MOVPE growth of GaP on Si with As initial coverage

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ABSTRACT

The growth of a GaP 50 nm layer on Si by metalorganic vapor phase epitaxy is studied using AsH₃ and PH₃ pre-exposure at low (550 °C) and high (800 °C) growth temperatures. The samples are characterized by transmission electron microscopy. The results obtained reveal that the use of As as a first coverage layer on top of misorientated Si-substrates favors the formation of a defect-free GaP epitaxial layer, for a wide range of AsH₃ pre-exposure times using high growth temperature (800 °C), even though relatively low Si substrate annealing temperatures are used (850 °C) and no homoepitaxial Si layer was first grown. The procedure presented in this work reduces the thermal budget and complexity compared to most previous GaP/Si routines.

1. Introduction

The integration of III-V semiconductors on silicon has been suggested as a promising technology to reduce the cost of optoelectronics, solar cells and high speed electronics, due to the optical and electronic functionality of III-V semiconductors combined with the mature and low cost silicon-based microelectronic technology [1,2]. For all the applications mentioned above, the suitable III-V materials exhibit a large lattice mismatch to Si which hinders their integration. For example, for multijunction solar cells the maximum theoretical efficiency for a III-V semiconductor on Si Dual-Junction Solar Cell (DJSC) is 40% for a GaAs_{0.8}P_{0.2}/Si solar cell [3] which presents a 3.24% lattice mismatch between both materials. A common approach is the formation of a virtual III-V substrate, by growing a GaP nucleation layer on the Si-substrate, acting as a template for the growth of the complete III-V semiconductor structure since this heteroepitaxial growth (GaP/Si) has the minimum lattice mismatch for a III-V on Si, i.e 0.36%. However, the system (GaP/Si) presents certain challenges that degrade the quality of the layers: i) the epitaxial strain or three dimensional growth, that leads to the formation of defects at the GaP/Si heterointerface or/and in the epitaxial layer [4–6]; ii) the growth of a polar III-V semiconductor (i.e. GaP) on a nonpolar substrate (i.e. Si) induces the formation of antiphase domains (APD) [5–9], which, if they are not annihilated or avoided will be detrimental for devices; and iii) the unwanted cross doping through the interface [9]. Recent and very promising studies opened the possibility of modifying the surface of a Si-substrate by As-coverage (close to 1 ML) and thermal treatments previous to the GaP deposit [10].

The development of well-controlled growth procedures to achieve

defect free GaP layers on Si is thus critical for the performance of the final devices and for industrial development.

The main requirements to achieve a successful growth of GaP on Si according to the literature are: i) the achievement of a clean Si surface free of any contaminants, especially C and O, since they can behave as nucleation centers for defects at the GaP/Si interface and ii) the formation of a single domain Si surface before III-V growth to avoid the formation of antiphase domains (APDs).

To achieve a clean Si surface most authors suggested a thermal treatment at high temperature (above 850 °C) under hydrogen not only to obtain an oxide and carbon-free surface but also to achieve double-step reconstruction on the Si wafer [5,6,9–14]. Some other authors also use homoepitaxial Si growth to bury any residual contaminant [4,7,8,15,16]. This last approach requires As-clean MOVPE reactors, and consequently growth interruptions and/or multi-reactor processes.

For the formation of a double-stepped Si surface to avoid APDs, the most common strategy is the use of misoriented Si wafers to enhance the formation of double steps at high temperature [5]; once this is achieved, the Si surface is pre-exposed to either group III or V elements in order to favor the formation of a given reconstruction of a Ga, As or P monolayer (ML). Regarding this pre-exposure or pre-nucleation step there is a wide range of approximations reported; how different pre-exposures affect subsequent growths has also been studied [17]. In MOVPE growth, most routines are based on group-V pre-exposure since the adsorption of group V elements with high vapor pressure on the surface is a self-limited phenomenon, contrary to exposure to group III atoms that tend to form clusters. The use of a P ML, either at high temperature [12–14] or low temperature [7,8,15] has been the most commonly reported strategy. In those cases in which low temperature

Table 1

Description of the pre-exposure routine for each sample.

Sample	Pre-exposure			
	Group V	Time (s)	Temp (°C)	Flow (moles/s)
As-30 s-800C	AsH ₃	30	800	$7.43 \cdot 10^{-6}$
As-360 s-800C	AsH ₃	360	800	$7.43 \cdot 10^{-6}$
P-30 s-800C	PH ₃	30	800	$3.71 \cdot 10^{-4}$
P-30 s-550C	PH ₃	30	550	$3.35 \cdot 10^{-4}$
As-30 s-550C	AsH ₃	30	550	$7.43 \cdot 10^{-6}$

GaP growth is required, tertiarybutylphosphine (TBP) is needed for an efficient pyrolysis of the P precursor. In comparison, only few works are based on As ML [6,10,11,18]. Just recently, the use of AsH₃ at high temperatures has been reported as giving promising results with Si substrate annealing below 850 °C [18]. In that work, the Si surface was exposed to AsH₃ at temperatures between 690 and 740 °C.

All these factors mentioned before increase the growth complexity, due to the time consumption, the thermal budget and the specific equipment requirements, making difficult the integration of GaP on Si technology with the standards required for the industry. Additionally, the number of parameters involved in the achievement of a defect free GaP layer is quite large (growth mode -continuous or pulsed-, growth temperature, pre-nucleation, etc) making the reported results non-easily transferrable to industry or even to other research reactors.

Accordingly, the main goal of this work is to set the basis for developing a GaP-on-Si growth procedure with: i) a lower thermal

budget by reducing the Si annealing temperature; ii) one step growth (no reactor changes or growth interruption); and iii) wide range of growth parameters.

In order to determine the limits of the growth parameters that allow a defect-free GaP/Si growth and to have a deeper understanding of the nucleation process, the AsH₃ pre-exposure time and growth temperature have been varied. PH₃ pre-exposure has been also tested at low (550 °C) and high temperature (800 °C), for comparison.

2. Experimental

Epilayers of GaP were prepared using a horizontal AIX200/4 MOVPE reactor on Si(100) substrates with a 2° miscut toward the nearest (111) plane. Wafers were deoxidized using an HF dip and preheated at 800 °C in a H₂ flow for 30 min in order to remove any residual traces of silicon oxide and to promote the reconstruction of the surface. Before the GaP growth initiation, the substrates were exposed to two types of preflows (AsH₃ or PH₃) at low temperature (550 °C) or high temperature (800 °C). The GaP layer was grown in continuous mode by supplying TMGa and PH₃ as source materials at a V/III ratio of ~4000. The target layer thickness was 50 nm. The temperature for the pre-exposure step and for the subsequent GaP growth was the same. In Table 1, the pre-exposure conditions for each sample are summarized.

The crystalline structure of the layers was characterized using transmission electron microscopy (TEM). Samples were examined in a Philips Tecnai F20 operated at 200 kV. Samples were prepared in cross-section by standard sample preparation methods, mechanical

Fig. 1. Cross-sectional TEM images along the [011] direction of sample As-30s-800C (AsH₃ pre-exposure during 30 s at 800 °C). Fig. 1a and b show low resolution BF images. Fig. 1c shows HRTEM and FFT analysis.

Fig. 2. Cross-sectional TEM images along the [011] direction of sample As-360s-800C (AsH_3 pre-exposure during 6 min at 800 °C). Figs. 2a and 2b show low resolution BF images. Fig. 2c shows HRTEM and FFT analysis.

Fig. 3. Cross-sectional TEM images along the [011] direction of sample P-30s-800C (PH_3 pre-exposure during 30 s at 800 °C). Fig. 3a shows low resolution BF image. Fig. 3b shows HRTEM analysis.

thinning and argon ion milling to electron transparency. High resolution TEM (HRTEM) images were also acquired for studying the local crystalline quality. Electron diffraction pattern and diffraction pattern simulations after fast Fourier transform (FFT) of HRTEM images were also used.

3. Results

In order to analyze the crystal quality of the GaP layers grown on Si as well as the properties of the interface, the different GaP/Si samples described in Table 1 were characterized by TEM.

Fig. 1 gathers the cross-sectional TEM images along the [011] direction for the sample pre-exposed to AsH_3 during 30 s at 800 °C

Fig. 4. Cross-sectional TEM images along the [011] direction of sample P-30s-550C (PH_3 pre-exposure during 30 s at 550 °C). **Fig. 4a** shows low resolution BF image. **Fig. 4b** shows HRTEM and FFT analysis of different regions.

(sample As-30s-800C). **Fig. 1a** and **b** show low resolution bright field (BF) images of the GaP layer deposited. Both images reveal the presence of a continuous and defect-free GaP layer, without any observable threading dislocations or stacking faults, which completely covers the Si surface. Additionally dark field images, not shown, reveal no APDs, as expected by using substrates with a 2° miscut toward the nearest (111) plane. **Fig. 1c** presents a characteristic HRTEM and the corresponding FFT analysis made in both the GaP layer and the Si substrate simultaneously. It shows the absence of crystallographic defects both in the interface and in the layer. The FFT analysis of the interface proves a good epitaxial growth of the GaP layer, since no rotation or double spots were observed.

In order to verify the influence of the AsH_3 pre-exposure time, an additional sample grown at the same temperature with the same molar flow but using a 6 min of AsH_3 pre-nucleation time was analyzed (sample As-360s-800C). Analogously to **Fig. 1**, **Fig. 2** presents TEM images along the [011] direction of sample As-360s-800C. **Fig. 2a** shows a general view of the surface and **Fig. 2b** presents a more detailed image. **Fig. 2c** presents a HTREM image and the FFT analysis made in both the GaP layer and Si substrate simultaneously.

The next step was to check if the use of PH_3 at high temperature also results in a defect free GaP on Si. **Fig. 3a-b** present cross-sectional TEM images of the sample pre-exposed to PH_3 at high temperature, 800 °C (sample P-30s-800C). **Fig. 3a** is a low magnification image

taken in BF along the [011] direction. In **Fig. 3a** an island-type growth of the GaP layer is clearly observable, these hillocks being interconnected by a thin 9 nm GaP layer. So, using PH_3 pre-exposure, a non-uniform GaP layer is obtained but still the islands formed seem to be of high crystal quality with well-defined and clean interfaces as shown by **Fig. 3b**.

Once the pre-growth/growth at high temperature had been tested, low temperature pre-growth/growth using AsH_3 as well as PH_3 were studied.

Fig. 4a-b show cross-sectional TEM images along the [011] direction of the sample pre-exposed to PH_3 at low temperature, 550 °C (sample P-30s-550C) and **Fig. 5a-b** are for the sample grown after AsH_3 pre-exposure at 550 °C (sample As-30s-550C). **Figs. 4a** and **5a** are low magnification images taken in BF along the [011] direction and **Figs. 4b** and **5b** are the corresponding HRTEM images with the FFT diagrams of different regions of the HRTEM image in order to determine the crystalline structure.

The images for both samples grown at low temperature (**Figs. 4** and **5**) are qualitatively similar despite the different pre-exposure species used. They show a continuous but rough GaP layer, plenty of defects such as stacking faults and twins. In most cases, defects seem to originate at the GaP/Si interface, although in some cases they start in the GaP layer. It can be observed that the nucleation layers present a high number of stacking faults along the {111} planes.

Fig. 5. Cross-sectional TEM images along the [011] direction of sample As-30s-550C (AsH_3 pre-exposure during 30 s at 550 °C). **Fig. 5a** shows low resolution BF image. **Fig. 5b** shows HRTEM and FFT analysis.

4. Discussion

Analyzing samples pre-exposed to AsH_3 (Figs. 1 and 2), it can be concluded that the duration of AsH_3 pre-exposure at high temperature is not critical to the crystal quality of the GaP layer and the GaP/Si interface, at least for the one molar flow of arsine and the one pre-exposure temperature used for both samples, although other authors have reported an increment in roughness with AsH_3 flows and times [20,21].

Summarizing the data about GaP nucleation at high temperature in Figs. 1–3, it seems that the use of AsH_3 pre-exposure leads to a continuous GaP layer without defects.

This result can be due to the combined influence of several factors: i) an effective removal of residual C and O at the Si surface by AsH_3 [19]; ii) stable As-Si bonds (stronger than P-Si) which, in turn, will favor the formation of a 2D nucleation layer during the exposure of Si wafers to an AsH_3 preflow [6]; and iii) the covalent radius of As atoms being only slightly larger than that of Si, which makes As atoms very likely to produce a continuous and stable coverage of Si surfaces even at high temperatures, favoring 2D-growth. Additionally, the GaP layer grows without defects for different AsH_3 exposure times. Warren et al. [18] published very good results of GaP on Si using AsH_3 for slightly lower temperatures and lower AsH_3 exposures, but also reported a decrease in layer quality with AsH_3 exposure time. It seems that using low flows, a high quality GaP/Si interface can be achieved even for high exposure times. This result is of relevance for the

development of a low budget multijunction solar cells process, since the formation of a Si p-n junction by diffusion in the same growth just before the GaP layer allows decreasing the duration of the complete routine since growth interruptions or extra equipment are not required.

Regarding the sample grown with PH_3 pre-exposure at high temperature (Fig. 4), the coalescence of islands is hardly obtained and a 3D-growth is commonly observed. According to previous studies, the use of low preflow times of PH_3 has been shown to result in island-type growth and a high density of V-shaped pit formation [13]. However, under certain conditions, PH_3 pre-flows can produce good results, both at high and at low temperatures [13–15]. It is important to remark that in those works at high temperature [13,14], the Si substrate was annealed above 850 °C before nucleation, so it seems that the substrate preparation using PH_3 requires higher annealing temperatures than when AsH_3 is used, increasing the thermal budget of the process.

Another interesting observation is that the use of low temperature growth using AsH_3 or PH_3 leads to the formation of a GaP layer with a lot of defects, especially {111} stacking faults. During three dimensional growth, the accommodation and coalescence of islands can favor the growth along the $\langle 111 \rangle$ direction. When a III or V atom arrives to a {111} plane, there are two equivalent positions in which the setting of the tetrahedral bonds characteristic of the zinc-blende structure are maintained. One of them results in the correct stacking of the atoms and the other one creates a stacking fault. If growth occurs along the $\langle 100 \rangle$ direction, the tetrahedral coordination is maintained in any

possible position for incorporating new atoms and the crystal structure of the substrate is also maintained. Therefore, the presence of stacking faults indicates growth following the $\langle 111 \rangle$ direction, and thus it is an indirect evidence of 3D-growth followed by island coalescence.

This result is coherent with the success of GaP/Si nucleation reported in [15], where very low temperatures ($\sim 450^\circ\text{C}$), specific precursors such as TBP, and pulsed growth (i.e. ALE) were needed to overcome the trend of GaP growing in 3D-mode at low temperature. In addition, very high Si annealing temperatures (above 850°C) or/and Si homoepitaxy were needed to achieve high quality GaP, increasing the complexity of the growth.

5. Summary and conclusions

We have studied the growth of GaP 50 nm layer on Si by MOVPE using AsH_3 and PH_3 pre-exposure before growth at both high (800°C) and low (550°C) temperatures. The characterization has been carried out by cross-sectional TEM. The results reveal that defect-free GaP on Si (without threading dislocations, stacking faults or other crystallographic defects) can be achieved for a wide range of AsH_3 pre-exposure times (30 s to 6 min using high temperature growth (800°C) with relatively low Si substrate annealing temperatures (850°C) and without prior homoepitaxial Si growth. Conversely, low temperature processes produce layers with high numbers of defects for both AsH_3 and PH_3 pre-exposures. Our AsH_3 pre-exposure routine at high temperature shows promising results due to the reduction in complexity compared to previous GaP/Si routines and opens a promising strategy for future industrial transfer, being of special interest for multijunction solar cells, since it will allow growing the complete structure in one single MOVPE reactor without growth interruptions.

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