**UNIVERSIDAD POLITÉCNICA DE
MADRID**

**ESCUELA TÉCNICA SUPERIOR
DE INGENIEROS DE TELECOMUNICACIÓN**

**APPLICATION OF ADVANCED THIN FILM
TECHNOLOGIES TO THE MANUFACTURE OF
MULTIJUNCTION SOLAR CELLS**

TESIS DOCTORAL

PENGYUN HUO

Ingeniero de Materiales

2016

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Instituto de Energía Solar
Departamento de Electrónica Física
Escuela Técnica Superior de Ingenieros de Telecomunicación

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AUTOR: **Pengyun Huo**
Ingeniero de Materiales

DIRECTOR: **Ignacio Rey-Stolle Prado**
Doctor Ingeniero de Telecomunicación

2016

**Tribunal nombrado por el Magnífico y
Excelentísimo Sr. Rector de la Universidad Politécnica
de Madrid.**

PRESIDENTE:

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SUPLENTE:

Realizado el acto de defensa y lectura de la Tesis en Madrid,
el día de de 2016.

Calificación:

EL PRESIDENTE

LOS VOCALES

EL SECRETARIO

AGRADECIMIEN

RESUME

La energía solar, en una u otra forma, es la fuente original de casi toda la energía en la Tierra. Además, es el más abundante y casi inagotable. La energía fotovoltaica (FV), siendo la tecnología que convierte directamente la luz solar en electricidad, es una alternativa prometedora para resolver el constante aumento de la demanda mundial de electricidad. En concreto, la energía solar fotovoltaica de concentración (CPV), como tecnología FV de tercera generación, es una de las tecnologías más prometedoras para reducir el coste de la electricidad solar. El uso de células solares multiunión (MJSC) con la más alta eficiencia de conversión y operando a alta o ultra-alta concentración son las estrategias típicas para reducir el coste de la CPV, y ambos factores están altamente relacionados con la resistencia en serie de la célula solar. Dado que la malla de metalización de la célula tiene una influencia determinante en la resistencia serie, el desarrollo de contactos capaces de proporcionar óptima resistencia de contacto metal-semiconductor y alta conductividad en la capa metálica son de gran relevancia.

En consecuencia, el problema fundamental que trata de resolver la presente tesis es la formación de contactos metálicos delanteros para ser usados en células multiunión para CPV que proporcionen baja resistencia específica de contacto (ρ_{CF}) y baja resistencia de hoja de metal (ρ_M) mediante la aplicación de la tecnología de depósito de películas delgadas mediante EBPVD.

El estado de la técnica en el IES-UPM en cuanto a contactos frontales de células solares de concentración está representado por capas de AuGe/Ni/Au depositadas por evaporación térmica. Sin embargo, esta tecnología no es capaz de evaporar metales refractarios y el control de velocidades de deposición elevadas y espesores altos resulta un reto. Por lo tanto, con el fin de depositar mejores metalizaciones, una nueva herramienta EBPVD Classic Doble 500 diseñada por Pfeiffer fue instalada y puesta en marcha, en el contexto de esta Tesis. Varios problemas, como el gran tamaño de haz de electrones, la deriva en el punto de impacto, retrasos en la apertura del obturador, etc., fueron identificados y resueltos.

Se han desarrollado y optimizado procesos de depósito por EBPVD para una amplia lista de materiales. Se ha determinado el tipo más adecuado de crisol en cada caso para evitar el entremezclado, contaminación o reacciones con el hogar de cobre durante la evaporación. El proceso de pre-fusión –i.e. proceso de fusión inicial de los gránulos para formar un "lingote" sólido y homogénea antes de comenzar el depósito– ha sido diseñado y optimizado para cada material. Casi todos los parámetros del proceso de evaporación se han probado y ajustado para producir un proceso optimizado de evaporación con control PID para cada metal. Como resultado, Al, Ti, Ag, Au, Pd, Ge, Ni, Cu pueden ser depositados adecuadamente ahora en el IES-UPM para formar contactos metálicos.

En consecuencia, cuatro sistemas de metalización, –Ti/Pd/Ag, Pd/Ti/Pd/Ag, Ge/Pd/Ti/Pd/Ag y Ge/Pd/Ti/Pd/Al– fueron propuestos y estudiados a fondo. Los contactos de Ti/Pd/Ag muestran muy buena resistividad del metal dado que la bicapa de barrera formada por Ti/Pd impide que Ga y As difundan hacia la Ag contaminándola y, por tanto, degradando su conductividad. Sin embargo, la resistencia de contacto específica de Ti/Pd/Ag es intolerablemente alta, incluso aplicado sobre $n^{++}\text{GaAs}$ muy dopado. Por lo tanto, se introdujeron otras capas interfaciales como Pd y Ge/Pd para disminuir la resistencia de contacto de metal-semiconductor. En comparación con el sistema clásico de metalización AuGe/Ni/Au (con $\rho_{CF} \sim 3 \cdot 10^{-6} \Omega \cdot \text{cm}^2$ y $\rho_M \sim 2 \cdot 10^{-5} \Omega \cdot \text{cm}$), la metalización Ge/Pd/Ti/Pd/Ag muestra una disminución de un orden de magnitud, tanto en la resistencia específica de contacto de metal-semiconductor como en la resistividad del metal. Tales valores de ρ_{CF} y ρ_M son suficientes para cumplir las exigentes demandas de metalizaciones de contacto de células solares CPV. Además, se estudió también la variante Ge/Pd/Ti/Pd/Al para disminuir aún más el coste y este sistema muestra un rendimiento similar a una fracción del precio.

Con el fin de implementar la nueva metalización en células solares de concentración, se estudió la compatibilidad de Ag y Al con los procesos (específicamente con los ataques químicos) utilizados en el proceso de fabricación de células solares llevado a cabo en el IES-UPM. En particular, Al resulta atacado rápidamente por HCl durante la etapa de aislamiento de mesas, y Ag se disuelve rápidamente por $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ durante la eliminación de la capa de contacto. Por lo tanto, se han diseñado procesos alternativos para evitar estos problemas. Finalmente, se utilizó el nuevo

proceso para implementar mallas de metalización, y se han conseguido fabricar con éxito células solares con una malla frontal de Ge/Pd/Ti/Pd/Al.

ABSTRACT

Solar energy, in one form or another, is the source of nearly all energy on the Earth. Moreover, it is the most plentiful and almost inexhaustible. Photovoltaics (PV), as a technology that directly converts sun light into electricity, is a promising approach to solve the steadily increasing world electricity demand. As the third generation PV technology, Concentrator photovoltaics (CPV) is one of the most promising technologies to reduce the cost of solar electricity. Using multijunction solar cells (MJSC) with the highest conversion efficiency and operating at high or ultra-high concentration are the typical strategies to reduce the cost in CPV, and both of them are highly related to the series resistance of the solar cell. Since the front grid of MJSC deeply impacts its series resistance, optimum semiconductor-metal contacts that provide highly conductive metallization are a must.

Accordingly, the fundamental problem addressed in the present thesis is the formation of front metal contacts to be used in MJSC for CPV that provide low specific contact resistance (ρ_{CF}) and low metal sheet conductivity (ρ_M) by applying EBPVD thin film technology.

The state-of-the-art contact films at IES-UPM are AuGe/Ni/Au stacks deposited by thermal evaporation. This technology is unable to evaporate refractory metals and the control of elevated deposition rates and thicknesses is challenging. Therefore, with the goal of depositing better metallizations, a new EBPVD tool Classic Twin 500 designed by PFEIFFER was set up and commissioned. Several problems, such as e-beam oversize, occasional impact point shifting, shutter delay problem, etc., were identified and solved.

The deposition processes by EBPVD for a broad list of materials have developed and optimized. The most suitable type of crucible liner has been determined for each material to avoid intermixing, contamination or reactions with the copper hearth during the evaporation. The pre-melting process –i.e. the melting of the pellets to form a homogenous solid “ingot” before the film deposition– has been designed and optimized for each individual material. Almost all the parameters of the evaporation

process have been tested to produce a new and optimized PID controlled evaporation process for each metal. Finally, Al, Ti, Ag, Au, Pd, Ge, Ni, Cu can be deposited properly to form metal contacts.

Consequently, four new metal stacks Ti/Pd/Ag, Pd/Ti/Pd/Ag, Ge/Pd/Ti/Pd/Ag and Ge/Pd/Ti/Pd/Al were proposed and thoroughly studied. Ti/Pd/Ag shows very good metal resistivity since the barrier bilayer formed by Ti/Pd prevents GaAs diffusing into Ag and thus poisoning the Ag top layer. However, the specific contact resistance of Ti/Pd/Ag, even on very highly doped n++GaAs, was unbearably high. Thus, another Pd and Ge/Pd interfacial layers were introduced to decrease the metal-semiconductor contact resistance. As compared to the classic AuGe/Ni/Au metallization system (with $\rho_{CF} \sim 3 \times 10^{-6} \Omega \cdot \text{cm}^2$ and $\rho_M \sim 2 \times 10^{-5} \Omega \cdot \text{cm}$), the Ge/Pd/Ti/Pd/Ag metallization shows a decrease of one order of magnitude in both the metal-semiconductor specific contact resistance and the metal resistivity. Such lower ρ_{CF} and ρ_M do achieve the challenging demands of contact metallizations for CPV solar cell. In addition, Ge/Pd/Ti/Pd/Al was also studied to further decrease the cost showing similar performance at a fraction of the price.

In order to implement the new metallization on concentrator solar cells, we studied the compatibility of Ag and Al with the processes (specifically chemical etches) used in the solar cell manufacturing process conducted at IES-UPM. In particular, Al is rapidly etched by HCl during the mesa isolation step, and Ag is rapidly dissolved by $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ during cap layer removal. Therefore, alternative processes have been designed. Finally, the new metallization grid pattern was used, and solar cells with a Ge/Pd/Ti/Pd/Al front grids have been demonstrated.

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1.1 Photovoltaics

Solar energy, in one form or another, is the source of nearly all energy on the Earth, and it is the most plentiful energy and almost inexhaustible. Photovoltaics, as a technology that directly converts sun light into electricity, is one of the most promising approaches to solve the steadily increasing world electricity demand. Besides, the photovoltaic conversion of solar energy stands out as a clean energy due to its limited impact on the environment as compared with other forms of electricity production. Furthermore, Photovoltaics can provide energy independence in remote area. All the merits pointed above added to some other characteristics such as modularity, easy-installation and reliability make that Photovoltaics will become a major source of electricity in the near term. Accordingly, the Photovoltaic (PV) market has grown significantly during the past decades. It is the fastest-growing energy source for renewable electricity generation, at an annual average growth rate of 6.8 % in 2015 [1]

However, the massive application of PV is still limited mainly due to its price. In order to be more cost effective, several PV technologies have been postulated as candidates to drop PV costs. The most mature technology –the so-called “first generation”– is the silicon wafer-based solar cell, and its economics have become dominated by the costs of silicon wafers which are already made in high volume and hence with limited potential for cost reduction. Another technology is that using thin-film solar cells –the so-called “second generation”–and offers prospects for a large reduction in material costs; nevertheless, its comparatively low conversion efficiency impedes its massive installation. One approach to progress further is to increase conversion efficiency by using novel solar cell architectures and materials. This is the so called “third generation” where multijunction solar cells, which convert more photons into current by adding more cells of different bandgap to a stack, stand out as the most credible technology. This idea can be backed with the aid of Figure 1-1 that shows the progress of research solar cell efficiency records over the last 45 years. In this chart the progress and efficiency achievements of multijunction solar cell can be evaluated with the current new record being 46.0%.

Figure 1-1 Evolution of research cell efficiency records for different PV technologies.[2]

1.2 Multijunction solar cells and Concentrator Photovoltaics

Multijunction solar cells (MJSC) comprised of III-V materials are routinely used in space applications, for example, on satellites, unmanned space probes, planetary landers, and the International Space Station (ISS) [1, 2]. In contrast, when these solar cells are used for terrestrial applications, in order to reduce the cost of such expensive solar cells, Concentrator Photovoltaics (CPV) technology is implemented, which is based on focusing sunlight on a small receiver (i.e. solar cell), and thus replace solar cell surface by inexpensive lens or mirror surface [3].

Figure 1-2 The principle of CPV, using Fresnel lens optics. (Courtesy of FhG/ISE, Freiburg, Germany).[4]

As shown in Figure 1-2, the principle of CPV to focus the direct sunlight collected by a large optics onto a small solar cell. The optics area to the solar cell area ratio is called geometrical concentration and its unit is typically referred to as suns or X. Therefore, CPV allows the use of the most efficient solar cell, which is more expensive than the normal silicon wafer solar cell, since it consumes much less semiconductor area to fabricate the solar cell; especially at the higher concentration ratios.

Generally, using solar cells with the highest conversion efficiency is the typical strategy to reduce the cost in CPV. Since the solar cell represents only a small fraction of the cost of the system (and they are small and thus cheap), the best efficiencies are affordable to attain the highest possible energy outputs.. Another key factor to reduce the cost CPV is to operate the MJSC at high or ultra-high concentration [5] [6], as the higher ratio of the lens to the solar cell area reduces the cost of cell material and a higher efficiency will be obtained due to V_{oc} increasing [7]. Figure 1-3 shows the cell efficiency and concentration impact on the CPV system price; increasing both of them will reduce the cost.

Figure 1-3 CPV cost as a function of solar cell efficiency for different concentration levels.[8]

1.3 Power losses arising from operating conditions and trade-off between grid shadowing and photo generation

Of course concentration cannot be increase unlimitedly. In addition to fundamental limitations in the optics –which restrict the maximum attainable concentration to ~46500 suns on the Erath surface– there are practical limitations on the solar cell that cause the efficiency to stabilize and the fall above a certain concentration level. As will be commented below the factor responsible for this fall in performance are the electrical losses caused by the series resistance of the device.

Table 1-1 lists the losses in solar cells; it includes optical losses, absorption losses, thermalization losses, recombination losses, and electrical losses.[8] Among them, the optical losses and the electrical losses are highly related to the metallization on solar cell, since the metallization area influences both the shadowing factor and the serial resistance of solar cell. Therefore, optimizing the metallization on solar cell is very important in order to minimize the impact of these losses.

Table 1-1 Losses in solar cell

<i>Optical losses.</i>	The metallic grid on the front surface will reflect some of the
------------------------	---

impinging light.

The antireflection coating on the surface will not be perfect for all wavelengths and also causes some loss.

Absorption losses. The photons with energy below the bandgap will be lost

Thermalization losses The excess energy of photons above the bandgap is lost in the form of heat.

Recombination losses. The excited carriers release their extra energy before reach the solar cell contacts

Electrical losses The current flowing through the semiconductor and metal layers causes resistive losses.

Figure 1-4 Sketch of the semiconductor structure of a GaInP/Ga(In)As/Ge triple-junction solar cell developed at IES-UPM with an efficiency of ~40% at 500 suns.[9]

Figure 1-4 shows the structure of triple junction solar cell in CPV, once the photons are converted into current through the top, middle and bottom subcell, in order to effectively draw the current from the device, the front and back metal contact are

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formed. The back contact fully covers the rear side of the cell whilst the front metal contact is designed as a grid or comb-like structure (as shown in Figure 1-6). This configuration intends to optimally solve a trade-off between reflection losses for which we would like sparse grids (i.e. if the grid is sparse few photons will impinge on the metal and will be reflected and lost) and electrical losses for which we would like dense grids (if the grid is dense the mean distance that a photogenerated carrier needs to travel to reach a contact will be short and so will be the ohmic losses in the semiconductor).

While the optical problem remains constant with concentration the electrical losses increase with concentration. This is so because the current produced by the solar cell grows linearly with light intensity and ohmic losses grow quadratically with current and therefore grow quadratically with concentration..

In other words, when the solar cell is operating under the high concentration, the current grows so high that the electrical power loss due to series resistance is magnified and becomes the most relevant limiting parameter [6]. Figure 1-5 shows the performance of some record III-V concentrator solar cells. As shown by this figure, initially the efficiency rises with concentration, as a result of the lower relative impact of recombination losses over concentration. However, at a given point, the efficiency starts to decline due to the fact that electrical losses grow since high concentration generates a high current flow and the increasing V_{oc} cannot counterbalance this loss.

Figure 1-5 Comparison of the performance of different III-V concentrator solar cells. It is indicated the number of junctions (from 1J to 3J), the type of structure (LM: lattice matched, LMM: lattice mismatched or IM: inverted metamorphic) and the lab or company who manufactured the cell [5].

The basic approach to tackle this limitation is to carefully design (and optimize) all the components of the solar cell that contribute to its series resistance, which are 1) the back contact; 2) vertical current flow in semiconductor layers including heterojunctions and tunnel junctions; 3) lateral current flow in the emitter and 4) the front contact. As mentioned above, the back contact is less of a problem since it fully covers the rear of the solar cell and thus has a large contact area. On the other hand, items 2) and 3) depend on the semiconductor structure and thus are deeply linked to the photovoltaic conversion process itself. Finally, the optimization of the front grid seems a technological challenge that can deeply impact the series resistance whilst it is to a great extent independent of the semiconductors structure (i.e. optimum grids could be applied to variety of III-V cell architectures).

Accordingly, the fundamental problem addressed in this thesis is the formation of front metal contacts with low series resistance and low metal area (shadowing factor) simultaneously. In order to clarify the needs of such contacts, Figure 1-6 shows the current flow in a multijunction cell and illustrates that the power loss due to series resistance in the front grid occurs in three segments: (1) resistance in the

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semiconductor layers associated to lateral flow of the current; (2) contact resistance at the semiconductor–metal interface; and (3) resistance in the metal gridlines. The losses labeled as (1), associated to lateral flow of current in the emitter, are related to the finger pitch or spacing that also determines the shadowing factor. However, losses (2) and (3) are only dependent on the technology used to manufacture the contacts. Thus, metal contacts systems providing low metal/semiconductor specific contact resistance and low metal sheet conductivity will be the best asset for any given concentrator solar cell technology.

Figure 1-6 Current flow in a multijunction cell. Current is collected by the gridlines and then it flows to busbar.

1.4 Current state-of-the art for manufacturing metal contacts for CPV solar cells at IES-UPM

The metal system currently under use at IES-UPM to implement front grid on III-V high concentrator solar cells is AuGe/Ni/Au, which forms excellent ohmic contacts on n-type GaAs. The AuGe/Ni/Au contact has been an extensively used system for several decades since its inception in 1967 [10-12], due to its low contact resistance and good adherence caused by the alloying process. However, the inter diffusion that takes place between Au and GaAs and Ni –being the latter an ineffective barrier layer during the annealing process–, brings about the mixing of the metal stacks and even may produce Au spiking into the GaAs layer. Both these facts impact the quality and reliability of the contact since the contamination of the top Au layer deteriorates the sheet conductance of the contact whilst Au spikes can produce short circuits or can cause thermal instability in the contact. In addition to these problems, it should be said that, being based on gold, the cost of this metallization is very high.

Figure 1-7 Efficiency vs. front contact metal/semiconductor specific contact resistance for a single junction 1mm^2 GaAs solar cell with an inverted-square grid at a concentration of 1000 suns[13]. The single junction concentrator solar cell represents the worst case in terms of impact of series resistance components since it is the device with the highest current density.

In the III-V semiconductor group at IES-UPM, AuGe/Ni/Au contacts were deposited by sequentially evaporating AuGe (200 nm), Ni (60 nm), and Au (500 nm) in a thermal evaporator followed by a subsequent annealing process at 370°C for 3 minutes under forming hydrogen. This was the baseline process for 1mm^2 concentrator solar cells intended to be operated at 1000 suns. The performance of such contacts can be summarized as follows. Its specific contact resistance is in the range of 10^{-5} - $10^{-6} \Omega \cdot \text{cm}$, a value which is good enough with lower results barely improving the solar cell performance. As shown in Figure 1-7, metal/semiconductor specific contact resistances lower than $\rho_{CF} < 10^{-5} \Omega \cdot \text{cm}^2$ cause minor improvements in efficiency, whilst for $\rho_{CF} \sim 10^{-6} \Omega \cdot \text{cm}^2$ improvements seem undetectable. Hence, attaining $\rho_{CF} \sim 10^{-6} \Omega \cdot \text{cm}^2$ guarantees no significant impact of the contact resistance on solar cell performance at 1000 suns. The second magnitude of interest of the metal system is its sheet resistance. In this case, the sheet resistances attained with AuGe/Ni/Au are in the range of $0.2 \sim 0.5 \Omega/\square$ depending on the thickness of metal layer deposited (500~1000nm) and this high value does impact the performance of solar cell. Figure 1-8 shows the simulation results of efficiency vs. light

concentration of a 1mm^2 GaInP/GaAs/Ge triple junction solar cell –with a structure similar to that in Figure 1-4– with an inverted-square metallization grid for different metal sheet resistances. It can be found that when the R_s decreases from $200\text{ m}\Omega/\square$ to $\sim 25\text{ m}\Omega/\square$, the efficiency of solar cell has a significant improvement ($\sim 2\%$ absolute). Thus, the design and implementation of a new metallization system able to provide lower sheet resistance and lower contact resistance is consequential.

Figure 1-8 Efficiency vs. light concentration of a 1mm^2 GaInP/GaAs/Ge triple junction solar cell with an inverted-square metallization grid for different metal sheet resistances. A specific metal semiconductor contact resistance of $\rho_{CF} \sim 10^{-6}\text{ }\Omega\cdot\text{cm}^2$.[14]

As mentioned above, the state-of-the-art front grid metallization in the Group of III-V semiconductors at IES-UPM is deposited by thermal evaporation. This technology is commonly used to deposit metal thin films due to its low cost and the simplicity of the equipment involved. However, it implies several difficulties when facing the design of a new metallization:

- 1) It is difficult to evaporate refractory metals with thermal evaporation due to its inability to reach high temperatures. Refractory metals are a key component to stop the diffusion between the metal and semiconductor

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layer in order to obtain high sheet conductance and maximize the reliability of the metallization.

- 2) The thermal evaporation tool of the Group of III-V semiconductors at IES-UPM can only evaporate three different metals per process, since it only has three boats. This limits the variety of metallization designs.
- 3) The evaporation rate by thermal evaporation is not able to be controlled precisely in some species and is subjected to the limitations stemming from the temperatures that can be achieved in the boat.

Therefore, in order to design and fabricate a new metallization properly with high advanced thin film technology a new technology was targeted, namely, electron beam thermal evaporation also termed as electron beam physical vapor deposition (EBPVD). Accordingly a new Classic 500 Twin EBPVD machine designed by PREFFER was acquired to be used to manufacture thin films (including contacts) on solar cells. Figure 1-9 shows the thermal evaporation machine used at IES-UPM (left) and the new Classic 500 Twin EBPVD machine (right). As will be discussed in detail in chapter 2, comparing the thermal evaporation, using EBPVD can: 1) evaporate refractory metals; 2) access more metal combinations; 3) reach high purity , and 4) control high evaporation rates precisely.

Thermal PVD → EB-PVD

- refractory metal
- more metal combination
- high purity
- control rate precisely

Figure 1-9 Thermal PVD (left) and EBPVD (right) of the Group of III-V semiconductors at IES-UPM.

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1.5 Goals for this thesis

As discussed above, in line with the research strategy of the III-V Semiconductor group at IES-UPM, the general goal of this thesis is to develop a new metallization system for solar cells by EBPVD, targeting on decreasing the series resistance limitation for multijunction solar cells working under high or ultra-high concentration. In particular, we target a new metallization system that can provide the following features:

1. A specific metal/semiconductor contact resistance of $\rho_{CF} \leq 10^{-5} \Omega \cdot \text{cm}^2$
2. A sheet resistance of $R_S \leq 30 \text{m}\Omega/\square$
3. Durable and reliable, to maximize the useful life of devices
4. Bondable, to facilitate the formation of the external connections
5. Low-cost, avoiding the use of large quantities of precious metals

Consequently, the implementation of this new metallization as well as its characterization is the subject of this doctoral thesis. In order to achieve this general goal, the specific goals established were the following:

1.5.1 Development of e-beam technology

As already described in section 1.4, in the III-V Semiconductor group at IES-UPM, the state-of-the-art front grid metallization was deposited by thermal evaporation. However, according to the demands posed by the new metallization, a new EBPVD technology needs to be used to overcome the drawbacks and limitations of thermal evaporation. Since we are facing the use of a new technology and a completely new machine, it is very important that the experimental tools and techniques are properly set-up, understood adequately, calibrated and well controlled. Moreover, subsequent characterization needs to be carried out correctly to ensure the obtained results are consequential.

A first goal of this thesis will be the set-up of a EBPVD technology at the III-V Semiconductor group at IES-UPM

1.5.2 Development of processing recipes for a large collection of metals

Once the basics of the EBPVD technology have been established and the tool has been commissioned and “tuned” processes to evaporate metals need to be developed,

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adjusted and optimized. The goal is to have a wide palette of materials to implement possible metallizations of interest in high concentrator solar cells.

1.5.3 Development of the new metallization

According to the result of simulations schematically presented in Figure 1-7 and Figure 1-8, when the metal/semiconductor specific contact resistance is in the range of $1 \times 10^{-5} \Omega \text{ cm}^2$ and the sheet resistance of metal grid is around $30 \text{ m}\Omega/\square$, the series resistance of the solar cell associated to its front grid is optimized. Further reductions in the specific contact resistance and sheet resistance have very little influence on the final results of the solar cell. Therefore, designing a new metallization to reach the above requirements is the key point of this thesis. In addition, high long-term stability, good bondability, and cost-effectiveness of the new metallization are also considered.

1.5.4 Apply new metallization into new high performance grid contacts for high concentrator solar cells

After designing and fabricating the new metallization, it has to be applied on solar cells and its actual performance should be compared with the present AuGe/Ni/Au technology. This will probably imply changes in the manufacturing process that will need to be envisaged.

1.6 Outline of the thesis

Following the four specific goals described above, this thesis is divided into four technical chapters proceeded by this and followed by a conclusion.

Chapter 2 is devoted to present an overview of the main experimental techniques, namely, Electron Beam Physical Vapor Deposition and some layer characterization methods such as TLM and Van de Pauw etc.. It is very important that the experimental tools and techniques used have been understood adequately, calibrated and well controlled, so that the new metal contact layer can be properly fabricated on the solar cells.

Chapter 3 describes the empirical information gathered about the metal deposition process by EBPVD of a large collection of materials. This information is given for each metal material of interest and mainly focuses on: 1) the properties of the

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material and the compatible crucible liner; 2) the pre-melting process with manual e-beam control; 3) the optimum evaporation parameters with PID control; and 4) any other concerns, tricks or caveats about each metal.

Chapter 4 presents the study of four new proposed metal contacts developed in this Thesis, namely, Ti/Pd/Ag, Pd/Ti/Pd/Ag, Ge/Pd/Ti/Pd/Ag and Ge/Pd/Ti/Pd/Al on n-type GaAs. Their target application is concentrator solar cells though they could be used in any electronic devices that handles high current densities and have grid-like contacts with limited surface coverage (i.e. as LEDs or lasers).

Chapter 5 deals with the use of Ge/Pd/Ti/Pd/Ag and Ge/Pd/Ti/Pd/Al grid contacts on solar cells its comparison with current AuGe/Ni/Au technology. To this end, the characteristics of solar cells with new and old metallization and their results and discussion are presented in this chapter.

The final chapter provides a critical review of the goals of the thesis and summarizes the main conclusions and final results of this work. The lines for future work that remain open or which follow-up to this research are also presented.

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Chapter 2. Basics of e-beam PVD and layer characterization

2.1 Introduction

In order to fabricate the solar cell properly with high advanced thin film technology, it is very important that the experimental tools and techniques used have been understood adequately, calibrated and well controlled. Moreover, subsequent characterization needs to be carried out correctly to ensure the obtained results are consequential. Therefore, in this chapter, an overview of the main experimental technique –Electron Beam Physical Vapor Deposition or EBPVD– will be presented, and the layer characterization methods such as TLM and Van de Pauw etc. will be also described.

2.2 Basic concepts of Physical Vapor Deposition

2.2.1 Definition and main techniques

Physical vapor deposition processes are atomistic deposition processes in which material is vaporized (by means of heating or sputtering) from a solid or liquid source in the form of atoms or molecules, transported in the form of a vapor through a vacuum or low pressure gaseous environment to eventually reach a substrate where it condenses [1]. Figure 2-1 shows the schematic of the PVD process. It mainly includes thermal vacuum evaporation, E-gun vacuum evaporation, and sputtering physical vapor deposition. Normally, the thickness of the film lies in the range from nanometer(a few atomic layers) to some micrometers; thicker layers are generally called coatings[2]. The substrate can be small or large and the shape can be flat or complex geometries. Typical deposition rates are 1~10 nm/s.

Figure 2-1 Tthe schematic of the PVD process.

2.2.2 Thermal evaporation

Vacuum evaporation perhaps is the simplest method to deposit a thin film; here the atoms or molecules from a thermal vaporization source reach the substrate without collisions with residual gas molecules in the deposition chamber[3]. It is identical to molecular beam epitaxy (MBE), the key difference is that vacuum evaporator is operated at higher base pressures and with much higher deposition rates than MBE counterparts. Figure 2-2 shows the schematic of thermal evaporation, the target source and substrate are loaded in a vacuum chamber. After the vacuum environment is built by the pump, the target source is heated by joule heating via a refractory metal (resistive element).

Figure 2-2 The schematic of thermal evaporation.[4]

For vacuum deposition, a reasonable deposition rate can be obtained only if the vaporization rate is fairly high. The desired equilibrium pressure of the evaporant is in the range of $\sim 10^{-2}$ mba[3], and it restricts materials species which can be evaporated from heated crucibles. For some materials, the low equilibrium pressure of the evaporant cannot meet the required level to be evaporated or, in other words, higher temperatures are needed to reach reasonable evaporation rates. The vapor pressure data for some materials of interest is shown in the Figure 2-3, and extensive data of other metal materials is included in (chapter 3). As shown in Figure 2-3, some

materials such as Al and Au are good for evaporating since low temperature is required to obtain the equilibrium pressure of evaporant. Meanwhile, Mo and W are virtually impossible to be evaporated by vacuum evaporation due to the high temperatures required.

Fig. 8.1 Vapor pressure curves for selected materials. Adapted from [2].

Figure 2-3 Vapor pressure curves for selected materials.[5]

2.2.3 Sputtering

Sputter deposition is a non-thermal vaporization process in which the surface atoms are physically ejected from a solid surface by momentum transfer from an atomic-sized energetic bombarding particle which is gaseous ion accelerated from a plasma.

Figure 2-4 The schematic of sputtering deposition.[5]

Sputtering deposition can be used to deposit a wide variety of metals, insulators and compounds. The composition in the deposited film is related to the target composition, making the control of composition is easier. Sputtering can be also used to clean the surface in situ prior to film deposition (i.e. ion milling). On the other hand, it has the disadvantage that plasma produces many high-speed atoms that bombard the substrate and may damage it. In addition, by using sputtering deposition the films on the substrate have a better step coverage. This may be an advantage or disadvantage, depending on the desired result.

2.2.4 E-beam evaporation

2.2.4.1 Fundamentals

Electron Beam Physical Vapor Deposition (EBPVD) is similar to vacuum thermal evaporation. It uses an electron beam (or e-beam for short) to impact on the target material to increase locally its temperature, causing atoms from the target to transform into the gaseous phase. These atoms then precipitate into solid form, coating everything in the vacuum chamber (within line of sight) with a thin layer.

Figure 2-5 electron beam evaporation.[6]

Electron beam (e-beam) evaporation can be used to develop a sufficiently high flux of evaporant from refractory materials since an intense beam of energy is applied locally to a target only in a very small region. Accordingly, only the central part of the target ingot is evaporated and the bulk remains solid (or liquid), but with a temperature gradient from the center to the rim, which is at much lower temperature. As the result, e-beam is required to be precisely controlled to impact only on a small central region of the target material.

Usually, multi pocket hearths are incorporated into the EBPVD for deposit multilayer film in a sequential manner, without breaking the vacuum between each layer and minimizing the contamination. On each hearth pocket a crucible is placed where only a single element should be loaded. It is extremely difficult to evaporate alloys with controlled composition by EBPVD since the vapor pressure of the separate components is, in general, not similar. Another possibility would be to use

two e-beams together to deposit the alloy film, but this would require an extremely precise temperature control in both pockets so that the alloy film composition can be accurately controlled and this is not easy to implement. Therefore, alloy films are seldom evaporated using vacuum e-beam evaporation and vacuum thermal evaporation is used instead.

For the EBPVD, high voltages (6-10KV) are used for beam formation which in turn produces X-rays. Such X-rays may cause damage in the substrate on which the film is deposited. Therefore, the distance between target material and substrate (i.e. the so called throw distance) should be long enough to minimize this influence. However, this requirement is in conflict with the material cost, since a longer target distance will cause a thinner film thickness with the same quantity of evaporated material.

2.2.4.2 Advantages for solar cell processing

During the solar cell manufacture processes, the contact metallization and the anti-reflection coating film fabrication are very important. The contact metallization has influence on the serial resistance and fill factor, and the anti-reflection coating film increase the incidence light. As one thin film technology, PVD is commonly used for both of them due to its high purity operation environment and high quality film obtained. In terms of fabrication of metallization, in order to get more sharp and well defined micron-sized lines for the front grid, photolithography and subsequent lift-off processes are necessary to be used. As a result, the evaporant needs a long mean free path to avoid agglomeration and should impinge perpendicularly on the masked substrate to totally avoid the step coverage (i.e. coating the photoresist walls). In this sense, a negative slope or a step overhang in the photoresist helps in this quest[7]. For this reason, EBPVD or thermal evaporation can be used. The chamber pressure of them are much lower than the requirement 1×10^{-4} mbar for the long free mean path. Meanwhile, a point source and substrate loaded in a dome curve shape are designed to keep the perpendicular incident angle of the evaporant atoms during EBPVD or thermal evaporation.

By comparison, sputter is not suitable since its high chamber pressure $\sim 10^{-2}$ mbar causes agglomeration and the random impinging incidence angle causes a good step cover, which leads to a problem during the lift off process. Table 2 shows a summary

of the merits and drawbacks for thermal evaporation, sputter deposition, and E-beam evaporation in concentrator solar cell processing.

Table 2 Comparison of thermal evaporation, sputter deposition, and E-beam evaporation.

Method	Pro	Con
Thermal Evaporation	<ol style="list-style-type: none">1. Simple to implement2. Poor step coverage (good for lift off)	<ol style="list-style-type: none">1. Limited source material (no high temperature)2. Evaporate alloys is difficult3. Contamination from crucible.
Sputter Deposition	<ol style="list-style-type: none">1. Evaporate alloys2. High temperature materials3. Less radiation damage	<ol style="list-style-type: none">1. Possible grumpy films2. Porous films3. Plasma damage/contamination4. Better step coverage (bad for lift off)
E-Beam Evaporation	<ol style="list-style-type: none">1. Refractory metals possible2. Evaporant travels in a straight line (good for lift off)3. Highest purity, less contamination from crucible	<ol style="list-style-type: none">1. Some CMOS processes is sensitive to radiation2. Evaporate alloys is difficult3. High material cost.

Comparing e-beam and thermal evaporation, EBPVD can evaporate more kinds of materials such as refractory metals. In addition, the EBPVD produces less contamination from the crucible and hearth. Although the X-rays produced may cause damage in the substrate, the relatively long throw distances needed for good lift-off also help in minimizing the X-ray damage. Conversely, these long throw distances cause the evaporated material to spread over large chamber areas and thus heavily impact material cost. However, large evaporation chambers also allow more wafers to be loaded in a single run in the fabrication process. In summary, EBPVD is the most versatile and effective technique to deposit high quality thin films for concentrator solar cell processing.

2.3 Description of the e-beam evaporator at IES-UPM

2.3.1 General description and overview of the machine

At IES-UPM, a Classic 500 Twin EBPVD machine designed by PREFFER is used to manufacture solar cells. It includes two chambers: one is used to deposit the metal layers to form the front and back contacts of the solar cell, and the other is for depositing the dielectric material and producing the antireflection coating to increase the absorption of incident light. Each chamber has independent pump and cooling water system and e-gun blocks, thus, the samples could be loaded and vacuum could be built separately. However, only one evaporation can be carried out at a time since only one power source and controller of e-gun is installed. Figure 2-6 shows the overview of Classic 500 Twin EBPVD machine at IES-UPM, It mainly includes four parts: a) the evaporation chambers; b) the vacuum system; c) the e-beam system; and d) the electric control system, and some accessory parts.

Fig. 2: Overview of High Vacuum Coating System Classic 500 Twin

1 Process chamber 1	7 Venting valve chamber 2
2 Rate/Thickness monitor	8 Venting valve chamber 1
3 Control unit E-gun	9 Earthing rod
4 Process chamber 2	10 Backing pump process chamber 1
5 Control units for the vacuum pumps	11 Container Meissner trap
6 Operation elements	

Figure 2-6 Overview of the Classic 500 Twin EBPVD machine at IES-UPM.[8]

2.3.2 The evaporation chambers

Figure 2-7 Process chamber of the Coating System Classic 500 Twin, a) metal chamber, b) dielectric material chamber.[8]

Figure 2-7 shows the evaporation chambers of the Coating System Classic 500 Twin; the left one is designed to deposit metals and the right one is for dielectric materials. As shown in Figure 2-7a the target material is loaded in the hearth (item no.3 in Figure 2-7a includes the e-gun and the multi-pocket hearth), and the substrate is loaded on the substrate plate on the top (item No.1 in Figure 2-7a). During the evaporation, the vacuum will be built through the flange connected with turbo pump (No.6); the deposition rate is detected by the coating thickness measuring head (No.2); the switch of deposition is controlled by the shutter (No.5) which shades the evaporant depositing on the substrate before and after the deposition process.

2.3.3 The vacuum system

The vacuum system is designed to build the lower pressure environment to generate a long mean free path and avoid agglomeration during the evaporation. The vacuum pressure needs to be lower than 1.33×10^{-4} mbar. In order to obtain such low vacuum

pressure, turbo molecular vacuum pumps are required, since the rotary vane vacuum pumps (also known as mechanical or roughing vacuum pumps) can only reach mid vacuum levels ($\sim 2 \times 10^{-3}$ mbar). The turbo molecular pump can be a very versatile pump. It can generate many degrees of vacuum from intermediate vacuum ($\sim 10^{-4}$ mbar) up to ultra-high vacuum levels ($\sim 10^{-10}$ mbar). Low pressure provides a non-contaminating environment and free of oxygen and water vapor, which is very important for the quality of the deposited thin film. In addition, vacuum eliminates convection and thus is helpful to reach the high temperatures needed to evaporate some materials (i.e. refractory metals), since there is no heat-transfer medium in the vacuum environment.

2.3.3.1 Turbo molecular vacuum pump

As shown in Figure 2-8, a turbo molecular vacuum pump (or simply turbo pump for short) includes a number of angled blades; when those blades rotate rapidly, the gas molecules enter through the inlet to the rotor and are subsequently ejected by the blades outwards through the exhaust, decreasing the number of molecules in the chamber and thus the pressure [9]. The turbo pump is required to work in combination with a rotary vane vacuum pump, which is also very important for reaching the low vacuum pressure level. The rotary vane vacuum pump has two functions: 1) it pumps chamber from atmospheric pressure to a pressure low enough to allow the high vacuum pump to operate; 2) it supports the high vacuum pump by providing a low enough pressure at the high vacuum pump's exhaust [10]. It is important to know that when the vacuum needs to be broken, before the rotation of blade stop, the inlet and exhaust pressure should change slowly. Therefore, nitrogen should not be injected immediately after stopping the turbo pump, since it will cause a large molecular flow to go through the pump and thereby cause a huge pressure on the blades and break them.

Figure 2-8 The schematic of a turbo pump.[9]

2.3.3.2 Meissner traps

Besides the turbo molecular pump and the rotary vane vacuum pump, the vacuum system of the Classic 500 Twin also includes another element, namely, a Meissner trap system with an Apollo 50 pressure vessel that stores liquid nitrogen, as shown in Figure 2-9. This element is only present in the metal chamber

Figure 2-9 Overveiw of vacuum system of Classic 500 Twin.

A Meissner trap is essentially a cooling coil attached to the chamber walls, through which a cryogenic liquid /gas flows (in our case liquid nitrogen from the pressure vessel). The low surface temperature of chamber walls helps capture gases and vapors by changing their state from gas to solid (the major residual gas component in chamber is water vapor) and thus further decrease the chamber pressure during or prior to the evaporation. It is an efficient method to “fix” water vapor. Normally, it is used to pump down a chamber from $\sim 10^{-3}$ to $\sim 10^{-8}$ mbar. Meissner traps help also decrease the pumping down time in industry.

2.3.3.3 The vacuum record data of the Classic 500 Twin at IES-UPM.

Figure 2-10 shows the vacuum record data of Classic 500 Twin at IES-UPM over a period of several months. As shown in Figure 2-10a, normally, it takes 70~120 minutes to reach a working pressure of $<10^{-6}$ mbar in the metal if the Meissner trap is not used. As shown in Figure 2-10b, the dielectric chamber normally takes between 60 to 90 minutes to reach the same working pressure of $<10^{-6}$ mbar. On the other hand, when the Meissner traps is used, working pressure of $<10^{-6}$ mbar are reached in ~ 30 minutes and the minimum pressure reachable is around 2×10^{-8} mbar, which is one magnitude lower than the vacuum pressure without Meissner traps. Lower pressures could not be obtained is due to seal rubber strip leaking. In addition, it takes more time to reach low pressure if the chamber was opened for long time during loading sample, since more contamination from the atmosphere went into the chamber.

Figure 2-10 The vacuum record data of Classic 500 Twin at IES-UPM during several months of 2012~2013. a) metal chamber, b) dielectric chamber, c) metal chamber by using Meissner trap.

2.3.4 The E-beam system

E-beam system is the core component of the machine. As shown is Figure 2-11, it is composed by 4 parts, 1) High voltage power supply (HVP), 2) Evaporation controller GENIUS with remote control, 3) Filament power supply (FPS), 4) Electron beam evaporator in Vacuum chamber and grounding Hook. The HPV is used to build High electric field in order to accelerate the electron, and the FPS was connected with the filament to produce the electron by thermionic emission.

Figure 2-11 The components of E-gun system[11] 1) High voltage power supply, 2) Evaporation controller GENIUS with remote control, 3) Filament power supply FPS, 4) Electron beam evaporator, 5) Vacuum chamber, 6) Grounding Hook.

2.3.4.1 Evaporator structure

Figure 2-12 The overview of electron beam evaporator, 1) Crucible cover, 2) Crucible, 3) y-coil 4) X-coil, 5) Magnet current connection, 6) Magnet (concealed shunt), 7) Feedthrough, 8) Rotary feedthrough, 9) Water outlet, 10) Water inlet, 11) Positioning unit, 12) Drive socket 13) Motor 14) Filament block.

Figure 2-12 shows the overview of electron beam evaporator. it mainly consist of 3 main components. 1) Driver unite, which is used to rotate the mutli-pockets hearth. 2) Water distributor for cooling the hearth during the evaporation. 3) Evaporator, it includes the mutli-pockets hearth, filament block and the magnetic coil.

During the evaporation, electrons emitted the filament are accelerated by high electric field and e-beam is formed though the filament block. Then the e-beam is deflected through $>180^\circ$ to avoid deposition of evaporated material on the filament[12], and finally impacted on the crucible by the static magnetic field with the magnet. Since the e-beam impact on target also generating some secondary electrons which could damage the substrate[13], the magnetic field was also used as a “electron trap” to capture the them. In order to control the e-beam precisely and

sweep the e-beam on the target, another dynamic magnetic field are also formed by the x-coils and y coils as shown in Figure 2-11. The dynamic magnetic is controlled by changing the current through coils with Evaporation controller --- Genius.

2.3.4.1 Evaporation controller --- Genius

Evaporation controller --- Genius is responsible for the control of the high voltage power supply, electron beam evaporator and filament power supply. Genius monitors the evaporation processes in the vacuum system, and all the operation elements are arranged on the remote control of evaporation controller (No.2) as shown in Figure 2-13. It manually control the evaporation process as well as to set all process and system parameters. As shown in Figure 2-13, the emission current of filament could be adjusted knob on the remote control from the 0~500mA, the range is deepened on the filament type, high emission current could obtain more power and high deposition rate. The impacted point could be controlled by the two joysticks, which can change the dynamic magnetic field. All the parameters such as voltage, pocket number, material and data are displayed on the screen.

Figure 2-13 Overview of evaporation controller --- Genius.[14]

Figure 2-14 Three modes to deflect the electron beam of an evaporator. [14]

The Genius already includes various modes to deflect the electron beam of an evaporator. As shown in Figure 2-14, the e-beam could be swept in three models. It is supposed that by applying the “spiral” and “circle” patterns, materials can be more homogenously evaporated. However, since the impacted point of e-beam in IES is oversize, the swept model does not work very well due to the consideration that avoiding e-beam to impact on the crucible.

2.3.4.2 The multi-pocket hearth.

Each chamber has an e-beam source with a multi-pocket hearth containing six pockets, as sketched in Figure 2-15. The multi-pocket hearth is used to load different

materials. The pockets can be rotated under vacuum, in order to change the target material and deposit multilayer films without breaking the vacuum.

Figure 2-15 (Left) E-beam source block with the multi-pocket hearth piece marked (Right) Top view of the multi-pocket hearth piece; the masked pockets have been shadowed in gray.

2.3.5 Deposition control

The deposition rate and the deposited film thickness are controlled by a SQC-310 thin film deposition controller. As sketched in Figure 2-16, the thin film deposition controller acts at three different levels: 1) measures the deposited thickness in real time; 2) calculates the deposition rate; 3) acts on the e-beam power supply to meet the predefined process parameters (i.e. increase its power when deposition rate must increase and vice versa).

Figure 2-16 Overview of SQC-310 thin film deposition controller.

The deposited film thickness is measured by quartz crystal microbalance (QCM), which measures a mass per unit area by measuring the change in frequency of a quartz crystal resonator. As the evaporated material builds up on the crystal, the resonance is disturbed by the addition of the thin film mass and consequently the frequency of oscillation decreases from the initial value. With some simplifying assumptions, this frequency change can be quantified and correlated precisely to the mass change using Sauerbrey's equation, which states that the decrease in frequency is linear with the increase in mass. As the area of the crystal sensor is known, and the material being deposited is also known by the controller, a change in mass can be translated into a change in deposited thickness using the density. Measuring deposited thickness in real time the evaporation controller can calculate the deposition rate. This deposition rate is adjusted to the desired (target) value using a PID controller that acts on the e-beam power supply.

2.4 Tool calibration and adjustment

In this section we intend to describe the calibration and troubleshooting process followed for the commissioning of the Classic 500 Twin EBPVD system. The problems faced during the commissioning process have been varied though, in general, they have been associated with the e-beam control (size and location) and the process control.

2.4.1 Electron beam control problem

2.4.1.1 The oversize impacting point on the target with the original filament

As shown in Figure 2-17, the e-beam impacting points is not only focused on the center of target, but one part of e-beam impacts on left rim of the crucible. The staff of the e-beam block manufacturer (Ferrotec) suggested that glow was due to secondary electrons. However, it seemed this evident was not the case since secondary electrons should be bent to a position ahead and collected by the copper hearth instead of only be focused on the left side of the crucible. The concentration of a high e-beam power on the left rim of the crucible could cause its uneven heating and subsequent cracking.

Figure 2-17 The e-beam impacting point is oversized in the metal chamber.

Figure 2-18 The comparison of the e-beam impacting size with the test protocol and specification.

Figure 2-18 shows the comparison of the e-beam impacting size with the test protocol and specification provided by the manufacturer. In comparison with the 3mm diameter on the specification, the real diameter measured in the e-beam test protocol is around triple, which would be still acceptable for our application. However, while evaporating Ag the e-beam size expands to 14.4mm and with an extra impacting region on left rim. The e-beam size expansion could be due to the fact that evaporating Ag needs more current than the 50mA which were used in the protocol and thus the aureole appears. Figure 2-19 shows the oversized e-beam impacting a point at the rim of the crucible in the dielectric chamber, where we found that the problem was the same.

Figure 2-19 The oversize e-beam impacting point in dielectric chamber

2.4.1.2 Better impacting point size with new filament.

As the oversized e-beam could crack the crucible, the filament of e-gun was changed to a new model. The new the e-beam impacting size was better than the old one, and the left impacting region disappeared. However, it is not perfect and the vertical size is still large . As shown in Figure 2-20, most power of e-beam is focused on the lower crucible region. When increasing the power step by step, there is more power on the upper region. If the e-beam is moved up a little bit so that most power impacts on the center of the crucible, the upper part of e-beam will touch the crucible rim.

Figure 2-20 The e-beam impacting size with new filament in metal chamber.

2.4.1.3 Electron beam shift problem

After several evaporation tests, we found that the e-beam impact point shifted up occasionally. The reason is unclear, though it seems to be a software bug in the Genius e-beam controller. As shown in Figure 2-21, the e-beam was located on the center after a calibration process intended to limit the risk of impacting the crucible rim. However, it shifted up occasionally during the next evaporation. As a result, the e-beam touched the crucible rim and broke it. (see chapter 3 about Ag.). In order to prevent this problem, it was decided to always carry out a preliminary test to find the actual beam position before each evaporation.

Figure 2-21 The E-beam shift up occasionally.

2.4.2 Shutter control problem

2.4.2.1 Shutter delay

We detected that a shutter opening delay occurs during the automatic mode of evaporation process with SQC-300 thin film controller. Once given the opening command, the shutter should open immediately but it remains closed for varying amount of time from 3 to 18 seconds. Obviously, during this period the reading of the QCM sensor is zero thickness. As a result, the controller steadily increases power of e-beam in order to get some thickness reading which cannot occurs since the shutter is actually closed. However, the target material is being actually evaporated at a high rate despite it does not reach the sensor and stiks on the shutter surface. Therefore, during this 3s-18s period of shutter delay, the e-beam can shoot up to an extreme current level as shown in Figure 2-22 and cause a big overshoot in the evaporation rate or even spoil the target material. Figure 2-22 shows that, if the shutter opening delays for 18s, the e-beam current can reach over 500mA.

Figure 2-22 The overshoot problem caused by the shutter opening delay.

After the checking of all parameters, the cause of the failure was not detected and PFEIFFER addressed the problem to the supplier of the SQC-300 thin film controller (Inficon). According to the response of the manufacturer (Inficon) there was a software bug, which was eliminated by upgrading to a new software version.

Figure 2-23 The feedback circulation loop is broken off by the shutter open delay during the first several seconds of the evaporation.

2.4.2.2 Imperfect shutter shading in the dielectric chamber.

The role of dielectric materials in solar cells is to implement highly efficient antireflection coatings. In some cases very thin layers (~ 3 nm) of specific materials need to be deposited to act as adhesives between the semiconductor and the antireflection coatings. This layers need to be thin to be optically transparent and not interfere with the antireflective behavior of the dielectric coating. However, we noticed that it was very difficult to precisely and reproducibly control the thickness of such thin layers of dielectrics since some material reached the substrate during the preheating process when the shutter was supposedly closed. This fact was difficult to be identified since the reading of the sensor was zero (i.e. the shutter worked

effectively for the sensor region which remains fixed but not for the rotating substrate holder). In order to solve the problem, a new shutter with bigger size was manufactured and installed.

2.4.3 Turbo pump error, warning F097.

The warning code F097 appeared after initiating the DCU (display control unit) of the PFEIFFER turbo molecular vacuum pump. It firstly appeared after the turbo pump was shut down without any control. The reason why the turbo pump stopped is still unclear and occurred occasionally for several times until all the cables in the pump were disconnected and reconnected again, after which it disappeared. However, the warning F097 still displays on DCU and there is no explanation of the meaning of this warning in the pump manual. It seems to be a software bug and does not influence the turbo pump control. In addition, it could be fixed by upgrading the software [15].

Figure 2-24 Screenshot of the turbo pump error warning F097 after initiating the DCU of the PFEIFFER vacuum pump.

2.4.4 Tooling factor Calibration

One of the key calibration steps in the commissioning of a PVD equipment is the calibration of the *tooling factor*. The tooling factor is a parameter that, for each material, corresponds to the relationship between the thicknesses deposited on the quartz sensor to the “real” thickness on the substrate. As Figure 2-25 shows, it is impossible to place a sensor in the same location as all the substrates in the chamber. Therefore, a correction for the difference in material deposited on the quartz sensor as compared to the substrate is necessary.

Figure 2-25 Different situations for the tooling factor calibration [16]

The tooling factor is calculated by [17]

$$F_m = F_i \times (T_m/T_i) \quad \text{Equation 2.1}$$

Being,

F_i : initial tooling factor, i.e. the tooling factor during the calibration test. If the default number is 100%, it will simplify the calculation.

T_m : film thickness measured on the substrate with a profilometer

T_i : Film thickness indicated by the rate monitor (quartz sensor)

The process followed for the calibration of the tooling factor for each material used in both chambers is as follows:

1. Place substrate and sensor in their normal position
2. Set the tooling factor in the evaporation controller to an approximate value; if unknown use 100%
3. Set the density and Z-Factor for the material
4. Choose T_m and deposit material (the optimum thickness will depend on the Profilometer or AFM instrument accuracy; films thicker than 100nm are recommend for the profilometer)
5. Calculate tooling factor by formula using Eq 1.1

6. Repeat the procedure above to fine tune the tooling factor until the result of the thickness read by the sensor is within the uncertainty associated to the thickness measurement.

Associated to this process the following caveats have been considered:

1. The target material quantity and the location of the e-beam in the crucible have influence on the deposited thickness. Therefore, the target material quantity and the location of the e-beam in the crucible should be kept the same during the calibration process.
2. For each material, the tooling factor calibration should be carried out independently. Different materials show different radiation patterns from the crucible and thus could show notable differences in their tooling factor. This is especially important for the dielectric materials, such as MgF_2 or ZnS .

2.5 Thin film characterization techniques

This section includes a brief description of all the experimental techniques and instruments used in this Thesis to characterize the properties of the thin films deposited by EBPVD. In brief, they are:

- Mechanical profilometer for thickness and surface roughness
- Van der Pauw, for thin film sheet resistance
- Resistivity bars, for thin film sheet resistance
- TLM or Transfer Length Measurement, for metal/semiconductor specific contact resistance
- ECV or Electrochemical CV profiling, to measure doping of semiconductor layers

2.5.1 Profilometer

A profilometer is a measuring instrument used to measure a surface profile using a mechanical sensing probe in the form of a stylus. It can be used to measure the thickness of a thin film, the depth of a mesa etch or the roughness of the film surface [18]. During the measurement, a diamond stylus moves down vertically until in contact with the sample and then scans laterally across the sample (or sample moves

relative to the stylus). The height position of the diamond stylus changes as it follows the sample surface, generating an analog signal, which is in turn converted to a digital signal and recorded. At IES-UPM, a KLA-Tencor AlphaStep D-120 Stylus Profiler was used. The most relevant parameters of this piece of equipment are shown in Table 2-3. The vertical resolution is 0.38Å; however, the step height repeatability is 6 Å or 0.1% (one-sigma, whichever is larger). As a result of these parameters, uncertainty in the measured thickness is acceptable (<10%) for heights above ~10 nm.

Table 2-3 AlphaStep D-120 Stylus Profiler specifications[19].

Vertical resolution:	0.38Å (least significant bit)
Lateral resolution:	100nm
Step height repeatability:	6 Å or 0.1% (one-sigma), whichever is larger
Stylus tip radius:	2.0 microns (standard)
Stylus force range:	0.03-10 mg

2.5.2 Van der Pauw method

The Van der Pauw method is commonly used to measure the sheet resistance of a wafer, thin film or any other 2D sample. It can be applied to samples of any arbitrary shape, on the condition that: 1) the sample is much thinner than its width/length (i.e. it is essentially a thin film); 2) the sample is homogeneous in thickness and singly connected, (i.e. it does not have any isolated hole); and 3) it has four very small contacts at the very perimeter [20-22]. Figure 2-26 shows some examples of patterns that are typically used for measurement by the Van der Pauw method. using any of these or similar patterns it can be shown that the actual sheet resistance R_s (measured in $\Omega/\square$) of the thin film can be calculated by [21]:

$$\exp \left[\frac{-\pi R_v}{R_s} \right] + \exp \left[\frac{-\pi R_h}{R_s} \right] = 1 \quad \text{Equation 2.2}$$

being R_v the vertical resistance and R_h the horizontal resistance that can be calculated as follows:

$$R_v = (R_{12,34} + R_{34,12} + R_{43,21} + R_{21,43}) / 4 \quad \text{Equation 2.3}$$

$$R_h = (R_{23,41} + R_{41,23} + R_{32,14} + R_{14,32}) / 4 \quad \text{Equation 2.4}$$

As these equations show, R_h and R_v are calculated by averaging the value of resistances of the type $R_{AB, CD}$, being A, B, C and D labels given to sequentially name the contacts of the Van der Pauw pattern (i.e A is next to B; B is next to C; C is next to D; and D is next to A). So to measure $R_{AB, CD}$, current should be injected between contacts C and D and voltage should be measured between contacts A and B:

$$R_{AB,CD} = V_{AB}/I_{CD} \quad \text{Equation 2.5}$$

Figure 2-27 shows how to measure $R_{12,34}$ on a disk pattern of a metallization sample for which V_{12} and I_{34} need to be measured. In order to get more precise values for R_v the four possible vertical combinations of resistances are averaged and the same is done for R_h .

Figure 2-26 Examples of Van der Pauw patterns[21].

Figure 2-27 Measure and calculate R_s by Van der Pauw method.

When $R_v = R_h = R$, Equation 2.2 can be simplified to $R_s = \pi R / \ln 2$, and R_s can be calculated easily. If R_v and R_h are not equal, Equation 2.2 can be solved by any computing software implementing an iterative method.

The result of the Van der Pauw method is the sheet resistance of the thin film (R_s) in Ohms per square. If the thickness of the layer (t) is known, it is straight forward to obtain the material resistivity (ρ):

$$\rho = R_s \cdot t \quad \text{Equation 2.6}$$

2.5.3 Sheet resistance bars

Another method which was also used to measure the sheet resistance and resistivity of metal thin films was the use of bar shaped patterns, as shown in Figure 2-28. A certain current (I) was injected from one end and flow outside through the other end; and voltages (V) between both ends and three points in the middle region were measured. Assuming that the contribution of the semiconductor to the film conductivity is negligible, the sheet resistance (R_s) could be calculated by:

$$\frac{V}{I} = R_s \frac{L}{W} \quad \text{Equation 2.7}$$

Being L the length between the two points of the voltage measurement, and W the metal bar width. As several measurements per bar and several bars are measured, the final value of R_s is obtained by averaging. Again, if the thickness of the layer is known, it is straight forward to obtain the material resistivity (ρ) using Equation 1.6.

Figure 2-28 Different bar patterns used to measure and calculate the sheet resistance of metal thin films

2.5.4 Transfer Length Measurement.

Transfer Length Measurement or Transmission Line Method (TLM) is a technique used in semiconductor physics to measure metal-semiconductor specific contact

resistance[20, 23-26]. As shown inFigure 2-29, the TLM pattern consists in a set of square or rectangular contacts defined on a semiconductor bar and separated by increasing distances ($L_1, L_2, L_3, \dots$). When current is injected between two adjacent contacts the associated resistance (R) has the following components:

$$R = 2R_M + 2R_C + R_{\text{semi}} \quad \text{Equation 2.8}$$

where R_M is the contact resistance between probe and metal; R_C is contact resistance between metal and semiconductor; and R_{semi} is the resistance of the semiconductor (as indicated inFigure 2-29). Since the R_M is small and thus negligible, Equation 1.8 can be further simplified to:

$$R = 2R_C + R_{\text{semi}} \quad \text{Equation 2.9}$$

However, if the probe does not contact on the metal properly, R_M will not be negligible and will introduce an error.

Figure 2-29 Patterns and measurement principle of TLM measurements.

Considering the geometry of the TLM pattern it is possible to find an expression for R_{semi} :

$$R = 2R_C + R_s \frac{L_i}{W} \quad \text{Equation 2.10}$$

where L_i is the length between the pads where current is injected; W is the pad width and R_s is the semiconductor layer sheet resistance. This equation states that R is a linear function of L_i as shown by Figure 2-30.

Analogously, the geometry of the TLM pattern allows finding an expression for R_C :

$$R_C = \frac{\rho_c}{L_T W} \quad \text{Equation 2.11}$$

where L_T is the so called transfer length; W is the pad width and ρ_c is the specific metal-semiconductor contact resistance, which reflects the metal-semiconductor contact resistance without the influence of the geometry of the metal pad. Since current crowding in the contacts implies a non-uniform distribution of the current under the contact, L_T is a parameter that represents the effective length of the contact where current flows between metal and semiconductor. It can be demonstrated [24], that L_T has the following expression:

$$L_T = \sqrt{\frac{\rho_c}{R_s}} \quad \text{Equation 2.12}$$

Using the above Equation it can be conclude that:

$$R_c = \frac{\rho_c}{L_T W} = \frac{R_s L_T}{W} \quad \text{Equation 2.13}$$

and therefore

$$R = R_s \frac{L}{W} + 2 \frac{R_s L_T}{W} = \frac{R_s}{W} (L + 2L_T) \quad \text{Equation 2.14}$$

The above equation represents the mathematical form of the graph in Figure 2-30. So doing a fit on this data (i.e. measuring the resistance of the TLM pattern over a range of different lengths) the parameters of Equation 1.14 can be obtained and thus ρ_C can be calculated.

Figure 2-30 Example of a TLM set of measurements and linear regression of the results.

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Chapter 3. Metal deposition by EBPVD

3.1 Introduction

In order to deposit the high quality metal layers needed to implement the contacts of high efficiency solar cells, the metal deposition process by EBPVD needs to be designed and optimized. Such design and optimization has to be performed for each individual constituent of the metallization, since each metal has different properties and behavior during the evaporation. Therefore, in this chapter, the empirical information gathered about metal deposition process by EBPVD is presented. This information is given for each metal material of interest and mainly focuses on: 1) the properties of the material and the compatible crucible liner; 2) the pre-melting process with manual e-beam control; 3) the optimum evaporation parameters with PID control; and 4) any other concerns, tricks or caveats about each metal.

3.2 Basic principles for EBPVD processes

3.2.1 On the use of crucible liners

3.2.1.1 The need for a crucible liner

The general recommendation for any EBPVD process is to locate the target material in a crucible liner (or simply *crucible* or *liner*) instead of putting it directly on the hearth pocket [1]. The reason for this is that 1) using a crucible liner for each material can avoid intermixing or contamination between target metals when a new one is needed to be loaded in the same hearth; thus using liners simplifies changing the material; 2) the crucible forms a thermal barrier between melt and water cooled hearth, which is so efficient that deposition rates can increase by 400% at the same power [2]; and 3) some metal material could form a metal alloy or react with copper hearth during the evaporation; as a result, the crucible is required to avoid hearth erosion or deterioration.

3.2.1.2 Crucible dimensions

The EBPVD machine at IES-UPM has two chambers, one for metal evaporation and a second one for dielectric materials. In terms of the metal chamber, the volume of hearth pocket is big (20 cm^3), since thicker metal films need to be evaporated and a lot of material is needed due to the long throw distance between hearth and substrate.

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In terms of crucible size selection, it would be natural to use a crucible liner that fits the hearth pocket. However, this is not always the best solution. A big crucible volume is able to load more metal material and subsequently decrease the frequency of loading and pre-melting material (in following sections we will comment on the pre-melting step). Nevertheless, a big crucible requires more initial material to be loaded (around 30% of the crucible volume, as a minimum) to avoid thermal stresses and cracking crucible. For noble metals such as Au, Pd, Pt, the cost of filling such 30% level of the crucible for 20cm³ is simply too much (see Table 3-4). Therefore, a smaller crucible dimension was used in these cases. The option chosen was to use crucible designed for the 7 cm³ hearth pocket, being the inner volume of such crucibles of 4.4 cm³, and the required initial volume is only around 1.5 cm³. The 7 cm³ crucible can be placed in a centered position of the 20 cm³ hearth. In this way, only the bottom of the crucible is in contact with the hearth pocket cooled copper base, while the side walls of the crucible should not touch the hearth walls. If one part of side wall contacts on the hearth pocket –which is water cooled–, it will cause non uniform heat transmission and may crack the crucible. Another approach is to design a copper adaptor piece to reduce the 20 cm³ pocket size to a 7 cm³ pocket size, as shown in Figure 3-20. As this figure shows, the 7cm³ crucible can fixed onto the adaptor piece and load those two crucibles together on the hearth pocket, and this produces a much more uniform heat transmission. More details on this approach will be given in 3.5.1. Although using the 7 cm³ crucible decreases the requirement of initial metal, it also decreases the heating transmission efficiency due to the decrease in contact surface with the cooled hearth. As a result, the evaporation velocity and PID control is more difficult.

Regarding the second chamber for dielectric material evaporation, the volume of hearth pocket is small (4 cm³), since only a few target materials is needed and the distance between hearth and substrate is short. Accordingly, 4 cm³ crucible liners were directly used in this case.

3.2.1.3 Crucible selection principles

The primary considerations [3-5] in selecting a crucible are chemical and thermal compatibility. Chemical compatibility is needed to ensure that crucible does not react with the material to be evaporated. Thermal compatibility is also important, and refers to the fact that material thermal expansion during the phase changing (ie.

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melting and solidification) does not crack the crucible. A refractory metal crucible (such as Mo or tungsten) can be used to avoid crack due to its good malleability; however, metal crucibles present some alloying problems and cannot be used for some target metal such as Al, which can readily react with the crucible metal during the evaporation. Finally, crucibles should not be filled greater than $\frac{3}{4}$ full with non-subliming materials [6] to avoid overfilling.

3.2.2 Crucible materials

3.2.2.1 Graphite crucible

In general, the most common material used in crucibles is graphite due to its low cost, inert chemical properties and its ability to withstand high temperatures. Graphite crucibles are typically used for melting non-ferrous —or non-iron— metals such as gold, silver, aluminum or brass.

Materials evaporated from graphite crucibles include[7]:

- Al-Ge alloys, Al-Si alloys, B, Be, Bi, CdS, CeO₂, Cr, Cu, Ge, In, Mg, Mo, Na₃AlF₆, Pd, Pt, Sb, SiO, SiO₂, Sr, Ta, Ti, Y₂O₃, Zn

3.2.2.2 FABMATE® Crucibles

Fabmate graphite is a specific type of high quality graphite manufactured by the company Pocographite through a proprietary process with a high purification and undergoing an amorphous carbon treatment, which infiltrates and locks onto the graphite and creates a grain-free, hard, thin coating surface protecting layer.

As compared to graphite crucibles, Fabmate crucibles have better strength, excellent machinability, show extended lives and are suitable for more materials.

Materials evaporated from Fabmate graphite crucibles include [8]:

- Ag, Al, AlF₃, Al₂O₃, Al/Si, As, Au, B, B₄C, Be, Bi, CdS, CeO₂, Cr, Cu, Fe*, Ga, GaAs, Ge, GeO₂, In, ITO, La₂O₃, Mg, MgF₂, MgO, Mo, NaF, Nb, Ni*, Ni/Cr*, Ni/Fe*, Pb, Pd, Pt, Rh, Se, Si*, SiO, SiO₂, Sn, Ta, Ta₂O₅, Tb, Te, Th, Ti, TiO, TiO₂, Ti₃O₅, WC, Y₂O₃, Zn, ZrO₂.

*One run material. Crucible liner may not survive subsequent runs.

3.2.2.3 Aluminum Oxide Crucibles (Al₂O₃)

Alumina (i.e. aluminum oxide) crucibles have wide applications due to their versatility and low material cost. Alumina possesses a high melting point, strong

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hardness, and good chemical stability, making it a good material to withstand high temperature and chemical corrosion. However, based on our experiments in IES-UPM, it is too easy to crack. The reason could be that the low malleability of this material is not suitable for the mechanical stress from the material expansion during the evaporation.

Metals evaporated from alumina crucibles include:

- Au, Ag, Al, Sb, As, Bi, Cd, Ca, Ce, Co, Cu, In, Ni, Pd, Se, Te, Tb, Ti, Sn

3.2.2.4 Tungsten crucibles (W) and Molybdenum crucibles (Mo)

Tungsten and molybdenum are refractory metals; both of them can withstand high temperatures (the thermal limit for Tungsten crucibles is 3250 °C). They are effectively indestructible and compatible with many materials. Although they have so many merits, their drawback is that they are very expensive. In addition, they many alloy with some metals and can degrade quickly, such as with Al and Pt.

3.2.2.5 Boron Nitride Crucibles (BN)[9]

BN is ceramic material, which is chemically inert material and is not wetted by metals. In this respect, it is used to make reaction vessels and crucibles.

BN crucibles could show some advantages to evaporate: Non-toxic, high purity, chemically inert, good thermal conductivity, tensile strength increases with temperature, excellent thermal shock resistance, high oxidation resistance.[10] It is typically used for evaporating Al, since its compatible with the high activity of melted Al.

3.2.2.6 Intermetallic Crucibles (BN-TiB₂)

Intermetallic crucibles show the advantages of ceramic crucibles, so it is highly chemical inert. At the same time, it is difficult to crack as a refractory metal crucible. Therefore, showing jointly the advantages of these two worlds, intermetallic crucibles have proven to be a reliable choice for the evaporation of aluminum [11]

3.2.2.7 Without crucible

Usually, using the crucible is more convenient for e-beam evaporation. However, in some cases, the material will be loaded on the hearth and evaporated directly without crucible. The reason for this maybe simply that the material does not react with copper or that simply the suitable crucible is hard to find, and its use does not

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provide a significant advantage. In such cases, the loaded metal does not generally react with the hearth, since the efficient water cooling system and the high thermal conductivity of copper promise a low temperature on the contact surface. In other words, the temperature of the interface between the hearth copper and the target material is not high enough to spark an alloying reaction, although the center area of target material is being evaporated. (see 3.4.1)

The above situation is based on a well-controlled e-beam shape on the target and enough material on the hearth. If the e-beam is swept too close to the sidewall of the hearth or the impacted on the bottom of the hearth directly due to insufficient material, this could lead to some reactions or break the hearth (i.e. evaporate the copper as a result of insufficient cooling power) (see Al 3.3.1, Ni 3.8.)

For the limitations and precautions described above, when the material is evaporated on the hearth pocket directly, it is almost impossible to use all the target material in the hearth. Therefore, if the material needs to be changed, the hearth should be cleaned carefully with fine sandpaper to avoid the mixing of both target materials.

3.2.3 Common causes behind crucible cracking

3.2.3.1 Material overfilled or not enough

Overfilling material can cause the melt to spill over the edge of the crucible. When a spill-over occurs, a thermal short is created between the crucible and the hearth. The resultant thermal stress causes the crucible to crack [1]. If the melt level is below 30%, the E-beam may strike the crucible bottom and breaks it.

3.2.3.2 Improper seating of the crucible on the hearth

Out of round or chiseled hearths often create non uniform mechanical stresses on the crucible walls. For the longest crucible life and for the most reproducible evaporation results, contact between the crucible liner and the copper hearth should be restricted to the bottom of the hearth cavity. A circular graphite or copper shim is frequently used to achieve proper contact[2].

However, based on the experiments at IES-UPM, it is not so easy to achieve that 20 cm³ crucibles only contact the bottom of the hearth, since the size of the crucible does not perfectly fit the hearth. In our experience non perfect seating of the crucible in 20 cm³ hearth pockets is commonplace and so is the cracking of crucibles made

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from fragile (i.e. ceramic) materials. As a consequence of this, crucible made from tougher materials are preferred at IES-UPM.

3.2.3.3 Storage and handling

Improper crucible handling and storage also can be the source of crucible life problems. Crucibles should be handled with tongs, gloves or finger cots; never with bare hands or fingers. Used crucibles available for reuse should be stored in a dry, oxygen-free environment [1].

3.2.3.4 E-beam sweeping out of region

Based on the experiments at IES-UPM, if the e-beam is swept out of the target material and impacts on the crucible sidewalls directly or even too close, the large temperature gradient and thermal stress may cause the crucible to crack.

3.2.3.5 Increasing e-beam power too quick

During the pre-melting process, increasing e-beam power too quick could lead to a non-uniform heating. In such case, some pellets have been melted while some pellets have not. The un-melted pellet only contacts with the crucible by small area (for example, only one corner of pellet), and high power could cause a huge thermal diffusion though a very small section area; then, as a result, the crucible is broken. Increasing e-beam power too quick could also cause huge volume change for some materials, and this may break the crucible either.

3.2.4 The pre-melting (dropping)

Before the evaporation process, the pellets of the target material need to be loaded into the crucible and be melted to form a homogenous solid “ingot”. In addition, this process needs to guarantee that no air bubbles remain trapped in the ingot, in order to obtain homogenous heating and avoid spatter out from the crucible during the real evaporation. This process is called the pre-melting (since the real melting takes place prior to the evaporation) or “dropping”. In this section, we describe our experimental findings about how to optimize the pre-melting.

3.2.4.1 Melt level.

Generally, the pellets of the target material are loaded in the crucible between until 30% to 80% of its internal volume is filled. Material spill-over may occur if the melt level is greater than 80% [2].

Cup Melt 60-70%

Lake Melt 70-80%

Ball Melt 80-85%

Figure 3-1 Three types of melting metal: cup melt, lake melt and ball melt, and safety limits for crucible filling [4].

Different metals tend to form different meniscus on the crucible when melt. As shown in Figure 3-1, there are three types of melting metal: cup melt, lake melt and ball melt. For the cup melt type (typical of Al), the safety filling level is lower than 70% since metal wets the crucible and may climb up the sidewalls and overspill. (see Al with Fabmate crucible in Figure 3-5)

3.2.4.2 Multistep pre-melting

For some materials (as for instance Ag), during the pre-melting process bubbles are difficult to be expelled if the material load in the crucible is too much. Therefore, a multistep pre-melting process can be used. (i.e. load 30% volume of the crucible with pellets of the target material and melt them; then fill with pellets until 60% volume of the crucible and melt them again).

3.2.4.3 On the selection of e-beam power, sweeping region and ramping velocity for the pre-melting process.

When the material is melted from pellets into a solid “ingot”, the e-beam power and ramping time need to be set. Due to the different properties of each material, these parameters vary. The basic principle is that the e-beam power should be controlled carefully and ramped slowly (i.e. increasing current no faster than around 10-20mA/s). If the e-beam power ramping velocity is too high, it could crack the crucible or cause a spatter problem due to condensed heating on the pellets. Based on our experiments at IES-UPM, it is recommended that the pre-melting of the pellets is carried out without sweeping the e-beam, since our e-beam impact area is large and thus moving it makes it easy to impact on the sidewall of the crucible.

In some cases, for some materials that need very high power to be melted, it is likely that the pellets in contact with the crucible sidewalls (or the hearth if no liner is used)

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could not be melted when using a non-sweeping e-beam impacting on the center of the target material, as the heat transmission between pellets is not very efficient (small contacted area). In this situation, sweeping is needed and should be controlled manually by an expert operator. The e-beam should be kept as far away from the hearth sidewall as possible.

Table 3-1 E-gun current (in mA) required for pre-melting metals and get different evaporation rates with an acceleration voltage of 10KV. Values determined empirically at IES-UPM.

Unit mA	crucible	Wet	sweep	melt	0.1 Å/s	1 Å/s	5 Å/s	10 Å/s
Al	No	no	no	60	200	263	384	442
Ti	No	no	no	no	55	86	146	205
Ag	TiB ₂ -BN (20 cm ³)	No	no	40	41	-	53	60
Ni	Cu pad (20 cm ³)	yes	no	30	30	115	246	330
Pd	Thicker graphite (inner 4.4 cm ³)	yes	yes	45	40	65	95	-
Au	Tungsten(7 cm ³)	yes	no	18	-	44	70	-
Ge	Copper (20 cm ³)	no	no	40	75	-	-	-
Cu	Fabmate (20 cm ³)	no	no	-	98	134	275	-

Table 3-1 lists the crucible choice, empirical e-beam current (power/10KV), and the corresponding evaporation rates for different metals at IES-UPM.

The standard procedure to perform the pre-melting is as follows:

In the first step, the e-beam power (i.e. current) is increased to the level of melting the target material (melt column in Table 3-1); then the liquid phase of the target material appears in the center region. Then, the power is kept at the melt level for a few minutes to preheat the target material and achieve a steady state in the thermal distribution in the target material.

In the second step, the power is increased to the 0.1 Å/s or 1 Å/s level and this power is used to melt all the pellets into the liquid phase. If some material (for example Pd), sublimates and cannot be melted at this power level, a higher power is used until a liquid phase appears. If the material needs sweeping to be melted, manual sweep should be used in this step. If there is an oxidation layer covering the target, (as

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for example occurs with silver oxide on the Ag target), the e-beam power needs to be increased to penetrate the oxygen layer to make the valid evaporation surface appear (see 3.5.2).

As a final step, after all pellets are melted into one ingot, the power should be increased to test the evaporation at typical rates (5-10 Å/s), and note down the parameters. For some materials, it is impossible to get high evaporation rates in our tool (see next section on the limitation of rates). In addition, the higher power in this step also helps to melt all the target material and eject the air bubbles which could be formed during the second step.

3.2.4.4 Limitations of the evaporation rate

In general, the optimum evaporation for metals is around 10 Å/s. However, for some materials, it is impossible to obtain such evaporation rates in our tool, since there are some factors that limit the evaporation rate reachable. We discuss them in the following sections.

3.2.4.4.1 E-gun output power and cooling system efficiency.

During the evaporation, the e-beam impacts on the target and produces heating in the center; meanwhile, cooling water is used inside the hearth to keep it at moderate temperature. Accordingly, when equilibrium is reached, a gradient in temperature exists from the center of target material to its rim (in contact with the crucible sidewalls and the hearth). If the water cooling has a high efficiency, when evaporating without crucible or using high cooling water flow, then the high temperature area (i.e. evaporation area) in the center of target material will be small. In this case, the maximum evaporation rate will be limited by the maximum e-beam power (maximum 10 KV*500 mA)

3.2.4.4.2 Presence of an oxide layer

Some metals such as Ag, readily react with oxygen and form an oxide crust on the metal ingot. This oxide layer does not evaporate and fully covers the surface of target material, hampering the evaporation of target material. After several evaporations, this oxide layer could cover most of the surface of the target material. As a result, the exposed area of target material will be reduced and the evaporation rate decreases.

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3.2.4.4.3 The surface shake

For some materials, such as Ge, it is hard to evaporate at rates higher than 4 Å/s. If evaporation rate is faster, the liquid metal surface shakes and causes the evaporation rate to oscillate quickly; in more extreme situations sparks of material are ejected and grains are deposited on the substrate instead of a homogeneous film. The adequate sweeping of the e-beam around the target can increase the valid evaporation area and evaporation rate, but it still cannot surpass rates higher than 5 Å/s.

In some other cases, the election of an unsuitable crucible also may induce the shake of the liquid metal surface. During the evaporation, the melted target material may “stick” on the sidewalls of the crucible since the liquid-crucible interfacial energy is lower than the liquid-vapor energy and vapor-crucible interfacial energy. Then, during evaporation, the surface of the liquid goes down due to less material in the crucible. These two forces could cause one region of the liquid near the sidewall of the crucible to suddenly fall down, and thus the liquid metal surface shakes (see 3.5.1).

3.2.4.4.4 Using small crucibles

Small crucibles (i.e. 7 cm³) hold ingots with less exposed surface to the e-beam and, as a result, less material can be evaporated at time. Therefore, it is estimated that the evaporation rates achievable would be lower. However, in the case of our tool since the cooling efficiency is lower for small crucibles (only the bottom of the crucible touches the hearth and thus gets cooling), the real evaporation rate is a trade-off between both effects.

3.2.5 Evaporation process design

After the pre-melting, the metal has been melted to form an ingot of the target material without bubbles, and almost all the parameters of the evaporation process have been tested; then a new PID controlled evaporation process for each metal needs to be set. This includes four steps: 1) temperature ramping up and soaking; 2) shutter opening; 3) deposition; and 4) temperature ramping down.

3.2.5.1 Ramp up and soak

The ramp and soak consists in the successive rises and plateaus of the e-beam power needed to melt and outgas the target material and reach the desired evaporation rate in a smooth and reproducible manner so that the thin film deposition starts in a

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reproducible and controlled way. Basically, there are 3 different types ramping up process [4]

3.2.5.1.1 Standard ramp up and soak

As shown in Figure 3-2, in the standard ramp and soak there are four steps (ramp1, soak1, ramp2 and soak2) before shutter opens and the deposition starts. In order to avoid splashing or a too fast change during the ramping up process, a preheat process –ramp1 and soak1– is carried out to fully melt the metal. Typically, it is required to ramp up the power slowly in around 3 minutes and then soak (hold the power constant) for around 30s. After the equilibrium of target material is built, the second ramp (i.e. ramp2) is carried out, when the target material is rapidly (30s) heated to reach the temperature at which the desired evaporation rate is reached. Finally, around 10-30s soaking time is used to fully stabilize the deposition rate. After that, the shutter is opened and the deposition starts.

Figure 3-2 Standard ramp up and soak process.

3.2.5.1.2 Overshoot of the e-beam power in the initial ramp

In some cases, for those materials which easily react with oxygen and form an oxide cover layer on the target material, an initial overshooting of the e-beam power (during ramp 1) is needed to penetrate or melt away the oxidation layer. A ramp and soak process following this strategy is presented in Figure 3-3. As this figure shows, the final ramp 1 e-beam power and thus the soak 1 e-beam power will be even higher

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than temperature in the soak2. Therefore, the corresponding soak1 temperature could be would be typically higher than the melting point of the target material.

Figure 3-3 Process with overshoot of the e-beam power in the initial ramp.

3.2.5.1.3 Cost-effective processes for noble metals

For noble metals, such as Au or Pd, as they are very expensive any material waste during the preheating process should be considered and avoided. In these cases, a process similar to the standard process in Figure 3-2 is adapted to minimize material loss. Therefore, as shown in Figure 3-4, the final temperature of ramp2 and soak2 should be chosen to reach an initial evaporation rate of just $0.1 \text{ \AA/s}$. In the case of our EBPVD tool, this process is especially difficult since small crucibles are used for Au and Pd, which are inefficiently cooled. This fact makes it difficult to control accurately the evaporation rate since inefficient cooling causes the heat accumulating in the liner and the evaporation rates changing with time going. So, in order to reproduce and control very low evaporation rates ($\sim 0.1 \text{ \AA/s}$), the e-beam power needs to be increased very slowly (5~10 min) to build the equilibrium state, as shown for ramp1 in Figure 3-4

Figure 3-4 Ramp and soak process for noble metals.

3.2.5.2 Deposition

After the shutter opens, the deposition starts. In this process, the proper PID parameters need to be set on the evaporation controller so that the evaporation rate can be effectively controlled (i.e. no oscillations or overshooting appear, keeps stable during the process, does not drift, etc.) and the desired thickness of the target material is deposited on the substrate. Once that is accomplished, the shutter will close. Caution should be taken with the e-beam shift problem (see section on e-gun problems in Chapter 2). In addition, in some cases (see Ag), the e-beam drills a hole in the center of the target material which could break the hearth, due to the large consumption of target material or non-sweeping. If this is likely to happen, more material needs to be filled or a change in the sweeping style is required.

3.2.5.3 Ramping down the e-beam power

Usually, after the shutter is closed, the e-beam can be stopped immediately. However, for materials that have a large difference between solid phase density and liquid phase density (such as Al or Ge), if the phase transformation is too quick, a hole or a pillar in the center of target ingot may be left due to the volume shrinkage or expansion. If a hole is left occurs, it could cause the e-beam to impact directly on the bottom of the crucible or hearth (see Al in Figure 3-7); on the other hand if a pillar is formed, it could leave stuck the rotation of the multi-hearth (see Ge in Figure 3-40).

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3.2.6 Calculation of material costs

In order to estimate the material cost of an evaporation process, a preliminary experiment was carried out with Al. The weight of the crucible loaded with Al was measured before and after the evaporation 3 times. In addition, the thickness of the deposited film was measured by a profilometer. Then the mass cost per nm of Al could be calculated. The mass cost per nm of Ti is calculated in the same way.

The comparison between the results obtained for Ti and Al shows that the ratio of mass cost and the ratio of density have positive correlation. Therefore, if it is supposed that such correlation index is a constant for other metals, such as Au or Pd, the material costs can be estimated without experiments. The results of these calculations are shown in Table 3-2.

Table 3-2 The cost of material in mass and price per nm.

material	price	Density (Solid)	Density (Liquid)	thickness	mass evaporated	mass cost	cost
	€/g	g/cc	g/cc	Å	g	mg/nm	€/nm
Al	1.00	2.70	2.38	1969.00	0.60	3.05	0.00305
Ti	5.00	4.51	4.11	966.67	0.58	5.98	0.0299
Ag1	1.00	10.49	9.30	-	-	13.92	0.01392
Ag2	3.00 ¹	10.49	9.30	-	-	13.92	0.04176
Au	45.00	19.30	17.31	-	-	25.61	1.15241
Pd	20.30	12.02	10.38	-	-	15.95	0.32377

¹ It is more expensive due to the supplier company and the higher purity of pellets.

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Ni	1.12	8.91	7.81	-	-	11.82	0.01324
Pt	57.80	21.45	19.77	-	-	28.46	1.64511
Ge	33.00	5.323	5.6	-	-	7.06	0.23308
Cu	0.79	8.96	8.02	-	-	11.89	0.00939

Since it is required to fill 30% - 80% volume of crucible with material pellets to avoid the cracking the crucible, the mass needed and its cost are calculated. The results based on filling 50% of the volume of 3 types of crucible are listed in Table 3-3 and Table 3-4.

Table 3-3 Required mass for the initial evaporation with 3 types of crucible.

Unit g	crucible 20 cm ³ inner 14.6cc				crucible 7 cm ³ inner 4.4 cm ³				crucible 4 cm ³ inner 2.1 cm ³			
material	solid		liquid		Solid		liquid		solid		liquid	
	14.6	50%	14.6	50%	4.4	50%	4.4	50%	2.1	50%	2.1	50%
Al	39.4	19.7	34.7	17.3	11.9	5.9	10.5	5.2	5.7	2.8	5.0	2.5
Ti	65.8	32.9	60.0	30.0	19.8	9.9	18.1	9.0	9.5	4.7	8.6	4.3
Ag	153.2	76.6	135.8	67.9	46.2	23.1	40.9	20.5	22.0	11.0	19.5	9.8
Au	281.8	140.9	252.7	126.4	84.9	42.5	76.2	38.1	40.5	20.3	36.4	18.2
Pd	175.5	87.7	151.5	75.8	52.9	26.4	45.7	22.8	25.2	12.6	21.8	10.9
Ni	130.1	65.0	114.0	57.0	39.2	19.6	34.4	17.2	18.7	9.4	16.4	8.2
Pt	313.2	156.6	288.6	144.3	94.4	47.2	87.0	43.5	45.0	22.5	41.5	20.8
Ge	77.7	38.9	81.8	40.9	23.4	11.7	24.6	12.3	11.2	5.6	11.8	5.9
Cu	130.8	65.4	117.1	58.5	39.4	19.7	35.3	17.6	18.8	9.4	16.8	8.4

Table 3-4 Cost for evaporation with 3 types of crucible.

Unit €	crucible 20 cm ³ inner 14.6cc				crucible 7 cm ³ inner 4.4 cm ³				crucible 4 cm ³ inner 2.1 cm ³			
material	solid		liquid		solid		liquid		solid		liquid	

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	14.6	50%	14.6	50 %	4.4	50 %	4.4	50 %	2.1	50 %	2.1	50 %
Al	39.4	19.7	34.7	17.3	11.9	5.9	10.5	5.2	5.7	2.8	5.0	2.5
Ti	329.0	164.5	300.0	150.0	99.2	49.6	90.4	45.2	47.3	23.7	43.2	21.6
Ag	153.2	76.6	135.8	67.9	46.2	23.1	40.9	20.5	22.0	11.0	19.5	9.8
Au	12680	6340	11373	5686	3821	1911	3427	1714	1824	912	1636	818
Pd	3563	1781	3076	1538	1074	537	927	464	512	256	443	221
Ni	145.7	72.8	127.7	63.9	43.9	21.9	38.5	19.2	21	10.5	18.4	9.2
Pt	18101	9051	16684	8342	5455	2728	5028	2514	2604	1302	2400	1200
Ge	2564.6	1282.3	2698.1	1349	772.9	386.4	813.1	406.6	368.9	184.4	388.1	194
Cu	12680	6340	11373	5686	3821	1911	3427	1714	1824	912	1636	818

3.3 Aluminum

3.3.1 Melting and pre-evaporation

The evaporation of Aluminum using E-beam is excellent. The only problem is the selection of the crucible since it alloys with many metals and wets graphite.

At IES-UPM, aluminum was evaporated with a graphite crucible. Since aluminum is known to “wet” graphite, the melt level needs to be reduced to avoid spill-over. Crucibles should only be filled to 70% of their height rather than 80% of the total volume. The Figure 3-5 shows that, if the aluminum is over filled, the crucible will be end cracked. When a spill-over occurs, a thermal short is created between the crucible and the hearth and the resultant thermal stress causes the crucible to crack

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Figure 3-5 Fabmate crucibles with different filling levels used to evaporate Al .

On the contrary, if the amount of aluminum is not enough, the crucible can be broken too (as shown in Figure 3-6). The reason could be that 1) since the e-beam impact area is not controlled well (it is not a small point, see chapter 2), the e-beam could impact on the crucible sidewalls as its diameter tapers towards the bottom; 2) the aluminum does not perfectly wet the crucible and the temperature difference between the wet part and non-wet part creates sufficient stress as to eventually crack the liner.

Figure 3-6 Cracked crucible after the evaporation of Al with a low filling level .

Another problem of using aluminum is that, after the evaporation, a hole is formed in the center of the ingot (as shown in Figure 3-7a.). If this happens, in a subsequent evaporation, before the aluminum is melted, the e-beam could impact on the bottom of crucible directly and damage it. The reason behind the formation of such hole in the center of the ingot can be explained considering that a gradient in temperature exists between the center of the ingot (hot) and the rim (cool since it is contact with the refrigerated hearth). This gradient in temperature produces an opposite gradient in density (the cooler molten Al is denser than the hotter Al in the center). When the evaporation finishes and the e-beam power is shut down, the cooler Al at the rim solidifies fast, leaving less dense liquid Al in the central region. As solidification progresses from the rim to the center, less mass of Al freezes and thus the height of the solid in those areas decreases. At the very center of the target, where the hotter

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(i.e. least dense) molten aluminum was seating, the Al mass solidifying is clearly lower than at the rim, and thus when freezing shrinks to create the center hole. Obviously, this process will occur with materials that exhibit a clearly lower density in liquid state than in solid. The solution to this problem is to decrease e-beam power during the cooling process smoothly as a ramp down process, instead of shutting down e-beam immediately. Figure 3-7b shows the result with such a ramp down process; it is obvious that the hole is much smaller than the case with abrupt shut down of the e-beam.

Figure 3-7 Hole formed in Al ingot after evaporation, a) cooling without ramp down; and b) cooling slowly with a ramp down process.

After several experiments, it turned out that evaporating Al in the fabmate crucible is was not easy to be well controlled. In addition, the fabmate crucible could only be used for a few runs since a reaction occurs to produce aluminum carbide, forming a transparent, yellowish film on the surface of the aluminum ingot. When such film covers the entire surface of the aluminum target, the evaporation rate is reduced to near zero.

Therefore, it was decided to evaporate Al in hearth directly without any crucible. As shown in Figure 3-8, Al is melted and evaporated in the hearth perfectly. Although Al is highly reactive when molten, it does neither wet nor react with the copper hearth, since the hearth is cooled and therefore the temperature on the contact interface is not so high as to make an alloy. In order to avoid high temperatures on the contact interface, the e-beam is not swept at high power ($>60\text{mA}$ @ 10kV).

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Figure 3-8 Evaporation of Al without crucible, directly in the hearth.

Figure 3-9 Evaporation of Al with a Cu crucible, e-beam sweep is restricted to the center region.

Since the hearth is made of copper, a Cu crucible was machined to test it as an alternative for the direct evaporation in the hearth. The result is shown in Figure 3-9. The Al alloys with Cu crucible during the evaporation, although it does not alloy with Cu hearth. The reason could be that the hearth is effectively cooled by the cooling water and consequently its temperature is low enough to inhibit the alloying reaction. On the contrary, the Cu crucible is not in direct contact with the cooling water causing a higher temperature during the evaporation and thus alloying.

3.3.2 Auto evaporation with PID control

Figure 3-10a shows that the evaporation rate can be kept stable at $10 \text{ \AA/s}$ with fabmate crucible. However, when Al is evaporated in the hearth directly, the evaporation rate fluctuates a lot, as shown in Figure 3-10b. The reason for such behavior could be that, without crucible, it is required to use a high e-beam power to evaporate the Al target and such high e-beam power is harder to control by the genius and PID feedback control system. The sensor detecting period could also have an influence on the figure, since a short detecting period could make the PID system too sensitive, causing the fluctuations seen in the evaporation rate. However, in this

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case, although the detecting period has been set longer, the fluctuation does not disappear.

Another drawback of evaporating Al without crucible is that the maximum power of the e-gun limits the highest evaporation rate reachable. Although it is possible to evaporate Al at 10 Å/s at the beginning (using 423mA@10kV), with time going, of the rate steadily decreases, and more power is needed to keep up the same rate. The reason for this is that as the Al in the ingot decreases the cooling efficiency increases. Finally, the required e-beam power will be out of range (>500mA.). In addition, higher e-beam powers lead to a higher risk of Cu/Al alloying if any copper part is accidentally reached by the e-beam.

Figure 3-10 Rate monitoring during the evaporation of Al with fabmate crucible (left) and directly in the hearth without crucible (right).

In summary, evaporating Al with a fabmate crucible tends to break the crucible after a few runs and has the risk of forming Al-C compounds but evaporation rate is well controlled and a higher rate can be obtained. On the contrary, evaporating without crucible does not have problem that cracking the crucible but evaporation rate is not as stable and limited on 5 Å/s.

3.3.3 Other Tips

Al also getters oxygen to form oxide layers if any oxygen is present during deposition. Therefore, after several evaporations, the oxide layer could grow thicker, cover the liquid Al during the evaporation, and cause the decline in the evaporation rate.

When evaporating aluminum the e-beam is not swept, as explained above. However, sweeping can be used to initially melt down the pellets with a lower e-beam power.

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3.4 Titanium

3.4.1 Melting and pre-evaporation

Figure 3-11 Evaporation of titanium in the fabmate crucible (left) and without crucible (right).

Figure 3-12 Relationship of vapor pressure and temperature, and Ti melting point.[4] the orange line is the minimum vaporant pressure when the quartz sensor can detect the deposition rate, the green line is the minimum vaporant pressure to deposited film at a reasonable rate. The green line is the maximum temperature that liner can endure.

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At IES-UPM, Titanium has been evaporated in Fabmate crucible and without crucible as shown in Figure 3-11. In both cases Ti was evaporated properly. As shown in Figure 3-12, the melting point is close to the evaporation temperature (marked as a green line in Figure 3-12, which is about 10^{-5} atmospheres). Therefore, when melting the Ti from pellets to ingot, the Ti will sublime a little bit before melting (this was anticipated in Table 3-1, where some rate was measured before the melting was observed). This phenomenon does waste some material, so the melting process should be carried out quickly.

The sweeping style of the e-beam is helpful to melt the pellets quickly, since the pellets near the cooled walls of the hearth or crucible are hard to melt without impacting them directly with the e-beam. However, when melting Ti pellets in the graphite crucible, in order to avoid impacting e-beam on the crucible directly and cracking it (what happened for Al with the graphite crucible, see Figure 3-6), the sweep is limited only to the center region. As a result, some pellets near the sidewalls of the fabmate crucible cannot be melted with low e-beam power as shown on Figure 3-11. Those pellets may melt unexpectedly after several evaporations, and thus it may cause a shake wave and make the PID control more difficult. One solution to this problem is to use a very high power e-beam to melt the central part of the Ti ingot, and let the heat transfer from the center to those rim pellets. However, since the evaporation temperature and melting point of Ti are very close (as shown in Figure 3-12), such high e-beam powers will evaporate Ti quickly and waste a lot of material.

Another solution is to evaporate Ti without crucible, and in this case it is not recommended to use a high power e-beam that could impact on the hearth wall. The pellets could be melted slowly into an ingot by again sweeping the beam around the center region.

As shown in Figure 3-13, there is a tiny hole in the center of the ingot after evaporating Ti without crucible. The formation mechanism is the same as with Al. However, since it is tiny, in this case there is no risk that the e-beam impacts on the bottom of the hearth; and thus it has no influence on the next evaporation.

Figure 3-13 Ti ingot after evaporation.

3.4.2 Auto evaporation with PID control

Figure 3-14 Rate monitoring during the evaporation of Ti with fabmate crucible (left) and without crucible (right).

Figure 3-14 shows that Ti can be evaporated with high control at 5 Å/s either with fabmate crucible or without crucible. However, it has been observed that in some cases, as shown in Figure 3-15, the initial rate suddenly decreases. The reason behind this drop could be that at the starting point only the central part of Ti has been transformed into liquid phase and is evaporating; with power increasing, the whole ingot of Ti transform into liquid phase and this transformation absorbs heat, so that the temperature in the center region decreases in a second, and leads to the rate decrease. The solution is increasing the soaking temperature and time, thereby letting the whole ingot transform into liquid before opening the shutter (ie. deposition), although this wastes some material.

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Figure 3-15 Rate monitoring during the evaporation of Ti without crucible and the initial sudden decrease in rate.

Titanium is very eager to absorb oxygen and form Titanium oxide. Therefore, in order to get the purest Ti deposition, a high e-beam power or a longer soaking time is used to capture any oxygen still present in the chamber before opening the shutter. In fact, when Ti starts to evaporate a drop is observed in the Chamber pressure as a result of its reaction (i.e. capture) with oxygen.

3.5 Silver

3.5.1 Melting and pre-evaporation

As shown in Table 3-7, Ag is an excellent material for EBPVD, being the recommend crucibles Al_2O_3 or Mo. Since it was difficult to find a commercial 20 cm^3 Mo crucible, alumina crucibles recommended by E-beam manufacture were initially used. However, based on the experiments developed at IES-UPM, it turned out to be almost impossible to evaporate Ag properly with a Al_2O_3 crucible. Figure 3-16 shows that the Al_2O_3 crucible is broken after melting Ag. The reason is unclear but it could be due to a small fraction of the e-beam area impacting on the crucible directly, despite the e-beam power is very low (from 0 to 20mA in 1 min.). Therefore, another melting experiment was carried out without sweeping e-beam. The results are shown in Figure 3-17. Despite the e-beam is not swept and more Ag was filled in the crucible to prevent e-beam impact on the crucible wall directly, the Al_2O_3 liner cracks again. This could be due to the problem mentioned in chapter 2 about the size of the e-beam impact area. Since the size of the e-beam is much larger than 3x3 mm (~9x9mm), despite it is located at the center of the crucible there is always a “branch” of the e-beam touching the rim of the crucible (as can be observed in Figure 3-17.d).

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It seems that even this small power is enough to crack alumina crucibles in our EBPVD tool.

Figure 3-16 (Top) Evaporation of Ag with Al_2O_3 crucible and sweeping e-beam trajectories. (Bottom) Resulting cracked crucibles.

Figure 3-17 Evaporation of Ag with Al_2O_3 crucible; the e-beam was not swept. (a) Initial filling of the liner; (b) hearth after evaporation where leaked Ag is visible; (c) crack in the liner from where Ag has leaked; (d) final aspect of the ingot where the fingerprint of the e-beam is observable.

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After several tests, it became obvious that it was impossible to evaporate Ag in our tool without cracking the Al_2O_3 crucible. As a result, Mo crucibles were chosen to evaporate Ag. However, we were only able to find small 7 cm^3 crucibles with conical shape in the market.. In this case, in order to let the 7 cm^3 Mo crucible fit the 20 cm^3 hearth, a copper adapter was machined (Figure 3-18) with the dimensions shown in Figure 3-19.

Figure 3-18 (Left) Cu adaptor and (right) Cu adaptor with 7cm^3 Mo crucible.

Figure 3-19 Dimensions of the Cu adapter.

Figure 3-20 shows the whole process for evaporating Ag in the small Mo crucible with a Cu adapter. The black points are e-beam current (*ie. power.*) and the red

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points correspond to the deposition rate. As shown in the graph, Ag evaporation rate could reach $15 \text{ \AA/s}$ and the Mo crucible neither cracks nor reacts with Ag. It seems that the 7cm^3 Mo crucible with a Cu insert is a good solution for evaporating Ag in our EBPVD tool. However, analyzing the relationship between current and deposition rate and time (not shown in Figure 3-20), we can find that after 15 minutes of process, a slight increase in the e-beam current has a big influence on the deposition rate. This situation makes the PID feedback system to have problems in the evaporation control, since it is too sensitive at this stage and, contrarily, very insensitive at the beginning (for times shorter than 15 min). The reason behind this phenomenon could be that the copper adaptor does not fully contact the hearth and crucible, and therefore the heat transfer is not good. At the beginning, the heat builds up in the center of the ingot and only heats the copper insert slowly giving rise to the “insensitive” stage. After 15 minutes, the thermal equilibrium has been established and any new heat is only used to evaporate Ag with relatively low cooling efficiency, causing the deposition rate to change significantly with small increases in the e-beam current.

Figure 3-20 Evaporate Ag in Mo crucible with another Cu pad.

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In order to tackle the problem of the difficult rate control, another Cu adapter was designed with the goal of increasing the cooling efficiency. This design, which is shown in Figure 3-21 and Figure 3-22, essentially consist in removing the bottom of the adapter to achieve direct contact of the Mo liner with the cooled bottom of the hearth. Unfortunately, the results of this evaporation were similar to those using the first Cu adapter design.

Figure 3-21 Dimensions of the second design of the Cu adapter.

Figure 3-22 (Left) Second Cu adaptor and (right) second Cu adaptor with 7cm³ Mo crucible.

Since using 7cm³ Mo crucible and Cu adapters to evaporate Ag produced problems to control the deposition rate, we decided to evaporate Ag in the hearth directly. Figure 3-23a shows this evaporation of Ag without crucible. In this approach, we found that only the center region of Ag ingot was melted and evaporated,; whilst the rim of the Ag ingot still remained in solid phase, as Figure 3-23b shows. As in other cases, this is again the result of the high cooling efficiency without crucible.

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Obviously, the e-beam produces a hole in the ingot since only center Ag has been evaporated and the solid Ag in the rim cannot fill the gap.

Figure 3-23 Evaporation of Ag without crucible, a) while being evaporated, b) after evaporation. E-beam mainly swept on the center region.

As a result of this problem, only a limited amount of Ag in the central region can be evaporated, although the hearth volume is 20cm^3 . Therefore, if the evaporation needs to consume a lot of Ag, –for example, for depositing a 1500nm Ag film– the e-beam will “drill” a hole in the center of the ingot and may reach the bottom of the hearth and damage the machine.

The high cooling efficiency also limits the deposition rate. As shown in Figure 3-25, with 89.7% of 500mA e-beam current output, the deposition rate is only of $5\text{ \AA/s}$. With the progress of the evaporation, less Ag is left in the center of the ingot (i.e. the hole grows deeper), and the e-beam is close to the bottom of the hearth causing more strong cooling efficiency. As a result, more current is required to keep the $5\text{ \AA/s}$ deposition rate until the current limit is out of range (no more than 500mA) and e-gun halts. In addition, as sketched in Figure 3-24, the solid Ag near the hole restricts the Ag evaporation angle and thus it reduces the deposition rate for some areas of the substrate holder and changes tooling factor since substrate and sensor are not located on top of the center of the hearth.

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Figure 3-24 Comparison of material being evaporated from the whole ingot surface and center region only.

Figure 3-25 Rate monitoring during the evaporation of Ag without crucible by PID control and e-beam sweeping in the center region.

In order to avoid the hole that appears in the center of the ingot, a bigger sweeping region of e-beam is required. However, a bigger sweeping region induces fluctuations in the depositing rate causing PID control to be more difficult (see description of the sweeping problem in chapter 2). Moreover, considering the high cooling efficiency in the hearth, the e-beam power density will be not enough to evaporate Ag near the cooled walls of hearth at a rate of 5Å/s . In addition, sweeping a high power e-beam ($500\text{mA}@10\text{KV}$) close to the hearth walls is risky. For all these reasons, we concluded that the evaporation of Ag directly in the hearth is not suitable to deposit films thicker than 1500nm . At IES-UPM, fabmate crucibles have also been tested for evaporating Ag. As shown Figure 3-26, Ag was successfully evaporated in a fabmate crucible. Since this crucible reaches a good balance in heat transfer, the deposition rate could reach a high value using a reasonable e- beam power. However, since Ag partly “sticks” on the wall instead of fully “wetting” the fabmate crucible,

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during the evaporation the part of Ag sticking may suddenly fall leading to fluctuations of the molten Ag surface. As a result, the deposition rate unexpectedly suffers ups and downs rendering the PID control more difficult (see 3.2.4.4.3). In addition, after pre-melting some bubbles seem to remain at the bottom of the ingot, as shown in Figure 3-26b. As a result of this, it is required to pre-melt Ag using the multistep process as described in 3.2.4.2.

Figure 3-26 Evaporation of Ag with fabmate crucible (a) top view of the Ag ingot in the liner; (b) bottom side of the ingot.

In a final quest for a process not subjected to the aforementioned limitations, Ag was evaporated in BN-TiB₂ intermetallic crucible. Such crucible shows the advantages of ceramic liners (i.e. they do not react with target material), whilst it is not so fragile as Al₂O₃. As a result, as shown in figure Figure 3-27 a successful, fast and reliable evaporation process could be developed for Ag.

Figure 3-27 Evaporation of Ag with a BN-TiB₂ crucible. (Left) top view of the Ag ingot in the liner; (b) ingot glow during evaporation.

3.5.2 Auto evaporation with PID control

Figure 3-28 Evaporation of Ag with BN-TiB₂ crucible after several evaporations; (a) before evaporation; (b) during evaporating; and (c) after evaporation.

As shown in Figure 3-28a and Figure 3-28b, after several evaporations there is an evident matte oxide layer covering the Ag: the reason is that Ag is eager to react with oxide in the atmosphere, especially during the opening of the chamber to load wafers or if the Ag target is kept out of the vacuum chamber. Comparing Figure 3-28 with Figure 3-27, we can see that the oxide layer (matte region) covers more area after several evaporations. As a result, a high power e-beam is required to penetrate the oxide and access the liquid Ag layer. Otherwise, the oxide layer will block the evaporating Ag even though the temperature is sufficient to melt Ag. Therefore, during the pre-heating process of evaporation by auto-control, the e-beam power of ramp1 should be higher than ramp 2 to crack the oxide layer firstly, as shown in Figure 3-3. Moreover, during the evaporation phase itself, with an oxide layer covering more area, less evaporating area is available in the ingot. Therefore, in order to evaporate Ag at the same rate, a higher e-beam power is required. Figure 3-29 shows that Ag was evaporated by PID auto control at a deposition rate $10\text{\AA}/\text{s}$ properly. However, the e-beam output current increase to 57.1% since more oxidation layer block evaporating Ag and less effusion cell is obtained.

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Figure 3-29 Rate monitoring during the evaporation of Ag by PID auto control using an intermetallic crucible.

3.5.3 Other tips

The e-beam shift problem (see chapter 2) could break the crucible as it is shown in Figure 3-30. Therefore, e-beam sweeping should be confined to the center region (or no sweeping) when evaporating Ag.

Figure 3-30 Crucible is broken by the e-beam shift problem.

Figure 3-31 Evaporation of Ag in 7cm³ Al₂O₃ crucible with Cu adapter.

Figure 3-31 shows the results of evaporating Ag in a 7cm³ Al₂O₃ crucible with a Cu adapter. The alumina liner ends broken again. It seems that Al₂O₃ crucibles are too fragile for the configuration of the e-beam in our tool.

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3.6 Gold

3.6.1 Melting and pre-evaporation

In the reference manual from a key e-gun supplier (Ferrotec), it is recommended to evaporate Au with Al_2O_3 , BN or vitrified carbon crucibles. Therefore, an Al_2O_3 crucible was first used to evaporate Au. Since the initial amount of Au is limited by its high cost (see Table 3-4), gold is totally uneconomical to be evaporated in a 20cm^3 . This is so because the limited amount of gold in the crucible would make very likely that the e-beam impacts on the bottom of crucible. The result of such melting of Au pellets in a 20cm^3 liner (and subsequent crucible cracking) is shown in Figure 3-32.

Figure 3-32 Evaporation of Au in a 20cm^3 Al_2O_3 crucible; the crucible cracks due to an inadequately low initial amount of Au.

In order to lower the initial cost and once know the fragility of alumina liners, a 7cm^3 tungsten crucible was selected to evaporate Au. Tungsten crucibles are almost indestructible, as confirmed by Figure 3-33, which shows that after evaporating, the 7cm^3 tungsten crucible remains undamaged.

Figure 3-33 Evaporation of Au in a 7cm^3 tungsten crucible.

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Since the 7 cm³ tungsten crucible does not fit the 20 cm³ hearth, it is located in the center, contacting with the bottom of hearth only. As a result the cooling efficiency is low and heat will accumulate with time going during the evaporation. This is similar to the silver evaporating in 7 cm³ Mo liners. When doing the initial pre-melting of the pellets, it is required to increase the e-beam power slowly in the first 10 minutes.

3.6.2 Auto evaporation with PID control

Figure 3-34 shows the evaporation of Au in a 7 cm³ tungsten crucible with a set point for the deposition rate fixed at 2.5 Å/s. It can be seen that there is a clear overshoot of the deposition rate at the beginning, whose amplitude decreases later. The reason for such is that the low cooling efficiency causes heat accumulation and a feedback delay, and therefore better PID parameters could decrease the overshoot. However, since this overshoot does not last long in the end it does not have a big influence on the deposited film thickness. Consequently, no further experiments were carried out for its improvement.

Figure 3-34 Rate monitoring during the evaporation of Au in a 7 cm³ tungsten crucible.

Since Au is very expensive, in order to avoid wasting material, the e-beam power for preheating should be lower than that of the depositing temperature and higher than the melting point (process described in 3.2.5.1.3).

3.7 Palladium

3.7.1 Melting and pre-evaporation

In the reference manual from Ferrotec, it is recommended to evaporate Pd with an Al₂O₃ crucible. According to our experiments with Ag and Au, alumina crucibles

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have revealed to be extremely fragile in our EBPVD tool and thus will crack again. As an alternative option, fabmate crucibles could be used to evaporate Pd. Due to the high cost of Pd, a 7 cm³ fabmate crucible was used to reduce the initial material needed and thus cost. Figure 3-35 shows the result of this evaporation of Pd in a 7 cm³ fabmate crucible. Obviously, the crucible is cracked, the reason is unclear, but again it could be due to the e-beam impacting on the crucible directly since the size of impacting point is big. In a second attempt Pd was evaporated in 15cm³ graphite crucible with extra thick walls (Figure 3-36). As the thickness of crucible wall is double, the crucible remained undamaged. The result is shown in Figure 3-36.

Figure 3-35 Evaporation of Pd in a standard 7 cm³ fabmate crucible.

Figure 3-36 Evaporation of Pd in a 15cm³ graphite crucible; the thickness of crucible sidewall is double.

As shown in Figure 3-37, the melting point of the Pd lies above the typical vapor pressure used during evaporation. This implies that Pd sublimates instead of evaporating. However, in order to obtain a high deposition rate, a temperature higher than melting point is required. As a result, the process of pre-melting Pd pellets into an ingot is necessary. During this process, the Pd pellets will start sublimating before being melted. A high e-beam power which can obtain a deposition rate of 2Å/s is

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required to melt all the Pd pellets in the crucible and thereby the waste of Pd is inevitable. In order to minimize the waste of Pd, the pre-melting process is carried out as quickly as possible. As a result, some pellets at the rim maybe not fully melted together in the ingot (as shown in Figure 3-38) since the temperature reached on that location is lower than melting point of Pd. The presence of those pellets can disturb the stability of evaporation in subsequent processes.

Figure 3-37 The relationship of vapor pressure and temperature and Pd melting point.[4]

Figure 3-38 Pd ingot after pre-melting where some pellets are still identifiable.

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Since the 15 cm³ crucible is only in contact with the bottom of hearth and the thickness of its walls is double than standard, the cooling efficiency is low and the heat will accumulate during the evaporation of Pd. It is a situation similar to the evaporation of Au in a 7 cm³ tungsten crucible. Analogously, when carrying out the initial pellet pre-melting process, it is better to increase the e-beam power slowly along the first 10 minutes of the process.

3.7.2 Auto evaporation with PID control

The evaporation of Pd by PID auto control is similar to the evaporation of Au in a 7 cm³ tungsten crucible, since both of them have low cooling efficiency and thereby a feedback delay.

3.8 Nickel

In the reference manual from Ferrotec, it is recommend evaporating Ni with Al₂O₃, BeO or vitreous carbon crucible. Since alumina crucibles always crack in our tool and the 20 cm³ BeO and vitreous carbon could not be found on the market, we decided to use a home made 20 cm³ Copper liner to evaporate Ni.

Figure 3-39 Evaporation of Ni in a Cu crucible; a) with low e-beam power and no sweeping; b) with high e-beam power and sweeping.

Figure 3-39a shows the result of evaporating Ni with low e-beam power and no sweeping. After the evaporation, the Ni ingot could be unloaded from the Cu crucible, and thus it seems that Ni does neither alloy nor react with Cu. However, after the Ni was evaporated with high e-beam power and sweeping (as shown in Figure 3-39b), the Ni ingot could not be unloaded from the crucible, suggesting that Ni alloys with Cu under high e-beam power. This experiment, in combination with the evaporation of Al in a Cu crucible, show evidences that high e-beam power

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impacting on any location near the Cu crucible or hearth could promote metal alloying with Cu and damage the crucible or hearth.

3.9 Germanium

3.9.1 Melting and pre-evaporation

In the reference manual from Ferrotec, it is recommended evaporating with alumina crucibles. Again, since the use of Al_2O_3 always resulted cracked liners in our tool, fabmate crucible were tested instead to evaporate Ge. In order to minimize the amount of Ge needed at the beginning, a 7 cm^3 fabmate crucible with a Cu adapter was selected for the initial tests. Figure 3-40 shows the result of this experiment. It can be seen that the fabmate crucible is undamaged and a “tail” of Ge appears in the ingot after evaporation. The reason for this could be the recrystallization of liquid Ge in the center. The density of liquid Ge is higher than solid Ge and, as a result, if the liquid Ge in rim region transforms to solid and leaves the hot liquid Ge only in the center, all the volume expansion accumulates in the center, and then the “tail” appears. It is just the opposite phenomenon causes the holes or voids when evaporating Al in fabmate liner (see Figure 3-5). This “tail” could grow higher than the level of the hearth, and get the rotation stuck when trying to change the target material.

Figure 3-40 Evaporation of Ge in a 7 cm^3 fabmate crucible with a Cu adapter.

Since the deposition rate is limited by the small evaporating area of the Ge target material in a 7 cm^3 crucible, the highest deposition rate with Ge in our tool is around 1 Å/s . If using more power, the Ge liquid will spill causing a splash of Ge in the chamber. In order to increase the evaporated area of Ge and obtain higher deposition rate, a 20 cm^3 Cu crucible was used to evaporate Ge. Figure 3-41 visually presents the results of this experiment. Small Ge particles can be seen on the liner walls in

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Figure 3-41b and Figure 3-41c, indicating that high e-beam power could cause Ge splashes in the chamber. The e-beam is only located in the center to avoid the e-beam heating the Cu crucible excessively and damaging it, ash appended with Al (see Figure 3-9). As shown in Figure 3-41c, after evaporation there is only a peak in the center of Ge target instead of a long tail; this is due to the fact that a smooth ramp down process was carried out after the evaporation was finished. In this way Ge cools down slowly, so the liquid Ge recrystallizes to solid phase step by step and more uniformly.

Figure 3-41 Evaporation of Ge in a Cu crucible, a) before evaporation, b) evaporating, c) after evaporation.

3.9.2 Auto evaporation with PID control

Considering the splash problem of Ge with the high e-beam power, the highest deposition rate that Ge could reach was $4.5 \text{ \AA/s}$. However, evaporating Ge at this deposition rate is unstable. This could be due to the fact that more germanium oxide is formed on the surface of the liquid Ge at high powers and this restricts the ingot area effectively contributing to the evaporation. Another possibility is that the low volume of material loaded in the liner forces the gradient of temperature to change very fast as material leaves the crucible and leads to a drastic reduction in the evaporation rate after several processes. Therefore, in auto evaporation mode with PID control, the set-point of deposition rate is limited to $2.5 \text{ \AA/s}$ to avoid splashing Ge.

3.9.3 Other tips

20 cm^3 Fabmate crucibles were not used since a volume lower than 30% of the crucible was loaded with Ge and this may cause the crucible cracking. As copper crucibles are stiffer, they were selected. It is supposed that fabmate crucibles could be used if more Ge was loaded.

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3.10 Copper

At IES-UPM, a fabmate crucible is used to evaporate Cu, since the standard recommendation is Al_2O_3 – and these always crack in our tool– and other options such as Mo or Ta crucibles are very difficult to find in the market in 20 cm³. As shown in Figure 3-42, the fabmate crucible does not crack after evaporation and the melted Cu does not stick on the fabmate wall. Copper vapor deposits on the inner wall of crucible and the forms a film and this film connects with the liquid Cu during the evaporation. As evaporation evolves, the liquid surface level decreases and this connection is torn (as circled in Figure 3-42), causing a huge fluctuation on the molten Cu surface. As a result, the situation with copper is similar to evaporating Ag in a fabmate crucible where PID auto control is difficult.

Figure 3-42 Evaporation of Cu in a fabmate crucible.

3.11 Summary

In this chapter, a complete survey of the empirical information we have gathered about evaporating different metals in a Classic 500 Twin EBPVD machine is presented. Many evaporation tests were carried out in order to implement reliable and reproducible processes to deposit metal thin film to form metal contacts for solar cells. In brief, Al, Ti, Ag, Au, Pd, Ge can be evaporated automatically without problem, and Cu and Ni can also be evaporated using the manual control of the tool. Table 3-5 and Table 3-6 list the parameters required for all those processes to be fed to our SQC-310 Thin Film Deposition Controller. In turn, Table 3-7 lists vacuum deposition techniques for thin film applications for all the metals which can be evaporated at IES-UPM [12-14].

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Table 3-5 Parameters for power ramp up used for depositing different metal materials.

		ramp1			ramp2		
	crucible	Power [%]	Time [s]	soak1 time [s]	Power [%]	Time [s]	soak2 time [s]
Al	no	40%	90	20	65%	30	10
Ti-1 ²	no	35.50%	90	30	12%	15	30
Ti-2 ³	no	8%	120	20	12%	60	20
Ag-1	20 cm ³ BN-TiB2	20%	60	10	7%	30	80
Ag-2	No	30%	60	5	50%	20	5
Au	7 cm ³ tungsten	3%	180	30	6.50%	60	5
Pd	7 cm ³ graphite	4%	600	30	7%	120	20
Ni	20 cm ³ Cu	6%	240	30	40%	60	10
Ge	20 cm ³ Cu	15%	120	0.2	35%	30	10
Cu	20 cm ³ fabmate	35%	120	30	56%	20	5

² high power in ramp1 to remove oxygen absorbed on Ti ingot surface, and more pure Ti film is obtained

³ low power in ramp1, introducing the absorbed oxygen on Ti ingot surface, however, it saves more Ti material.

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Table 3-6 Parameters of PID control and ramp down used for depositing different metal materials.

		PID			ramp3 (down)			idle	
	crucible	P	I	D	Power [%]	Time [s]	soak1 time [s]	Power [%]	Time [s]
Al	no	25	0.5	0	0	0	0	0	0
Ti-1	no	25	0.5	0	0	0	0	0	0
Ti-2	no	25	0.5	0	0	0	0	0	0
Ag-1	20 cm ³ BN-TiB ₂	20	0.5	0	0	0	0	0	0
Ag-2	no	25	0.5	0	0	0	0	0	0
Au	7 cm ³ tungsten	10	0.5	0	0	0	0	0	0
Pd	7 cm ³ graphite	25	0.5	0	2%	10	0	0.10%	20
Ni	Cu	35	0.5	0	0	0	0	0	0
Ge	20 cm ³ Cu	25	0.5	0	2%	20	0	0.10%	10
Cu	20 cm ³ fabmate	25	0.7	0	10	18	0	1%	41

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Table 3-7 Vacuum deposition techniques for thin film applications, obtained from E-gun manufacturer Ferrotec [6].

EVAPORATION MATERIAL	Melting Point °C	Density g/cm ³	TEMPERATURE (°C) @ VAP. PRESSURE			EVAPORATION TECHNIQUES				REMARKS n = Index of Refraction
			10 ⁻⁸ Mbar	10 ⁻⁶ Mbar	10 ⁻⁴ Mbar	ELECTRON BEAM	CRUCIBLE	COIL	BOAT	
Au	1062	19,32	807	947	1132	Excel.	Al ₂ O ₃ , BN Vit. Carbon	W	W, Mo Coated Al ₂ O ₃	Films soft, not very adherent.
Al	660	2,7	677	821	1010	Xint.	TiB ₂ -BN , ZrB ₂ , BN	W	TiB ₂ , W	Alloys and wets; tungsten- stranded superior
Ag	961	10,49	847	958	1105	Excel.	Al ₂ O ₃ , Mo	W	Ta, Mo	Evaporates well from any source.
Ti	1675	4,5	1067	1235	1453	Excel.	TiC	—	W	Alloys with refractory metals; evolves gas on first heating.
Pd	1550	12,4	842	992	1192	Excel.	Al ₂ O ₃ , BeO	W	W	Alloys with refractory metals; rapid evaporation suggested. Spits in EB.
Ni	1453	8,9	927	1072	1262	Excel.	Al ₂ O ₃ , BeO, Vit. Carbon	W	W	Alloys with refractory metals. Forms smooth adherent films.
Ge	937	5.35	812	957	1167	Ex	Quartz , Al ₂ O ₃	W, C, Ta	-	Excellent films from E- beam guns.
Cu	1083	8.92	727	857	1017	Ex	Al ₂ O ₃ , Mo, Ta	W	Mo	Adhesion poor. Use interlayer (Cr). Evaporates using any source material.

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Chapter 4. Development of new metallizations on n-type GaAs for high current density devices

4.1 Introduction

Ohmic contacts are key components for high current density devices [1, 2]. Moreover, in the case of LEDs and solar cells this problem is specially demanding since the layout of the front contact has the shape of a grid (i.e. does not fully cover the front side) and thus the problem of high current densities is aggravated by an electrode with limited contact area [3-5]. Therefore, the search for metallization systems with low contact resistance, high metal sheet conductivity, good bondability, reliable and cost-effective is still an interesting and longstanding research topic [6-10]. For ohmic contacts on GaAs, the AuGe/Ni/Au contact has been an extensively used system for several decades since its inception in 1967 [11-13] due to its low contact resistance and good adherence caused by the alloying process. However, the interdiffusion that takes place between Au and GaAs and Ni –being the latter an ineffective barrier layer during the annealing process–, brings about the mixing of the metal stacks and even may produce Au spiking into the GaAs layer. Both these facts impact the quality and reliability of the contact since the contamination of the top Au layer deteriorates the sheet conductance of the contact whilst Au spikes can produce short circuits or can cause thermal instability in the contact. For these reasons, efforts have been conducted to minimize the diffusion in the AuGe/Ni/Au system such as optimizing the contact thermal processing [14] or introducing another refractory metal (for example, Pt) as a barrier layer [15].

An alternative line of investigation has been the quest for new metallization systems that include robust diffusion barriers between the GaAs and the contact metal stack. For example, contacts using Ti/Pt barriers on GaAs have been intensively studied [15-20]. The key merits of this system are that the TiPt bilayer acts as an effective barrier layer between the GaAs and the upper layers responsible for the contact sheet conductance and, moreover, Ti promotes the adhesion to GaAs resulting in a contact with good lateral homogeneity, no spiking and good bondability. On the other hand, the limitation of this contact is that very high doping levels in the semiconductor

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($N_D \sim 10^{20} \text{ cm}^{-3}$) are required to increase the tunneling probability over the Schottky barrier that forms between Ti and GaAs [21].

When it comes to minimizing the specific metal-semiconductor contact resistance, another interesting metallization system that has been widely studied lately is that based on PdGe, which has been reported to show very low metal-semiconductor specific contact resistance ($\sim 10^{-7} - 10^{-6} \Omega \cdot \text{cm}^2$) [22-24]. In this system, the ohmic contact is formed by solid phase regrowth [25-27]. Initially, at low temperatures, the Pd dissolves the GaAs forming PdGaAs compounds. At higher temperatures the inward diffusion of Ge comes into play and Germanium reacts with the PdGaAs to produce the more stable PdGe compound and thus promotes the subsequent recrystallization of GaAs (i.e. solid phase regrowth) that becomes very highly doped as a result of the incorporation of large amounts of Ge. Moreover, if excess Ge is present, a thin epitaxial Ge layer also grows on top of the n++GaAs, forming a Ge-GaAs heterojunction that further contributes to the lowering of the metal-semiconductor barrier height [25-27]. Since all these reactions take place in a quasi-planar front, PdGe-based contacts show no spiking and smooth surfaces comparable to unalloyed contacts [25-27] and can be combined with diffusion barriers such as TiPt [28] or W [29] to increase its bondability and sheet conductivity.

Accordingly, in this chapter, new metallization systems Ti/Pd/Ag, Pd/Ti/Pd/Ag, Pd/Ge/Ti/Pd/Ag on n-type GaAs were proposed and examined on the purpose of producing contacts that provide both minimum metal-semiconductor specific contact resistance and excellent lateral conductivity, intended to be used electronic devices that handle large current densities, especially for those with grid-like contacts with limited surface coverage such as solar cells, lasers or light emitting diodes. With this goal we explore the performance of the contact as a function of the n-GaAs layer doping level, analyzing 1) the Schottky/Ohmic nature of the contact; 2) the metal-semiconductor specific contact resistance and 3) the influence of contact formation conditions on the sheet resistivity of the metallization.

4.2 Experimental Procedures

A set of n-GaAs layers were grown by metalorganic vapor phase epitaxy (MOVPE) on semi-insulating (100) GaAs wafers with a miscut of 2° towards the nearest (111)A

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plane. The epilayer thickness was of 400 nm and three different doping concentrations of 1.3×10^{18} , 2.5×10^{18} , 3.1×10^{18} , and $1.6 \times 10^{19} \text{ cm}^{-3}$ were fabricated to observe the doping level influence on the contact quality. Such doping levels were chosen to sweep typical contact layer doping levels used in MOVPE. After epitaxial growth, the doping level in the *n*-GaAs layers was confirmed by electrochemical capacitance–voltage profiling using a WEP Control CVP21 tool. Contact areas were defined by using conventional photolithographic techniques. Prior to contact deposition, the substrates were cleaned using $\text{H}_2\text{SO}_4\text{:H}_2\text{O}_2\text{:H}_2\text{O}$ (2:1:50) and $\text{HCl:H}_2\text{O}$ (1:1) to remove the native oxide layer, and a completely hydrophobic surface was obtained; deionized water rinsing and blow drying with nitrogen followed. Ti/Pd/Ag, Pd/Ti/Pd/Ag, and Pd/Ge/Ti/Pd/Ag metal stacks were deposited in our multi-pocket electron beam evaporator at a base vacuum of 1×10^{-6} mbar. Immediately after evaporation, the patterns suffered a lift-off process to remove the metal from unwanted areas. The samples were annealed individually by RTA in forming gas ($\text{H}_2\text{:N}_2$, 1:9) at different temperatures (300-750°C) and times (20-180 s). In order to compare the quality of the metallization obtained, samples with the classic contact structure AuGe/Ni/Au (200/60/500 nm) were also fabricated on the highest doped samples ($1.6 \times 10^{19} \text{ cm}^{-3}$) and RTA processing at 375 °C for 180 s followed. For electrical characterization, the transmission line model (TLM) was applied to measure specific contact resistance and the Van der Pauw method [30] together with line shaped patterns were used to measure the metal layer sheet resistance. In the latter case, the metal resistivity was then calculated as the sheet resistance times the nominal thickness of metal layer. To isolate the TLM and Van der Pauw patterns a mesa etching was conducted with $\text{NH}_4\text{OH:H}_2\text{O}_2\text{:H}_2\text{O}$ (2:1:10). The electrical characterization was carried out using the 4-wire method by sweeping current and measuring voltage with a Keithley 2062 programmable power supply. A profilometer KLA-Tencor AlphaStep D-120 Stylus Profiler was used to measure the surface roughness. More details and short descriptions about the experimental techniques can be found in Chapter 2 of this Thesis.

4.3 Ti/Pd/Ag contacts to n-type GaAs.

4.3.1 Background

In the field of silicon solar cells –in particular, in high efficiency or concentrator designs– this problem was solved using the system Ti/Pd/Ag to define front grids on *n*-Si, with evidence of excellent metal/semiconductor specific contact resistance, good bondability and demonstrated long term stability [23][24]. These properties can be cursorily explained as follows: 1) Ti is a refractory metal that while having an firm adhesion to Si, does not show intermetallic reactions (at least for $T < 500^\circ\text{C}$), providing excellent stability and total absence of spiking at the metal semiconductor interface; 2) high doping levels in Phosphorus-diffused solar cell emitters and Ti ability to dissolve the native SiO_2 produce extremely thin Schottky barriers and very low specific contact resistances; 3) Ti/Pd works as a diffusion barrier layer, separating the Si and top Ag layer, and thus avoiding cross contamination; and 4) pure Ag has a large conductivity, ideal to produce contacts with low metal resistivity. In summary, the Ti/Pd/Ag metallization has been reported to work very well on $n^+\text{Si}$.

Figure 4-1 Energy band diagrams of Ti/*n*-GaAs contacts for various doping levels in the GaAs layer (left $N_D = 1 \times 10^{18} \text{ cm}^{-3}$; center $N_D = 3 \times 10^{18} \text{ cm}^{-3}$; right $N_D = 1 \times 10^{19} \text{ cm}^{-3}$). The zero energy level is the Fermi energy level. All the diagrams have been calculated assuming the Ti/*n*-GaAs barrier layer to be $\phi_{M-S} = 0.8 \text{ eV}$. The resulting effective barrier thickness (W_{M-S}) for each doping level are also included in the plots.

Moving on to GaAs, Ti has been extensively studied to fabricate highly stable Schottky contacts on moderately doped *n*-GaAs [25-27] for its ability to produce inert and highly stable interfaces. Figure 4-1 shows the energy band diagrams of

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Ti/*n*-GaAs contacts for various doping levels in the GaAs layer (left $N_D=1\times 10^{18} \text{ cm}^{-3}$; center $N_D=3\times 10^{18} \text{ cm}^{-3}$; right $N_D=1\times 10^{19} \text{ cm}^{-3}$). All the diagrams in this figure have been calculated using Snider's 1D Poisson solver [28] assuming the Ti/*n*-GaAs barrier layer to be $\phi_{M-S} = 0.8 \text{ eV}$ [26][27]. Obviously, the resulting effective barrier thickness (W_{M-S}) –defined here as the depth at which the conduction band energy reaches the Fermi level energy– is the parameter that controls the conduction of charge carriers across this interface by governing their tunneling probability. For moderately doped *n*-GaAs layers (data not shown), W_{M-S} can extend over a hundred nm but it also can reach values lower than 300Å for dopings higher than $1.5\times 10^{18} \text{ cm}^{-3}$, indicating that (as occurs with $n^+\text{Si}$) heavy doping in the contact layer is an effective way to control the transition from Schottky to ohmic behavior.

Therefore, the aforementioned working principles of the Ti/Pd/Ag metal system on $n^+\text{Si}$ also hold for $n^+\text{GaAs}$, and therefore this metal system shows some potential for our target application. First, it should be noted that Ti also shows firm adhesion to GaAs and does not react with it at least for $T<500^\circ\text{C}$ [25], providing excellent stability of the metal semiconductor interface. Second, Ti affinity for oxygen also provides an advantage on GaAs, since it can be used to getter oxygen during the e-beam evaporation process and to dissolve the native GaAs oxides produce clean sharp metal-semiconductor interfaces. Third, as shown in Figure 4-1 high doping levels in the *n*-GaAs produce very thin Schottky barriers with potentially low specific contact resistance. In addition, Ti also works as a diffusion barrier in GaAs [15-17, 25], separating the semiconductor and the top metal layer in charge of providing good sheet conductance; the endurance of this barrier is further enhanced by the presence of a layer of Pd [17]. Finally, pure Ag has a large conductivity, ideal to produce contacts with low metal resistivity.

In fact, pursuing some of these ideas, there are some works in the literature reporting the use of Ti/Pd/Au on p-GaAs [29], and other Ti-based contacts on GaAs, such as Ti/Pt for p-GaAs [30][31] and Ti/Pt/Au for *n*-GaAs [15][16]. In these systems either gold (and not silver) is used as the conductive layer or Pt (and not Pd) is used as the diffusion barrier layer. Although Pt has shown to have superior performance than Pd working as a diffusion barrier (because the Pd-Pd bond strength is about ¼ of that of the Pt-Pt bond), the fact is that Pd has demonstrated to be successful under moderate RTA temperatures ($<500^\circ\text{C}$) and is more cost-effective [29][30].

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Despite its potential advantages, a thorough study of Ti/Pd/Ag metallization characteristics on *n*-GaAs is lacking, and would offer a more cost-effective alternative than systems using Pt and Au. Accordingly, in this section we present an assessment of Ti/Pd/Ag contacts to *n*-GaAs as a function of the *n*-GaAs doping level and contact annealing treatment; analyzing the impact of these variables on the Schottky/Ohmic nature of the contact; its specific contact resistance and the influence of contact formation on the metal resistivity and morphology (i.e. bondability) of the metallization.

4.3.2 Results and Discussion

In the first set of experiments, Ti/Pd/Ag layers (50/50/1000 nm) were deposited on three *n*-GaAs layers with different doping levels (1.3×10^{18} , 3.1×10^{18} and $1.6 \times 10^{19} \text{ cm}^{-3}$) and subsequently annealed by RTA at 400°C for 100 s. Figure 4-2 shows, for each sample, representative *I*-*V* curves taken between two adjacent TLM contacts, which were 100 μm apart.

Figure 4-2 *I*-*V* curve of Ti/Pd/Ag contact resistance as a function of *n*-GaAs doping. Pad separation is 100 μm .

Figure 4-2 evidences that when the doping level is not high enough, Schottky contacts are obtained. Nevertheless, for the sample doped $1.6 \times 10^{19} \text{ cm}^{-3}$, the contact is ohmic and shows little influence of the RTA process (curves for annealed and non-annealed samples virtually overlap in Figure 4-2). The specific contact resistance and metal resistivity of these samples are included in Table 4-1. As anticipated by Figure

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4-2, the specific contact resistance (ρ_c) for the sample doped $1.6 \times 10^{19} \text{ cm}^{-3}$ experiences only small changes before and after RTA, going from $\rho_c = 1.9 \times 10^{-3} \Omega \cdot \text{cm}^2$ to $\rho_c = 1.5 \times 10^{-3} \Omega \cdot \text{cm}^2$. However, despite being ohmic, these values of ρ_c are still quite high, as compared to the reference AuGe/Ni/Au contact (last row in Table 4-1). On the contrary, the values of metal resistivity ρ_M are significantly better and quite homogeneous for all samples in Figure 4-2. All values of ρ_M are around $2.4 \times 10^{-6} \Omega \cdot \text{cm}$, which is about one order of magnitude lower than the metal resistivity of the AuGe/Ni/Au reference contact. Notably, this metal resistivity range is reasonably close to the tabulated value for pure bulk Ag ($1.6 \times 10^{-6} \Omega \cdot \text{cm}$). Given the fact that even small impurity concentrations tend to affect the conductivity of thin films, it seems plausible that the Ag layer is not contaminated by GaAs, supporting the idea that TiPd works fine as a barrier layer, hindering the diffusion of Ga and As atoms into Ag layer. Of course this result is not an unequivocal proof for lack of significant diffusion though it is certainly in line with the results with Ti/Pd/Au reported by Chor et al [29] and Jones et al. [30], where no significant contamination of the Au layer could be measured for RTA processing temperatures of 500°C or less. On the contrary, the metal resistivity of AuGe/Ni/Au system is one order of magnitude lower than that of pure bulk gold. This seems to be an indirect evidence of Ni not being as an effective diffusion barrier and thus gold overlayer conductivity being degraded by Ga and As, Ge and Ni contamination.

Table 4-1 Comparison of contact properties of Ti/Pd/Ag on *n*-type GaAs with different doping levels and annealing conditions. The time included in the third column is the so called *soaking time* for the RTA process (i.e. the time for which the temperature remains constant, not including ramp-up and ramp-down times). The results of the classic AuGe/Ni/Au metallization have been included for reference in the last row.

System	Doping concentration N_D [cm ⁻³]	RTA	Specific contact resistance ρ_c [Ω·cm ²]	Metal resistivity ρ_M [Ω·cm]
Ti/Pd/Ag (50/50/1000 nm)	1.3×10 ¹⁸	375 °C 180s	-	2.36×10 ⁻⁶
		400 °C 100s	-	2.38×10 ⁻⁶
		430 °C 100s	-	2.47×10 ⁻⁶

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		460 °C 100s	-	2.49×10^{-6}
		-	-	2.02×10^{-6}
Ti/Pd/Ag (50/50/1000 nm)	3.1×10^{18}	400 °C 100s	-	2.48×10^{-6}
		500 °C 100s	-	2.14×10^{-6}
		750 °C 30s	9.2×10^{-4}	7.19×10^{-5}
		-	1.9×10^{-3}	1.98×10^{-6}
Ti/Pd/Ag (50/50/1000 nm)	1.6×10^{19}	400 °C 100s	1.5×10^{-3}	2.23×10^{-6}
		500 °C 100s	4.9×10^{-4}	2.23×10^{-6}
		750 °C 30s	1.3×10^{-4}	9.31×10^{-5}
		-	-	-
AuGe/Ni/Au (200/60/500 nm)	1.6×10^{19}	375 °C 180s	2.9×10^{-6}	2.22×10^{-5}

Figure 4-3 *I-V* curves of Ti/Pd/Ag contact resistance as a function annealing temperature and doping level. The *n*-GaAs layer doping concentration is: (a) $N_D=1.3 \times 10^{18} \text{ cm}^{-3}$; (b) $N_D=3.1 \times 10^{18} \text{ cm}^{-3}$; (c) and $N_D=1.6 \times 10^{19} \text{ cm}^{-3}$. Pad separation is 100 μm in all cases. Please note the different voltage scale in the three figures.

To assess the impact of annealing conditions on the Ti/Pd/Ag contact quality, different RTA processes have been carried out. Figure 4-3a shows the results for the contacts made on GaAs doped $1.3 \times 10^{18} \text{ cm}^{-3}$. In all cases Schottky-like behavior is observed. For increasing temperatures a slight decrease in the turn-on voltage (i.e. on the barrier height) is observed. At this point, it seemed plausible that further increasing the annealing temperature would eventually make the contact ohmic.

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Therefore, the experiment was repeated and higher temperatures were explored for the RTA. In order to further facilitate the formation of ohmic contacts (i.e. in order to increase tunneling probability), highly doped samples ($N_D=3.1\times10^{18}\text{ cm}^{-3}$) were used in this new set of experiments. The result of this experiment can be seen in Figure 4-3b. As shown in this figure, when the annealing temperature is raised to 750 °C, which is the optimum temperature for a Ti contact on degenerated doped *n*-GaAs as reported by J. Zhou and co-workers [15], the contact becomes ohmic and $\rho_c = 9.2\times10^{-4}\text{ }\Omega\cdot\text{cm}^2$. However, for lower temperatures (400°C and 500°C), Schottky contacts are obtained as displayed in Figure 4-3b.

Finally, Figure 4-3c summarizes the same set of experiments for the sample doped $1.6\times10^{19}\text{ cm}^{-3}$. As shown in Figure 4-3c and Table 4-1, an increase in annealing temperature mildly decreases ρ_c . After annealing at 750 °C, a minimum ρ_c value is reached of $1.3\times10^{-4}\text{ }\Omega\cdot\text{cm}^2$, which is similar to the results obtained with Ti/Pt/Au on *n*-GaAs ($\sim1.0\times10^{-4}\text{ }\Omega\cdot\text{cm}^2$) [15][16]; still far from the values of the reference AuGe/Ni/Au contact ($\rho_c= 2.9\times10^{-6}\text{ }\Omega\cdot\text{cm}^2$) and metallization systems based on Pd/Ge on *n*-GaAs ($\sim3.0\times10^{-7}$) [19][21][34]. Obviously, the high ρ_c limitation places restrictions on the use of this metallization system, however, it could be acceptable in some cases. For example, according to the calculation reported by H. Cotal et al. [16] it could be used with low or medium concentrator photovoltaic (CPV) solar cells operating below 500 suns. Nevertheless, given the fact that many CPV manufacturers are moving their designs to ultra-high concentration levels (above 1000 suns), ρ_c needs to be improved to values below $1\times10^{-5}\text{ }\Omega\cdot\text{cm}^2$.

Table 4-1 also summarizes the results of metal resistivity of the experiments in Figure 4-3a to 3.c. A first fact observable in this table is that annealing temperatures lower than 500°C seem not to affect significantly the metal resistivity of the layer. The metal resistivity barely increases after annealing below 500°C. Furthermore, the average metal resistivity of all these experiments from 375°C to 500°C is $2.4\times10^{-6}\text{ }\Omega\cdot\text{cm}$ with a standard deviation of around 6%, which is in agreement with the uncertainty expected in the deposited thickness in our e-gun evaporator. In other words, if there is a change in metal resistivity associated to annealing the samples for temperatures from 375°C to 500°C, it is non observable due to our uncertainty in the deposited thickness. However, this situation changes for the samples processed at

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750°C. In such case, the metal resistivity is highly degraded increasing by more than a factor of 30.

Figure 4-4 Surface roughness of Ti/Pd/Ag contacts deposited on $3.1 \times 10^{18} \text{ cm}^{-3}$ doped n-type GaAs with different annealing conditions.

In order to gain insight into these changes of the metal resistivity, the surface roughness of samples annealed at different temperatures was measured using a profilometer, as shown in Figure 4-4. This figure shows that sample roughness increases with annealing temperature and surface roughness (RMS) increases from 4.9 to 892 nm, reaching a deleterious morphology for samples annealed at 750°C. In addition, the color of the metallization changed from silver to bronze-green after annealing 750°C evidencing some chemical (intermetallic) reactions between the components of the metal system possibly as a result of the blurring of the Ti/Pd barrier layer [35][36]. In summary, morphology degradation together with the degradation of Ag conductivity as a result of contamination could explain the degradation measured and calculated in the metal resistivity.

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In conclusion, the good metal resistivity of the Ti/Pd/Ag system shows promises to develop ohmic contacts to electronic devices that handle large current densities. The lowest values reached for the metal/semiconductor specific contact resistance are still far from the records reported in the literature though would be enough to be used in low or medium concentration solar cell (<500 suns).

4.4 Ti/Pd/Ag contacts modified with Pd or Ge/Pd interfacial layers to n-type GaAs.

4.4.1 Background

In the former section, we studied Ti/Pd/Ag contacts to n-GaAs as a possible low cost and high reliability alternative to Ti/Pt/Au (and alike) contacts [21]. The combination of TiPd acted as an excellent diffusion barrier that preserved the sheet conductivity of the top Ag layer thus yielding excellent lateral metal resistivity values (i.e. virtually those of bulk silver). On the other hand, the Ti/GaAs contact produced modest values of the specific metal-semiconductor contact resistance ($\rho_c \sim 0.5-1 \times 10^{-3} \Omega \cdot \text{cm}^2$). These results suggested that this system exhibited good potential for its application in high current density devices –especially for those with grid-like contacts with limited surface coverage such as solar cells, lasers or light emitting diodes– provided that its high metal-semiconductor specific contact resistance could be improved.

In order to enhance the metal-semiconductor conductivity of TiPdAg based contacts, we decided to explore systems of the type X-TiPdAg, X being a compound intended to form an interface to GaAs with minimum metal-semiconductor losses and compatible with Ti (both chemically and as a diffusion barrier). With this purpose, two interfacial metal layers, namely, Pd and PdGe, have been explored. The interest of Pd stems from the fact that it would not add significant complexity to the system (since it is already used as part of the diffusion barrier) and, as reported by E.F.Chor et al. [31], a Pd interfacial layer allows achieving a low ρ_c to GaAs. The reason given by E.F.Chor et al. [31] for this low ρ_c was the absence of oxide on the metal-semiconductor interface caused by Pd penetrating native oxides and dispersing them uniformly and the formation of PdGaAs phases as described section 4.1. On the other hand, introducing a PdGe interfacial bilayer would increase moderately the

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complexity of the system (a new element, namely Germanium, is added) but, as discussed above, the merits associated to the solid phase regrowth process would be achieved producing a much lower metal-semiconductor specific contact resistance. Of course, in both cases, the impact of such interfacial layers on the robustness of the TiPd diffusion barrier is anticipated to be low, preserving the quality of the sheet resistance attained with Ti/Pd/Ag systems.

Accordingly, in this section, we present the assessment of Pd/Ti/Pd/Ag and Pd/Ge/Ti/Pd/Ag contacts to n-GaAs with the final target of producing contacts that provide both minimum metal-semiconductor specific contact resistance and excellent lateral conductivity.

4.4.2 Results and Discussion

As discussed above, the Ti/Pd/Ag metal system [21] produces contacts with very good metal sheet conductivity, however, its metal-semiconductor specific contact resistance ($\sim 10^{-3} \Omega \cdot \text{cm}^2$) is far from state of the art vales. In order to improve the specific contact resistance, a 50 nm Pd layer was introduced between GaAs and Ti/Pd/Ag. Figure 4-5 shows the comparison of I-V curves of representative samples of Ti/Pd/Ag and Pd/Ti/Pd/Ag with and without RTA on n-GaAs layers with different doping levels. As illustrated in Figure 4-5(a), when the n-GaAs doping level is $3.1 \times 10^{18} \text{ cm}^{-3}$, both types of metal systems show Schottky behavior before annealing, with the system with the Pd/n-GaAs interface (green triangles in Figure 4-5(a)) exhibiting a slightly higher barrier height than the system with the Ti/n-GaAs interface (black squares in Figure 4-5(a)). This is in good agreement with the expected Schottky barrier heights for these two contacts, namely, $\phi_B \sim 0.8\text{-}0.85 \text{ eV}$ for Ti/n-GaAs [32] and $\phi_B \sim 0.85\text{-}0.9 \text{ eV}$ for Pd/n-GaAs [33]. After RTA no big changes are observed in either contact since the I-V curves of all samples in Figure 4-5(a) almost overlap. This result was surprising since we expected that the widely reported reactions that occur between Pd and GaAs producing PdGaAs phases [31] would impact more significantly the barrier height. However, similar results have been reported in Pd/n-GaAs contacts made on lightly doped GaAs ($N_D = 3 \times 10^{16} \text{ cm}^{-3}$) where a reduction of only $\sim 0.02 \text{ eV}$ was observed on the barrier height after annealing under similar conditions [34]. So, in essence, our results indicate that the

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introduction of a Pd layer between n-GaAs and the Ti/Pd/Ag has little influence on the contact resistance when deposited on the lowly doped n-GaAs.

Figure 4-5 Comparison of I-V curves of Ti/Pd/Ag and Pd/Ti/Pd/Ag with and without RTA on n-GaAs. The n-GaAs layer doping concentration is: (a) $N_D = 3.1 \times 10^{18} \text{ cm}^{-3}$; (b) $N_D = 1.6 \times 10^{19} \text{ cm}^{-3}$. As sketched by the inset, I-V curves were measured between pads separated 100 μm .

On the contrary, the situation on the highly doped samples changes notably as shown in Figure 4-5(b). As illustrated in this figure, all the contacts made on n-GaAs with $N_D = 1.6 \times 10^{19} \text{ cm}^{-3}$ have ohmic behavior and, as compared to the I-V curves of Ti/Pd/Ag, the I-V curves of Pd/Ti/Pd/Ag exhibit lower contact resistance. Hence, the

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specific contact resistance and sheet metal resistivity were calculated. A summary of the mean values obtained from representative samples of each type are listed in Table 4-2. As shown in this table, the specific contact resistance of Pd/Ti/Pd/Ag on highly doped n-GaAs ($1.6 \times 10^{19} \text{ cm}^{-3}$) is $5.8 \times 10^{-4} \Omega \cdot \text{cm}^2$ and, after RTA, it decreases to $9.7 \times 10^{-5} \Omega \cdot \text{cm}^2$. This value is lower than the Ti/Pd/Ag specific contact resistance after RTA by a factor of 15. This difference can only be attributed to a drastic change in the barrier height of the sample with the Pd interface layer, a fact that didn't occur in the moderately doped sample of Figure 4-5(a). The physical processes behind the decrease in specific contact resistance (i.e. in the barrier height) could be related to the ability of Pd to dissolve surface native oxides of GaAs and the formation during RTA of PdGaAs phases with a lower barrier height with GaAs [31]. Our results suggest that the intensity of these phenomena (presumably the formation of PdGaAs phases) is modulated by the doping of the n-GaAs layer. Our speculation at this point to explain these results is that the doping in the n-GaAs influences the amount and type of PdGaAs phases that the RTA forms at the Pd/n-GaAs interface and thus determines the specific contact resistance. Microstructure analyses by TEM are underway to clarify this issue.

In regard to the metal sheet resistivity, all the samples of Ti/Pd/Ag and Pd/Ti/Pd/Ag have similar performance. Before RTA, the metal resistivity is $\sim 2.0 \times 10^{-6} \Omega \cdot \text{cm}$, and after RTA, it increases a little reaching $\sim 2.4 \times 10^{-6} \Omega \cdot \text{cm}$. The small difference may be due to deterioration of Ag conductivity caused by limited diffusion from the GaAs to the Ag layer during the RTA. Nevertheless, these values are still nearly one order of magnitude better than the classic metallization AuGe/Ni/Au, which shows a sheet resistivity of $2.22 \times 10^{-5} \Omega \cdot \text{cm}$. These results confirm that introducing a Pd interfacial layer has barely any influence on the performance of the TiPd bilayer that works as an effective barrier layer to restrict the contamination of Ag by GaAs.

Table 4-2 Comparison of contact properties of Ti/Pd/Ag and Pd/Ti/Pd/Ag on n-type GaAs with different doping and annealing conditions. The results of the classic AuGe/Ni/Au metallization have been included for reference in the last row.

System	Doping concentration n	RTA	Specific contact resistance, $\rho_c [\Omega \cdot \text{cm}^2]$	Metal resistivity $\rho_M [\Omega \cdot \text{cm}]$
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N_D [cm^{-3}]				
Ti/Pd/Ag (50/50/1000 nm)	3.1×10^{18}	-	-	2.02×10^{-6}
		400 °C 100s	-	2.48×10^{-6}
	1.6×10^{19}	-	1.9×10^{-3}	1.98×10^{-6}
		400 °C 100s	1.5×10^{-3}	2.23×10^{-6}
Pd/Ti/Pd/Ag (50/50/50/1000 nm)	3.1×10^{18}	-	-	1.94×10^{-6}
		400 °C 100s	-	2.43×10^{-6}
	1.6×10^{19}	-	5.8×10^{-4}	1.96×10^{-6}
		400 °C 100s	9.7×10^{-5}	2.31×10^{-6}
AuGe/Ni/Au (200/60/500 nm)	1.6×10^{19}	375 °C 180s	2.9×10^{-6}	2.22×10^{-5}

However, although the introduction of the Pd layer decreased considerably the metal-semiconductor specific contact resistance of the contact (by a factor of 15), the final value reached is still far from that of the classic metallization AuGe/Ni/Au with $\rho_c = 2.9 \times 10^{-6} \Omega \cdot \text{cm}^2$. Therefore, with the target of obtaining lower specific contact resistances, an interfacial Pd/Ge bilayer was introduced between n-GaAs and Ti/Pd/Ag metal system. According to the literature, in order to obtain the lowest contact resistance, Ge must be in excess in the PdGe bilayer (i.e. the atomic ratio in the layers must be Pd/Ge <1, which corresponds to a thickness ratio of Pd/Ge <2/3) [22, 27, 35]. Accordingly, a Pd/Ge thickness ratio around 1/2 was widely used in these works (45/90, 50/100, 60/130, 75/135nm) [22, 27, 35] and hence all the Pd/Ge layers in our samples were fabricated with such thickness ratio of 1/2. As shown in Table 4-3, the standard thickness combination chosen in our experiments was 50/100nm. However, for the samples doped $2.5 \times 10^{18} \text{ cm}^{-3}$ (namely, samples *c*, *d* and *e* in Table 4-3), three different thickness of Pd/Ge (50/100, 30/60, 15/30 nm) were fabricated to study the impact of total thickness for the bilayer as will be discussed below.

Figure 4-6 shows the I-V curves of representative samples of this contact as a function of n-GaAs doping level, PdGe thickness and RTA conditions. A summary of the mean values obtained from representative samples of each type are listed in

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Table 4-3. As Figure 4-6 shows, the I-V curves of all samples show ohmic behavior with three slopes that correspond to the three different doping levels used in the n-GaAs contact layer. As shown in Table 4-3, the specific contact resistances of all these samples are much lower than in the case of a single Pd interfacial layer (Table 4-2). In fact, the best values reached for the specific contact resistance ($1.5\text{-}1.7\times 10^{-7} \Omega\cdot\text{cm}^2$) are only slightly higher than the best reported for PdGe contacts [22, 27, 35]. We interpret this fact as an indirect proof of lack of influence of the upper layers in the contact region and in turn an indirect proof of the TiPd bilayer working successfully as a diffusion barrier, effectively separating the contact interface region and the sheet conductivity region.

Figure 4-6 I-V curves of Pd/Ge/Ti/Pd/Ag contact resistance as a function annealing time and doping level and PdGe thickness. Pad separation is 100 μm in all cases. The details of doping concentration and Ge/Pd thickness from sample (a) ~ (f) are listed in the figure and the other details are listed in Table 4-3. The I-V curves of the classic AuGe/Ni/Au metallization have also been included as (g).

Table 4-3 Comparison of contact properties of Pd/Ge/Ti/Pd/Ag on n-type GaAs with different doping level, Pd/Ge metal bilayer thickness and annealing time. The results of the classic AuGe/Ni/Au metallization have been included for reference in the last row.

Doping	System	RTA	Specific	Metal
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concentration N_D [cm^{-3}]			contact resistance, ρ_c [$\Omega \cdot \text{cm}^2$]	resistivity ρ_M [$\Omega \cdot \text{cm}$]	No.
1.3×10^{18}	Pd/Ge/Ti/Pd/Ag (50/100/50/50/500 nm)	300°C, 20s	8.7×10^{-7}	1.94×10^{-6}	<i>a</i>
		300°C, 60s	1.8×10^{-6}	1.95×10^{-6}	<i>b</i>
2.5×10^{18}	Pd/Ge/Ti/Pd/Ag (50/100/50/50/500 nm)	300°C, 20s	1.7×10^{-7}	2.04×10^{-6}	<i>c</i>
	Pd/Ge/Ti/Pd/Ag (30/60/50/50/500 nm)	300°C, 20s	1.5×10^{-7}	N.A.	<i>d</i>
	Pd/Ge/Ti/Pd/Ag (15/30/50/50/1000 nm)	300°C, 20s	1.1×10^{-5}	1.90×10^{-6}	<i>e</i>
1.6×10^{19}	Pd/Ge/Ti/Pd/Ag (50/100/50/50/500 nm)	300°C, 20s	2.5×10^{-6}	1.91×10^{-6}	<i>f</i>
1.6×10^{19}	AuGe/Ni/Au (200/60/500 nm)	375°C, 180s	2.9×10^{-6}	2.22×10^{-5}	<i>g</i>

As shown in Table 4-3, when the doping level is low ($1.3 \times 10^{18} \text{ cm}^{-3}$), the specific contact resistance is $8.7 \times 10^{-7} \Omega \cdot \text{cm}^2$ after RTA at 300 °C, 20 s. Extending the RTA time to 60 s does not improve the results, which are in fact a factor of two larger. For this reason we decided to fix our alloying times to 20s [27] [36] . When the doping level is $2.5 \times 10^{18} \text{ cm}^{-3}$, the results are much better: sample *d* (30/60nm) has a specific contact resistance value as low as $1.5 \times 10^{-7} \Omega \cdot \text{cm}^2$, whilst sample *c* (50/100nm) reaches virtually the same value ($1.7 \times 10^{-7} \Omega \cdot \text{cm}^2$). These values are an order of magnitude lower than those attained with the classic AuGe/Ni/Au (sample *g* with $\rho_c = 2.9 \times 10^{-6} \Omega \cdot \text{cm}^2$). However, for sample *e* with Pd/Ge thickness of 15/30nm, the results deteriorate to $1.05 \times 10^{-5} \Omega \cdot \text{cm}^2$. This increase of two orders of magnitude in the specific contact resistance seems to suggest that the Pd/Ge interfacial bilayer is not thick enough in this case (15/30 nm) for the solid phase regrowth process to proceed appropriately. Finally, for the highly doped samples ($1.6 \times 10^{19} \text{ cm}^{-3}$), the values of the specific contact resistance obtained despite being very low ($2.5 \times 10^{-6} \Omega \cdot \text{cm}^2$) do not reach the record values reported for the PdGe system. So, in this case the ultra-high doping in the n-GaAs does not lead to the best contact (as opposed to what occurred with the Pd/Ti/Pd/Ag system). Again, this leads us to think that the

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microstructure of the contact –i.e. relative abundance and type of the PdGaAs phases– is impacted by the doping of the n-GaAs layer and, in this case, the phases associated to the very high doping are not the best to favor the solid phase regrowth (in particular the second part associated to the formation of PdGe, recrystallization of n++GaAs and formation of the Ge-GaAs heterostructure). However, it should be noted the value of the specific contact resistance obtained with sample *f* is in the same range as that of AuGe/Ni/Ge, even a little lower and good enough for the requirement of most high current density devices [21].

Regarding the contact sheet resistivity, as shown in Table 4-3, all the Pd/Ge/Ti/Pd/Ag samples have a metal resistivity around $1.9\sim 2.0\times 10^{-6}\ \Omega\cdot\text{cm}$, which is almost the same as Ti/Pd/Ag without RTA and very close to the tabulated value for pure bulk Ag ($1.6\times 10^{-6}\ \Omega\cdot\text{cm}$). It should be also noted that these resistivities are, on average, around 20% lower than those measured in the annealed Ti/Pd/Ag and Pd/Ti/Pd/Ag systems (see Table 4-2). We link this result to the fact that the PdGe contact demands lower RTA temperatures (300°C vs. 400°C) and therefore contamination of the top metal layer is less likely to occur.

In conclusion, as compared to the classic AuGe/Ni/Au contact layer, Pd/GeTi/Pd/Ag shows a factor 20 lower specific contact resistance, one magnitude lower metal resistivity and does not use gold. As a result of such good electrical properties, plus its cost-effectiveness and long-term durability, and high bondability, it exhibits high potential for applications on electronic devices that need to handle high current densities.

4.5 Pd/Ge/Ti/Pd/Al contacts to n-type GaAs.

In an attempt to further increase the cost effectiveness of the metalization developed we investigated the use of aluminum (instead of silver) as the conductive overlayer in the metallization. The choice of aluminum to perform this purpose can be understood with the aid of Table 4-4. This table represents a cost-performance comparison of different materials to implement the conductive layer in a metallization taking silver as a reference. The calculations in this table assume that the resistivity of the thin film is comparable to that of the pure bulk material, which is rather optimistic for some materials such as gold. Therefore, this table should be taken as a semi-

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quantitative guide for benchmarking materials more than a design tool. As this table shows, the cost of a thin film layer of Al that produces a sheet resistance of $30\text{m}\Omega/\square$ (this value is a typical target in IES-UPM's concentrator solar cell technology) is around 15% of the same using silver. This represents the lowest among the materials analyzed.

Table 4-4 Cost-performance comparison of different materials to implement the conductive layer in a metallization. The fourth column represents the nominal layer thickness needed to attain a sheet resistivity of $30\text{m}\Omega/\square$. The fifth column represents the cost of such layer taking silver as a reference.

Material	Bulk resistivity ¹ [$\Omega\cdot\text{cm}$]	Cost ² [€/gr]	Density [gr/cm ³]	Thickness for $R_s = 30\text{m}\Omega/\square$ [nm]	Cost of $30\text{m}\Omega/\square$ layer [%]
Silver (Ag)	$1.6\cdot 10^{-6}$	3	10.5	535	100%
Copper (Cu)	$1.7\cdot 10^{-6}$	0.8	9	570	25%
Gold (Au)	$2.3\cdot 10^{-6}$	45	19.3	770	4000%
Aluminum (Al)	$2.7\cdot 10^{-6}$	1	2.7	900	15%

¹ This is the bulk resistivity. Thin film resistivities are expected to be notably higher.

² the price is obtained from supplier the Kurt J. Lesker Company

Table 4-5 Comparison of contact properties of Pd/Ge/Ti/Pd/Al, Pd/Ge/Ti/Pd/Ag and AuGe/Ni/Au metallization on n-type GaAs.

System	Doping concentration N_D [cm ⁻³]	RTA	Specific contact resistance, ρ_c [$\Omega\cdot\text{cm}^2$]	Metal resistivity ρ_M [$\Omega\cdot\text{cm}$]	Top layer Thickness for $R_s = 30\text{m}\Omega/\square$ [nm]	Top layer cost of $30\text{m}\Omega/\square$ layer [%]
Pd/Ge/Ti/Pd/Al (30/60/50/50/500 nm)	$2.5\cdot 10^{18}$	300°C, 20s	$2.3\cdot 10^{-7}$	$3.57\cdot 10^{-6}$	1190	15%
Pd/Ge/Ti/Pd/Ag (50/100/50/50/500 nm)	$2.5\cdot 10^{18}$	300°C, 20s	$1.7\cdot 10^{-7}$	$2.04\cdot 10^{-6}$	680	100%
AuGe/Ni/Au (200/60/500 nm)	$1.6\cdot 10^{19}$	375°C, 180s	$2.9\cdot 10^{-6}$	$2.22\cdot 10^{-5}$	7400	30000%

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Table 4-5 shows the contact properties of Pd/Ge/Ti/Pd/Al metallization on n-type GaAs and, for comparison, the results of Pd/Ge/Ti/Pd/Ag and AuGe/Ni/Au are also shown in Table 4-5. It can be found that the specific contact resistance of Pd/Ge/Ti/Pd/Al is $2.3 \times 10^{-7} \Omega \cdot \text{cm}$, which is similar to the result of Pd/Ge/Ti/Pd/Ag. This phenomenon indicates that using Al to substitute the top Ag does not have a significant influence on the way the Pd/Ge layer achieves a low metal/semiconductor specific contact resistance. Furthermore, the metal resistivity of Pd/Ge/Ti/Pd/Al is $3.57 \times 10^{-7} \Omega \cdot \text{cm}$, which is close to that of bulk Al and 1.75 times the result of Pd/Ge/Ti/Pd/Ag. Considering that the ratio of resistivities of bulk Al to bulk Ag is 1.68, this result is reasonable, and it also confirms that the Ti/Pd barrier is working efficiently to stop the top metal layer and GaAs diffusing into each other. Although $\rho_{M, \text{Pd/Ge/Ti/Pd/Al}}$ is a little higher than $\rho_{M, \text{Pd/Ge/Ti/Pd/Ag}}$, it is acceptable for the application of IES-UPM's concentrator solar cell technology, since it produces a sheet resistance of $30 \text{ m}\Omega/\square$ (ie. target value at IES) by a thickness of about $1.2 \mu\text{m}$, and such a thickness can be obtained at IES (thicker than $1.5 \mu\text{m}$ is not easy to obtain due to problems during the lift-off process). On the contrary, the Pd/Ge/Ti/Pd/Ag only need $0.7 \mu\text{m}$ Ag layer to reach the same value. However, using Al as top layer only costs 15% to Ag. Therefore, considering the top metal layer is the main component of the metallization regarding to metal cost, Pd/Ge/Ti/Pd/Al is undoubtedly more cost-effective.

4.6 Conclusion

The metallization stack Ti/Pd/Ag on n-type Si has been readily used in solar cells due to its low metal/semiconductor specific contact resistance, very high sheet conductance, bondability, long-term durability and cost-effectiveness. In this chapter, the use of Ti/Pd/Ag metallization on n-type GaAs is examined, targeting electronic devices that need to handle high current densities and with grid-like contacts with limited surface coverage (i.e. solar cells, lasers or light emitting diodes). Ti/Pd/Ag (50/50/1000nm) metal layers were deposited on n-type GaAs by electron beam evaporation and the contact quality was assessed for different doping levels (from $1.3 \times 10^{18} \text{ cm}^{-3}$ to $1.6 \times 10^{19} \text{ cm}^{-3}$) and annealing temperatures (from 300°C to 750°C). The metal/semiconductor specific contact resistance, metal resistivity and the morphology of the contacts were studied.

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The results show that samples doped in the range of 10^{18} cm^{-3} had Schottky-like I - V characteristics and only samples doped $1.6 \times 10^{19} \text{ cm}^{-3}$ exhibited ohmic behavior even before annealing. For the ohmic contacts, increasing annealing temperature causes a decrease in the specific contact resistance ($\rho_{c, \text{Ti/Pd/Ag}} \sim 5 \times 10^{-4} \Omega \cdot \text{cm}^2$). In regard to the metal resistivity, Ti/Pd/Ag metallization presents a very good metal conductivity for samples treated below 500°C ($\rho_{M, \text{Ti/Pd/Ag}} \sim 2.3 \times 10^{-6} \Omega \cdot \text{cm}$); however, for samples treated at 750°C , metal resistivity strongly degrades due to morphological degradation and contamination in the silver overlayer. As compared to the classic AuGe/Ni/Au metal system, the Ti/Pd/Ag system shows higher metal/semiconductor specific contact resistance and one order of magnitude lower metal resistivity.

To further reduce the metal/semiconductor specific contact resistance, the interfacial layer Pd or Pd/Ge was added between GaAs and Ti/Pd/Ag. These metal systems Pd/Ti/Pd/Ag and Pd/Ge/Ti/Pd/Ag have been designed with the goal of producing an electric contact with a) low metal-semiconductor specific contact resistance, b) very high sheet conductance, c) good bondability, d) long-term durability and f) cost-effectiveness. The structure of the contacts consists of an interfacial layer (either Pd or PdGe) intended to produce a low metal-semiconductor specific contact resistance; a diffusion barrier (TiPd) and a thick top layer of Ag intended to provide the desired high sheet conductance, limited cost and good bondability. The target applications are electronic devices that handle high current densities and have grid-like contacts with limited surface coverage (i.e. solar cells, lasers or light emitting diodes). The results show that both systems can achieve very low metal resistivities ($\rho_M \sim 2 \times 10^{-6} \Omega \cdot \text{cm}$), reaching values close to that of pure bulk silver. This indicates the TiPd bilayer acts as an efficient diffusion barrier and thus the metal sheet resistance can be controlled by the thickness of silver deposited. On the other hand, the use of Pd as interfacial layer produces contacts with moderate specific contact resistance ($\rho_c \sim 10^{-4} \Omega \cdot \text{cm}^2$) whilst the use of GePd decreases the specific contact resistance to $\rho_c \sim 1.5 \times 10^{-7} \Omega \cdot \text{cm}^2$. As compared to the classic AuGe/Ni/Au metallization system ($\rho_c \sim 2.9 \times 10^{-6} \Omega \cdot \text{cm}^2$, $\rho_M \sim 2.22 \times 10^{-5} \Omega \cdot \text{cm}$), the Ge/Pd/Ti/Pd/Ag system shows a decrease of one order of magnitude in both the metal-semiconductor specific contact resistance and the metal resistivity. Furthermore, the properties of Pd/Ge/Ti/Pd/Al were also investigated targeting a further reduction of the cost. The results show that replacing the Ag top layer by Al does not influence the function of Pd/Ge as contact

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layer, being its specific contact resistance ($\rho_c \sim 2.3 \times 10^{-7} \Omega \cdot \text{cm}^2$) similar to Pd/Ge/Ti/Pd/Ag. Regarding the metal resistivity, it is ($\rho_M \sim 3.57 \times 10^{-6} \Omega \cdot \text{cm}$) a little higher than Pd/Ge/Ti/Pd/Ag because of the higher Al metal resistivity. Nevertheless, due to the low cost of Al and its lower density, depositing Al as top layer only cost 15% to Ag to obtain the same targeted metal resistivity.

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Chapter 5. Implementation of metallization grids on III-V solar cells

5.1 Introduction

In the last chapter we have presented several metallization systems that are able to provide the desired low levels of metal/semiconductor specific contact resistance and metal sheet resistance. In this chapter, we will discuss the implementation of actual metallization grids on high concentrator multijunction solar cells using these metallization systems. In essence, the first question that we intend to answer is: “Are the metallization systems developed compatible with the standard solar cell processing sequence at IES-UPM?” In order to answer this question it is needed to review the fabrication sequence used at IES-UPM to manufacture multijunction solar cells. This sequence is schematically shown in Figure 5-1. As this figure shows, the grid contact is the third stage in the fabrication process. Therefore, once the grid has been deposited it should be compatible with 1) the mesa isolation process and 2) the selective removal of the cap layer. Both this processes use chemical etchants that will (or may) be in contact with the contact metal. Therefore, the new metallization should withstand such etches without significant degradation.

Accordingly, in this chapter we will review in detail these two processes to analyze the compatibility of the current chemical etches used at IES-UPM with the new metallizations. As will be shown, some incompatibilities have arisen and therefore alternatives have to be explored and tested.

In the final part of this chapter, we present the implementation solar cells with front grids using these new metallizations and compare their performance with solar cells with conventional AuGe/Ni/Au grids, as a proof of concept for the technology.

Figure 5-1 Schematic representation of the fabrication process of multijunction solar cells at IES-UPM. The figures depict the cross-section of an epiwafer, where two solar cells are to be fabricated, at different stages in the fabrication process. The dark blue stripe corresponds to the GaAs cap layer; light blue band is the top cell; red band is the middle cell, and green band is the bottom cell.

5.2 Preliminary tests on metal resistance to different etchants

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As has been stated at the introduction, one of the key goals of this chapter is to study the compatibility of the metals used in our new metallizations under different etching solutions. In this respect, the big concerns are about layer producing the low sheet resistivity made of Au, Al, Ag or Cu. This is so because Pd is difficult to etch (needs aqua regia) and Ti is typically etched with HF, which we don't use in our multijunction solar cell processing.

As stated above, Ag, Al, Cu are the most common metals that can provide the high conductivity and low-cost needed for the top layer of the metallization. However, all those three metals are not as inert as gold. Therefore their compatibility with the most common etching chemicals, namely, $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$, citric acid and HCl, needs to be assessed. Therefore, we carried out a preliminary experiment in which Ag, Al, Cu pellets were immersed into these three different etching solutions, and the weight loss was monitored against etching time. The results of this experiment are summarized in Table 5-1 were measured in order to calculate diameter decreasing and the etching rate. (the pellet geometric shape is supposed as a ball)

Table 5-1 Etching rates (i.e. compatibility) of Ag, Al, Cu under different etching solution

	Citric acid $\text{C}_6\text{H}_8\text{O}_7:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ 1:1:2	Amonia hydroxide $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ 2:1:10	Hydrochloric acid HCl
Ag	Very slow	yes	no
Al	no	Very slow	Yes
Cu	yes	yes	no

As expected, this preliminary experiment anticipates that Ag shows problems with Amonia hydroxide; Al will experience difficulties when exposed to hydrochloric acid and Cu seems not to be an adequate option in any case that involves H_2O_2 (as expected as it is readily oxidized in hydrogen peroxide).

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After this preliminary assessment we can proceed with the detailed analysis of the steps of our solar cell fabrication process that involve some degree of exposure of the grid contact to chemical etches, namely, the cap layer removal and the mesa etch.

5.3 Cap layer removal

Figure 5-2 selective etching of the cap layers (also termed the contact layer) over the AlInP window layer.

In order to obtain a good ohmic contact, an additional GaAs n++ layer is usually grown on top of the window layer of the top subcell, as shown in Figure 5-2. Once the ohmic contact is formed, the unused area of the contact layer needs to be removed since otherwise it would absorb the incident light and decrease the solar cell efficiency. Therefore, a selective etching process is required, which removes the GaAs n++ layer and keeps intact the AlInP window layer. In this process, the grid metal acts as a mask to protect the n++GaAs under the grid fingers that we need to keep (as shown in right part of Figure 5-2). Therefore, a first processing requirement for a grid metallization is that it can withstand the selective etchants used to remove the cap layer. In the following subsections we examine how the metallizations developed perform when exposed to typical selective etchants used in III-V technology.

5.3.1 Selective etching reagent

5.3.1.1 $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$

The solution used for cap layer selective removal at IES-UPM is $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ (2:1:10). However, this reagent does dissolve silver metal, which is the key for the high sheet conductivity through the following reaction[1]:

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Thus, an alternative chemical is required and therefore the performance of some alternative solutions is analyzed in the next sections.

5.3.1.2 Selective etchants based on acetic acid, phosphoric acid or sulfuric acid

■ Etching of III/V-Semiconductors (Overview)											
Material Etchant	GaAs	InP	InGaAs	InGaAsP	GaInP	GaAsP	AlGaP	AlGaAs	AlInP	InAlAs	InGaAlAs
HCl* : H ₃ PO ₄ * : H ₂ O											
H ₃ PO ₄ * : H ₂ O ₂ * : H ₂ O											
H ₂ SO ₄ * : H ₂ O ₂ * : H ₂ O											
C ₆ H ₈ O ₇ : H ₂ O ₂ * : H ₂ O											
HCl* : HNO ₃ * : H ₂ O											
HNO ₃ * : H ₂ SO ₄ * : H ₂ O											
HCl* : *H ₂ O ₂ : H ₂ O											
HCl* : H ₂ O											
BHF : H ₂ O											
	etches		depends on composition					selective against (etch stop)			

Figure 5-3 The etching agents for the III/V-Semiconductors.[2]

As shown in Figure 5-3, GaAs can be etched by various types of acidic solutions; meanwhile, AlInP can be etched by HCl. However, there is no conclusive information about the resistance of AlInP under some other acids such as H₂SO₄ or H₃PO₄. Therefore, some new chemical solution were tested to selective etch GaAs on AlInP and the subsequent results are listed in Table 5-2 Etching results Table 5-2.

Table 5-2 Etching results under different solutions.

	Acetic acid etch	Phosphoric acid etch	Sulfuric acid etch	Amonia hydroxide etch
	CH ₃ COOH:H ₂ O ₂ :H ₂ O	H ₃ PO ₄ :H ₂ O ₂ :H ₂ O	H ₂ SO ₄ :H ₂ O ₂ :H ₂ O	NH ₄ OH:H ₂ O ₂ :H ₂ O
	10:3:10	3:1:10	5:1:10	2:1:10
Ag	-	no	-	yes
GaAs n++	no	yes	yes	yes
AlInP	-	yes	yes	no
substrate	-	No	yes	no

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As shown in Table 5-2, the acetic acid is too weak to etch the GaAs layer, and the $\text{H}_3\text{PO}_4:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ and $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ solutions etch both GaAs and AlInP. Thus, none of them could be used for the selective etching of the cap layer.

5.3.1.3 Citric acid and hydrogen peroxide ($\text{C}_6\text{H}_8\text{O}_7:\text{H}_2\text{O}_2$)

Some researches [3-6] have shown that the combination of citric acid and hydrogen peroxide is another option to implement a selective etching process on GaAs. Therefore, citric acid was tested to etch the GaAs cap layer. The granular citric acid (monohydrate) was mixed 1:1 with deionized (DI) water by weight, and the mixed citric acid solution was in turn mixed with H_2O_2 by ratio (5:1). The results of this etchant on the Ag metallization are shown in Figure 5-4. After 150s etching in the mixture of citric acid and peroxide, the surface of the metallization has become rougher, indicating that the solution of $\text{C}_6\text{H}_8\text{O}_7:\text{H}_2\text{O}_2$ reacts with Ag to a certain extent. This result was also confirmed by measurements with the profilometer, which show that the thickness of metallization decreased 50 nm after the etching process (i.e. the Ag etching rate is $\sim 3.3 \text{ \AA/s}$).

Figure 5-4 Pd/Ge/Ti/Pd/Ag metallization etched by $\text{C}_6\text{H}_8\text{O}_7:\text{H}_2\text{O}_2$ (5:1).

Notably, one part of metallization has been deeply etched s, as it is shown in Figure 5-5. A deep trench was found one the fingers of the grid, indicating that at this particular point, the Ag was totally etched by the $\text{C}_6\text{H}_8\text{O}_7:\text{H}_2\text{O}_2$ solution. The reason for this anomalous behavior is still unknown, though we hypothesize it might be actually related to a pore in the photoresist during the mesa etch rather than an etch during the cap layer removal.

Figure 5-5 Deeply etched Pd/Ge/Ti/Pd/Ag metallization by $C_6H_8O_7 : H_2O_2$ (5:1).

5.3.2 New metallization system designed for the selective etching.

Except searching a new etching agent, an alternative method to fabricate a solar cell is modifying the metallization structure to augment its endurance against the etching reagent. In the following subsections we present some alternatives explored.

5.3.2.1 Protect Ag with another Au layer

Since the Ag layer is easily etched by $NH_4OH:H_2O_2:H_2O$, a thin gold overlayer could be deposited to protect the Ag. However, if the gold does not conformally cover the metallization, the lateral side of metallization can be still accessed (and thus etched) by the $NH_4OH:H_2O_2:H_2O$, and metallization layer will be eventually dissolved due to the high etching rate of Ag in the etching solution. (The Ag is fully dissolved in only single seconds)

On the contrary, it is estimated that a top Au layer could be beneficial to the etching process by citric acid ($C_6H_8O_7:H_2O_2$), since the lateral etching in this case could be neglected due to the slow etching rate. However, depending on the RTA temperature used, the Au layer would diffuse into the silver layer losing its passivation function.

5.3.2.2 New metallization Pd/Ge/Ti/Pd/Al

Another modification is using Al instead of Ag as the layer to achieve a high sheet conductance. Although the conductivity of Al layer is not as good as Ag, it is still good conductor and is much more cost effective as has been shown in the last chapter. Therefore, another set of selective etching experiments were conducted on Pd/Ge/Ti/Pd/Al metal grids.. Figure 5-6 shows the results of etching Pd/Ge/Ti/Pd/Al

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with $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$. As the profilometer scans show, it was found that the metallization Pd/Ge/Ti/Pd/Al remained virtually intact on the solar cell after the etching process. The photographs on the left side of the figure also indicate that there is no visual change either.

Figure 5-6 Etching Pd/Ge/Ti/Pd/Al with $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$.

To confirm that Al is durable against $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$, the sheet resistance (R_s) was measured by line shaped patterns before and after etching for 10s and 60s. Figure 5-7 shows the results of this experiment. As this figure shows, it was found that R_s almost doesn't change, it only increases a little with increasing etching time. As the profilometer scans revealed no loss in Al thickness (Figure 1-6), we attribute the slight increase in R_s to the GaAs under the metallization being etched by $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ during the etching process (note that the sheet resistance measurement actually measures the parallel resistance of the metal layer and the n++GaAs cap layer underneath).

Figure 5-7 Sheet resistance of metallization before and after etching 10s and 60s.

5.4 Wet-etch isolation process (etching mesas)

CPV solar cell fabrication includes a wafer dicing step to separate individual cells. Moreover, to achieve the effective singulation of solar cells without performance and yield losses is very important. The saw-dicing process generates defects at the edge of the semiconductor and uncontrolled fragmentation, chipping or stress-induced cracks. Such damage could cause short-circuits or increase perimeter recombination. Therefore, one extra process such as etching trenches into the III-V layers to define the perimeter of MJSC is required before the dicing process is required [7]. This is the so called mesa isolation. Wet-etch is normally used for this purpose since its implementation is straightforward.

Accordingly, it is precisely the mesa etching process the one that defines the active area of the solar cell. In this respect, in a concentrator solar cell we typically want the active area to be totally surrounded by the busbar. In other words, there should be no photovoltaic active area beyond the busbar. In a real CPV cell this would not make much difference since the light is concentrated onto the designated area. However, in lab cells (as those manufactured at IES-UPM) aimed for calibrated measurements, any area

beyond the busbar would be added to the active area and will contribute poorly to the performance of the device as a result of perimeter recombination.

Accordingly, the ideal situation for a mesa etch is depicted in Figure 5-8 (b) where a perfect alignment between the metal grid and the mesas has been achieved. On the contrary, Figure 5-8 (a) represents a case where some photoactive area remains at the left rim of the device, beyond the busbar (indicated by the arrow). In order to prevent this from happening, the manufacturing process at IES-UPM intends to achieve the situation Figure 5-8 (c), where some undercutting is allowed in the semiconductor to guarantee that no active edges are left.

Figure 5-8 Illustration of the mesa alignment problem using the crosssection of a solar cell. (a) Imperfect mesa alignment where the arrow points some photoactive area that remains after the mesa etch; (b) the ideal situation where grid and mesas are perfectly aligned; and (c) a situation in which some undercutting of the mesas is allowed to prevent the existence of photoactive areas at the edge. Lateral and depth dimensions are not drawn to scale.

Mesa etches are isotropical, therefore the lateral penetration of the etch is the same as its depth (neither Figure 5-8 nor Figure 5-9 are draw to scale; in both cases the depth scale uis greatly magnified). Therefore, the way in which the situation of Figure 5-8 (c) is implemented is by using a photolithography mask to define the mesas that is the same size as the device area (or only slightly larger). In this way, the lateral penetration of the mesa etch will eliminate any photoactive area at the edges at the expense of causing some undercutting beneath the busbar. There are two extreme situations as reflected in Figure 5-9. The alignment of the mesa mask can be perfect, as in Figure 5-9 (a), and the undercutting appears in both ends or the is a slight misalignment, as in Figure 5-9 (b),

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and the undercutting concentrates at one end. The photolithography mask for the mesas must be designed so that in both these extreme cases the lateral penetration is enough to eliminate any possible rest of active area at the edges.

Figure 5-9 Possible situations with the mesa photolithography mask alignment.

The evident consequence of these alignment requirements is that the metallization is exposed (at least at the edges or from below) to the mesa etch reagents and therefore it must withstand their chemical action. This is not a problem in conventional gold-based metalizations but has to be demonstrated for Ge/Pd/Ti/Pd/Ag and for Ge/Pd/Ti/Pd/Al.

5.4.1 Problems with lateral etching.

During the mesa etching process, HCl and $\text{NH}_4\text{OH}_4:\text{H}_2\text{O}_2$ are needed to etch different layers in the multijunction solar cell structure. In particular, the mesa etching process is as follows:

- 1) 35s in $\text{NH}_4\text{OH}_4:\text{H}_2\text{O}_2$ to remove the cap layer.
- 2) 30s in HCl to etch the GaInP top cell.
- 3) 5s in $\text{NH}_4\text{OH}_4:\text{H}_2\text{O}_2$ to etch the GaInAs tunnel junction p region.
- 4) 4s in HCl to etch the GaInP tunnel junction n region.
- 5) 3min. in $\text{NH}_4\text{OH}_4:\text{H}_2\text{O}_2$ to etch the Ga(In)As middle cell and adjacent tunnel junctions.
- 6) 4s in HCl to etch the GaInP buffer layer.
- 7) 16s in $\text{NH}_4\text{OH}_4:\text{H}_2\text{O}_2$ to etch the GaInAs and GaAs tunnel junction.
- 8) 2s in HCl to etch the GaInP window layer.
- 9) 2min. in $\text{NH}_4\text{OH}_4:\text{H}_2\text{O}_2$ to etch the Ge bottom cell.

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Since the classic metallization on GaAs is AuGe/Ni/Au and Au is inert, there were no problems in using the procedure describe above with repeated immersions in HCl and $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2$ chemicals. However, as the new metallizations include either Ag or Al, it is found that lateral etching during the formation of the mesas damages the new metallization, since $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2$ etches Ag and the HCl etches the Al. For instance, Figure 5-10 shows the effects of etching mesas with $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2$ and HCl in a solar cell with a Pd/Ge/Ti/Pd/Al grid contact. It can be found that the metallization grid remains on the semiconductor virtually unaffected after the first 35s of etching with $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2$ and 30 s of etching in HCl. However, it was destroyed after the whole etching process due to the Al reacts with HCl.

Figure 5-11 depicts our vision on how this process occurs. Initially the metal is protected by the resist and no metal etching can proceed. However, after a certain time the lateral penetration of the etch allows the metal can be reached by the chemicals from underneath. At this point the dissolution of Al progresses very fast and the metallization is damaged.

Figure 5-10 Etching mesa results of Pd/Ge/Ti/Pd/Al with $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2$ and HCl.

Figure 5-11 Etching the metallization from a lateral side during the mesa etching process.

To overcome the problem that the solution etches the metallization through semiconductor, one extra resin layer was deposited to stop the lateral side etching on the semiconductor. The schematic diagram is shown in Figure 5-12. After the initial trench was formed, another layer of resin was deposited to protect the semiconductor lateral side. This approach does work on the first etching steps and thus confirms that the access to the metal form below is the origin of the problem. However, when the etching proceeds the trench grows deeper and the resin cannot protect the larger lateral area anymore, since the maximum thickness of resin layer is around the $3\text{ }\mu\text{m}$ and the depth of trench is about $6\text{ }\mu\text{m}$.

Figure 5-12 Schematic diagram illustrating the deposition of an extra resin layer to protect the lateral side of the semiconductor.

At this point, the sensibility of Al layers to our mesa etches remains an issue still to be solved.

5.4.2 Etching mesas with a new metallization grid

To design a new mask for the metallization grid pattern is an alternative method to avoid that the wet-etch solution destroys the metallization. We used a new metallization grid design (the one used at NREL, see picture in Figure 5-13) in which the metal stays “far” from the semiconductor perimeter (i.e. there is enough semiconductor between the perimeter and the metal that prevents the metallization from being etched by the etching solution through the lateral side. Figure 5-13 shows the result of etching mesas for the metallization Pd/Ge/Ti/Pd/Al with new grid pattern, it can be found that after etching, the metallization is perfect.

Figure 5-13 Results of etching mesa for the metallization Pd/Ge/Ti/Pd/Al with the new grid pattern.

This approach allows us to manufacture solar cells with the new metallizations to be compared with the conventional approach. However, it lacks of the accurate control of the active area needed for lab cells.

5.5 Solar cell results

5.5.1 Solar cell fabrication

With the objective of testing the suitability of the newly developed metallization and the subsequent adaptations made in the fabrication process we faced the fabrication of triple junction solar cells. The triple-junction semiconductor structure used in this experiment was state-of-the-art and is similar to that depicted in the “Introduction” chapter.

In order to avoid the contact between critical chemicals a special photolithography mask –designed at NREL– was used. Figure 5-14 shows the details about how this mask works. The solar cell active area is almost square ($3220\mu\text{m} \times 3480\mu\text{m} \sim 11\text{mm}^2$). The metal grid is defined so that always stays far from the active area rim; as shown in the right part of Figure 5-14. In this respect there is some sort of safeguard active area at the perimeter of the devices that prevents the chemicals used in the mesa etches to be in contact with the grid metal.

Figure 5-14 Solar cell active area configuration used in these experiments

The structures were processed into solar cells with the active area described in Figure 5-14 in two versions: one variant having Ge/Pd/Ti/Pd/**Al** front grids and the second variant having Ge/Pd/Ti/Pd/**Ag** front grids. The manufacturing sequence was as follows:

1. *Back contact definition.* Thermally evaporated gold contacts were deposited on the back germanium surface with a thickness of 600nm. During the evaporation the front side was protected with Shiphley Microposit 1828 photoresist which was rinsed in acetone after the metal was deposited. RTA alloying followed and was performed at 200°C during 2 minutes, under forming gas.
2. *Grid definition.* Grid photolithography was made on the front side of the samples using positive Shiphley Microposit 1828 photoresist. Despite not being optimum positive photoresist had to be used since the mask of Figure 5-14 was only available in the positive version. E-beam evaporated Ge/Pd/Ti/Pd/**Al** (50/100/50/50/500 nm) or Ge/Pd/Ti/Pd/**Ag** (50/100/50/50/500 nm) contacts were subsequently deposited. Only 500nm were deposited in order to facilitate the lift-off. Lift-off was carried out in acetone using ultrasounds. RTA alloying followed and was performed at 300°C during 20 seconds, under forming gas.

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3. *Mesa isolation.* Mesa photolithography was made on the front side of the samples using positive Shiphley Microposit 1828 photoresist. The wet mesa etching process applied to isolate the devices and minimize the perimeter recombination consisted of an optimized sequence of etching processes using $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ (2:1:10) and $\text{ClH}:\text{H}_2\text{O}_2$ (1:1), just as described in previous sections. After the mesas were finished, photoresist was rinsed in acetone.
4. *Cap layer removal.* The cap layer was etched using the metal grid as a mask. For grids using Aluminum, $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ (2:1:10) was used as an etchant for 50 seconds. For grids using silver, a citric acid mixture $-\text{C}_6\text{H}_8\text{O}_7:\text{H}_2\text{O}_2$ (5:1)– was used as an etchant for 3 minutes.

As is illustrated by Figure 5-15, the mask used contains a layout of 11 solar cells and auxiliary devices including Hall-Van-der-Pauw patterns, TLM patterns and sheet resistance bars. In particular, solar cells are set in four different rows, each row including devices with a different number of fingers in the grid. Thereby, the influence of the metal resistance can be assessed in a diversity of ways.

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Figure 5-15 (Left) Mask configuration including devices with different number of fingers. (Right) Outcome of the manufacturing process on a typical sample.

5.5.2 Solar cell characterization

5.5.2.1 Specific metal/semiconductor contact resistance (TLM)

The specific contact resistance of the metal/semiconductor contacts manufactured was measured using the auxiliary TLM patterns present in the mask (see Figure 5-15). The results of this measurement are summarized in Table 5-3 for both the metallizations with Al overlayer and with Ag overlayer. As expected, in all cases we measure specific contact resistances in the $10^{-6} \Omega \cdot \text{cm}^2$ range, as was the target of this thesis. A first conclusion that can be drawn is that no step of the solar manufacturing process causes an unexpected deterioration of the contact resistance.

Table 5-3 Metal/Semiconductor specific contact resistance measured in $\Omega \cdot \text{cm}^2$.

Pattern	Silver over-layer (Ge/Pd/Ti/Pd/Ag)	Aluminum over-layer (Ge/Pd/Ti/Pd/Al)
1e	5.73×10^{-6}	5.82×10^{-6}
1p	4.51×10^{-6}	6.23×10^{-6}
Average	5.12×10^{-6}	4.97×10^{-6}

5.5.2.2 Sheet resistance

The sheet resistance of contacts manufactured was measured using the auxiliary bar-like patterns present in the mask (see Figure 5-15). The results of this measurement are summarized in Table 5-4 for both the metallizations with Al overlayer and with Ag overlayer. In addition, measurements were taken before and after the cap layer removal to assess the possible impact of this process on the metal thickness and thus conductivity. As expected due to the limitation of 500 nm of Ag or Al in this experiment, in all cases we measure sheet conductance in the 50-70 $\text{m}\Omega/\square$ range. Again these were the values expected according to the targets of this thesis- A second conclusion that can be drawn is that the solar manufacturing process reaches the target values for sheet resistivity an unexpected deterioration of the contact resistance.

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Table 5-4 Sheet resistance measured in milliohms /square.

Pattern	Silver over-layer (Ge/Pd/Ti/Pd/Ag)		Aluminum over-layer (Ge/Pd/Ti/Pd/Al)	
	Before cap layer removal	After cap layer removal	Before cap layer removal	After cap layer removal
1e	38.53	-	63.01	72.69
2e	41.33	713.70	-	-
1p	42.88	59.80	55.99	-
2p	106.02	115.68	62.15	74.56
3p	39.16	-	-	-

5.5.2.3 Dark I-V

Dark I-V curves were measured on cells on the wafer (i.e. cells were neither diced nor soldered onto a carrier) with a probe station. These curves are summarized in Figure 5-16 (a) for Al-based metallizations and Figure 5-16 (b) for Ag based metallizations. Two facts are observable in these pictures. First a slight difference in series resistance is observable depending on the number of fingers. This fact indicates that due to the good quality of the contact, some current spreading through the grid fingers occurs even in the dark I-V measurement. The second fact is that a curve that was measured before the cap layer was removed (green line in both Figure 5-16 (a) and (b)) presents a series resistance very similar to that of the curves with the etched cap indicating that no significant undercutting of the cap layer under the fingers has occurred. Both these facts anticipate a successful processing of the solar cell devices.

(a)

(b)

Figure 5-16 (a) Representative dark I-V curves of solar cells with Ge/Pd/Ti/Pd/Al front grids with different number of fingers. The green line represents the situation of the sample before the cap layer was removed. (b) Representative dark I-V curves of solar cells with Ge/Pd/Ti/Pd/Ag front grids with different number of fingers. The green line represents the situation of the sample before the cap layer was removed in the sample with Al overlayer.

5.5.2.4 Light I-V

As a final proof of the success of the new processing sequence implemented, light I-V curves were measured on the cells still on the wafer (i.e. the solar cells were neither diced nor soldered onto a carrier). No antireflection coating was deposited onto the solar cells. These curves are summarized in Figure 5-17 (a) and (b) for Al-based metallizations and Figure 5-18 (a) and (b) for Ag based metallizations. Instead of presenting the Y-axis as current in [A], we have chosen to represent the current normalized as a percentage of the average I_{SC} of the cells measured with the lowest fill factor (i.e. those with 11 fingers). Figure 5-17 (a) represents the successful measurement of a one-sun I-V curve of several solar cells with Al-based metallizations and 11 fingers. Correspondingly, Figure 5-17 (b) represents the same for devices with 16 fingers. As expected the I_{SC} lowers ~2% as a result of the increase in the shadowing factor. Figure 5-18 (a) and (b) show the same situation for devices with Ag-based metallizations. In this case, as shown by Figure 5-18 (a) the I_{SC} produced by the device with eleven fingers is ~96.5% instead of the expected 100%. Analogously, Figure 5-18 (b) shows that the I_{SC} produced by the device with sixteen fingers is of is ~92% instead of the expected 98%. A careful analysis of the surface of these solar cells revealed that the etching of the capping layer was not totally perfect and residues remained close to the surrounding the fingers and busbar. Obviously, the presence of this unetched GaAs residues accounts for the loss in photocurrent. In summary, despite the processing of the cells with Al-based metalizations turned out to be successful the processing of the cells with Ag-based metalizations was not satisfactory. Further work needs to be done to fine tune this process.

(a)

(b)

Figure 5-17 (a) Representative one-sun I-V curves of solar cells with Ge/Pd/Ti/Pd/Al front grids with 11 fingers (b) The same for cells with 16 fingers. Since solar cells have no ARC currents have been normalized to the cells with the lower shadowing factor for easier comparison.

(a)

(b)

Figure 5-18 (a) Representative one-sun I-V curves of solar cells with Ge/Pd/Ti/Pd/Ag front grids with 11 fingers (b) The same for cells with 16 fingers. Since solar cells have no ARC currents have been normalized to the cells with the lower shadowing factor for easier comparison.

5.5.2.5 Concentrator I-V measurements

Obviously, the final proof of the suitability of the new metallizations and their associated manufacturing process has to be provided by concentrator measurements in

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which it should be shown how these improvements in contact technology produce, in the end, the expected outcomes in terms of increases in cell efficiency. Unfortunately, by the time this thesis had to be handed in the manufactured devices were being encapsulated to face the concentrator measurements and thus these results could not be included in the thesis.

5.6 Conclusions

The goal of this chapter was to implement the new metallizations developed into high concentrator solar cells. In order to do this, we have reviewed will the manufacturing sequence of concentrator solar cells paying special attention to the cap layer removal and the mesa isolation processes. During these two steps the contacts (or some parts of them) may be exposed to chemicals that can degrade them.

The results of these analyses could confirm that Al is durable against the $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ used for cap layer removal but is rapidly etched by the HCl used during the mesa isolation step. Therefore, the photolithography mask used must guarantee a perfect isolation of the Al layer during the mesas.

Conversely, these analyses could confirm that Ag has no problem with HCl but is rapidly dissolved in $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ used for cap layer removal. Accordingly new cap layer etches based on citric acid solutions have been implemented. Of course, again the photolithography mask used during the mesa etching step must guarantee a perfect isolation of the Ag layer during the mesas where $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ is heavily used.

In the final part of this chapter, we presented the implementation solar cells with front grids using these new Al-based and Ag-based metallizations. Results of the contact resistance and metal sheet resistance were within the ranges predicted. However, whilst Al-based solar cells performed well demonstrating the viability of the process, Ag-based devices suffered from a deficient etching of the cap layer that yielded a loss in photocurrent. Further work needs to be done to overcome this problem.

5.7 Reference

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Chapter 6. Summary, conclusions and future works

6.1 Summary and conclusions

The main goal and contribution of this thesis has been the development of a new contact metallization for multijunction solar cells by applying new EBPVD thin film technology, with the target of increasing CPV solar cell performance by reducing the series resistance. We can conclude that this goal has been achieved. In order to show a general perspective of the work presented, in the following sections the main results are summarized.

6.1.1 EBPVD tool has been commissioned and understood

Before this thesis, in the III-V Semiconductors Group at IES-UPM, the state-of-the-art front grid metallization was deposited by thermal evaporation. However, this technology is limited since is unable to evaporate refractory metals and the control of high deposition rate and thicknesses is difficult. Therefore, according to the demand of depositing new metallization, a new EBPVD tool Classic Twin 500 designed by PFEIFFER was set up and commissioned. In order to fabricate the solar cells properly, it is very important that the new experimental tools and techniques used have been understood adequately, and are well calibrated and controlled. The water system, vacuum system, e-gun system, and deposition control system have been checked and calibrated. Several problems were identified and solved: 1) a new e-beam block installed to solve the problems of e-beam oversize in the original one; 2) e-beam impact point shifts occasionally; 3) warnings in the turbo pump have been found and managed; 4) the software of SQC-300 controller has been updated to solve shutter delay problem; 5) a new bigger shutter was installed to increase the shading area in order to avoid the deposition of material before shutter opens; 6) the tooling factor for the thickness sensor has been calculated and examined.

6.1.2 Recipes to evaporate a wide range of materials have been developed

Deposition processes by EBPVD for a broad list of materials have developed and optimized. The most suitable type of crucible liner has been chosen for each material to

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avoid intermixing, contamination or reactions with the copper hearth during the evaporation. In order to deposit the film properly, the metal pellets (source material) have to be melted to form a homogenous solid “ingot” before the film deposition. This pre-melting process has been designed and developed for each individual material, including melt level, selection of e-beam power, sweeping region and ramping velocity, limitation of the evaporation rate, etc.

Once the pre-melting process has been done, almost all the parameters of the evaporation process have been tested to produce a new and optimized PID controlled evaporation process for each metal. This includes four steps: 1) temperature ramping up and soaking; 2) shutter opening; 3) deposition; and 4) temperature ramp down. Each step varies depending on unique properties of each material. Subsequently, a preliminary calculation about cost of deposition for each metal film has been carried out.

In essence, after a wealth of experiments and tests, a palette of interesting metal materials, namely, Al, Ti, Ag, Au, Pd, Ge, Ni, Cu can be deposited properly to form metal contacts on multijunction solar cells.

6.1.3 Several metallization systems have been studied

Before this thesis. in the III-V Semiconductor Group at IES-UPM, AuGe/Ni/Au contacts were deposited as front grids on high concentrator solar cells. Its specific contact resistance is in the range of 10^{-5} - $10^{-6} \Omega \cdot \text{cm}$, a value which is good enough with lower results barely improving the solar cell performance. However, its sheet resistances are in the range of $0.2 \sim 0.5 \Omega/\square$ depending on the thickness of metal layer deposited (500~1000nm) and this high value does impact the performance of solar cell. Therefore, four new metal stacks Ti/Pd/Ag, Pd/Ti/Pd/Ag, Ge/Pd/Ti/Pd/Ag and Ge/Pd/Ti/Pd/Al were proposed and thoroughly studied, to achieve:

1. A specific metal/semiconductor contact resistance of $\rho_{CF} \leq 10^{-5} \Omega \cdot \text{cm}^2$
2. A sheet resistance of $R_S \leq 30 \text{m}\Omega/\square$
3. Durable and reliable, to maximize the useful life of devices
4. Bondable, to facilitate the formation of the external connections
5. Low-cost, avoiding the use of large quantities of precious metals

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Figure 6-1 summarizes the different metallization stacks studied in this thesis to achieve the aforementioned properties, while Table 6-1 compiles their respective performance.

Figure 6-1 Different metallization stacks analyzed in this thesis.

Table 6-1 Comparative performance of all metal stacks studied.

	Ti/Pd/Ag	Pd/Ti/Pd/Ag	Ge/Pd/Ti/Pd/Ag	Ge/Pd/Ti/Pd/Al
Best ρ_{CF} [$\Omega \cdot \text{cm}^2$]	10^{-4}	10^{-4}	10^{-7}	10^{-7}
Best ρ_M [$\Omega \cdot \text{cm}$]	1.98×10^{-6}	1.94×10^{-6}	1.90×10^{-6}	3.57×10^{-6}
Best R_s for 1 μm thick film [$\text{m}\Omega/\square$]	20	20	19	36
Behavior with GaAs doping	Schottky for $N_D < 10^{19} \text{ cm}^{-3}$	Schottky for $N_D < 10^{19} \text{ cm}^{-3}$	Ohmic for $N_D > 10^{18} \text{ cm}^{-3}$	Ohmic for $N_D > 10^{18} \text{ cm}^{-3}$
Comments	Only ohmic for GaAs doped $N_D > 10^{19} \text{ cm}^{-3}$ and RTAs above 500°C that degrade contact morphology	Only ohmic for GaAs doped $N_D > 10^{19} \text{ cm}^{-3}$ and result of RTA 400 °C is better than Ti/Pd/Ag. RTAs above 400°C is not examined	Good ohmic contact, sample with doping level $2.5 \times 10^{18} \text{ cm}^{-3}$ has the lowest ρ_{CF} , higher or lower doping increase ρ_{CF} to $10^{-6} \Omega \cdot \text{cm}^2$	behaves similar to Ge/Pd/Ti/Pd/Ag ρ_M is higher relating to high bulk ρ_M of AL.

Ti/Pd/Ag was examined firstly. This stack showed very good metal resistivity ($\rho_M \sim 2.3 \times 10^{-6} \Omega \cdot \text{cm}$, corresponding to a $R_s \sim 23 \text{ m}\Omega/\square$ with 1μ thickness). This was attributed to the fact that barrier bilayer Ti/Pd prevents GaAs diffusing into Ag and thus poisoning the Ag top layer. However, its specific contact resistance achieved was high (best values in the range of $\rho_{CF} \sim 10^{-4} \Omega \cdot \text{cm}^2$). Accordingly, two new metal layers Pd and Ge/Pd were introduced to increase the metal-semiconductor contact conductance. Finally, the Ge/Pd/Ti/Pd/Ag metallization with low sheet resistance and low specific contact resistance ($\rho_M < 1 \times 10^{-6} \Omega \cdot \text{cm}$ and $\rho_{CF} < 10^{-6} \Omega \cdot \text{cm}^2$) were obtained, since the solid phase regrowth process of PdGe forming a highly doped GaAs⁺⁺ layer or Ge-GaAs heterojunction that further contributes to the lowering of the metal-semiconductor barrier height. As compared to the classic AuGe/Ni/Au metallization system ($\rho_c \sim 3 \times 10^{-6} \Omega \cdot \text{cm}^2$, $\rho_M \sim 2 \times 10^{-5} \Omega \cdot \text{cm}$), the Ge/Pd/Ti/Pd/Ag metallization shows a decrease of one order of magnitude in both the metal-semiconductor specific contact resistance and the metal resistivity. Such lower R_s and ρ_{CF} does achieve the challenging demands of contact metallizations for CPV solar cell. In addition, Ge/Pd/Ti/Pd/Al was also studied to further decrease the cost.

6.1.4 Manufacturing issues to use these new metallizations have been identified and sorted out (at least partially)

In order to implement the new Ge/Pd/Ti/Pd/Ag (or Al) metallization on concentrator solar cells, it must be compatible with the standard solar cell processing sequence at IES-UPM. This sequence includes two critical processes for the grid, namely, the mesa isolation process and the selective etching of the cap layer. Both of them use chemical etchants that will (or may) be in contact with the grid metal. Therefore, the new metallization should withstand such etches without significant degradation.

In terms of the cap layer removal, the state-of-the-art selective reagent used in the *III-V Semiconductor Group at IES-UPM* is $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ (2:1:10), does dissolve silver metal, which is the key for the high sheet conductivity. As a result, some new chemical solutions were tested to selective etch the GaAs cap layer on the AlInP window layer.

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Finally, a solution based on citric acid – $C_6H_8O_7:H_2O_2$ (5:1)– was found though it may etch Ag to a certain extent. Depositing another Au layer to protect Ag was also examined, but it did not work due to and the high etching rate of $NH_4OH:H_2O_2:H_2O$ (2:1:10) on the lateral side, however, the Au layer may be beneficial to the etching process by citric acid ($C_6H_8O_7:H_2O_2$). Another solution is using other top metal layer such as Al or Cu instead of Ag, since our etching experiments show that Al is durable against $NH_4OH:H_2O_2:H_2O$.

In terms of the isolation process, mesa etches are isotropic and thus the lateral penetration of the etch is the same as its depth. As the etching solution of HCl and $NH_4OH_4:H_2O_2$ are needed to etch different layers in the multijunction solar cell structure, both Al and Ag are damaged through the lateral side due to $NH_4OH_4:H_2O_2$ etching Ag and HCl etching Al. Finally, a new metallization grid pattern was used, in which the metal stays “far” from the semiconductor perimeter. Accordingly, the etching solution is not able to reach the metallization and the grid is perfect after the isolation process.

6.1.5 Implementation of these systems on solar cells has been achieved

In order to implement the new metallizations developed into high concentrator solar cells, we have reviewed the manufacturing sequence of concentrator solar cells paying special attention to the cap layer removal and the mesa isolation processes. During these two steps the contacts (or some parts of them) may be exposed to chemicals that can degrade them.

The results of these analyses could confirm that Al is durable against the $NH_4OH:H_2O_2:H_2O$ used for cap layer removal but is rapidly etched by the HCl used during the mesa isolation step. Therefore, the photolithography mask used must guarantee a perfect isolation of the Al layer during the mesas.

Conversely, these analyses could confirm that Ag has no problem with HCl but is rapidly dissolved in $NH_4OH:H_2O_2:H_2O$ used for cap layer removal. Accordingly new cap layer etches based on citric acid solutions have been implemented. Of course, again the photolithography mask used during the mesa etching step must guarantee a perfect isolation of the Ag layer during the mesas where $NH_4OH:H_2O_2:H_2O$ is heavily used

Chapter 6 Summary, conclusions and future works

In the final part of this chapter, we presented the implementation solar cells with front grids using these new Al-based and Ag-based metallizations. Results of the contact resistance and metal sheet resistance were within the ranges predicted. However, whilst Al-based solar cells performed well demonstrating the viability of the process, Ag-based devices suffered from a deficient etching of the cap layer that yielded a loss in photocurrent. Further work needs to be done to overcome this problem.

6.2 Future works

This thesis has contributed to develop a new contact metallization on multijunction solar cell by applying new EBPVD thin film technology. Accordingly, it is natural to follow up to develop EBPVD tools for depositing anti-reflection coating layers on the solar cell. Besides, several parts of this work can still be improved. This section synthesizes then all the works that can be addressed in the near future.

6.2.1 Further development of the cap layer removal and mesa isolation process

As has been detailed part of the problems to used the new metallizations used in the conventional fabrication sequence of high concentrator III-V solar cells used at IES-UPM is the reactivity of either Al or Ag to some chemicals used. Therefore, some research lines of potential interest to solve these problems include:

- Explore the use of *gold flash* to protect the metallization for chemical etches, i.e. create a protective gold crust a few nm thick to isolate Al o Ag from the
- Explore the use of dry etching to eliminated the problems with chemical etches
- Explore other conductive layers such as copper and new etching solution to be compatible with cap layer removal and mesa isolation process

6.2.2 Study the durability and reliability of the new contacts

The durability and reliability of the new contacts with high current flow and heating is necessary to be carried out, in order to ensure it can withstand the high concentration CPV operating conditions for long times.

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The new metallizations have been characterized by EDS and the results show that there is sulfur contamination in them. The role and influence of this sulfur contamination needs be understood.

6.2.3 Expand this study to dielectrics for ARCs

- Another obvious application of this the EBPVD technology developed is its use in the deposition of dielectric thin films for antireflection coatings. In this respect. The preliminary calibration of dielectric chamber of our EBPVD tool has been carried out. However, it is still necessary to further fine tune the calibration due to the large impact that ARC thickness has on light absorption. .
- Development of new deposition processes for new material.
- Design new ARC films based on new materials, replacing the current one ZnS and MgF_2 to increasing light absorption and film durability.
- Study a new shutter design to decrease lack of uniformity in dielectric film thickness deposited in the different locations in the spinning disk.

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CONTRIBUTION

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