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A GaAs metalorganic vapor phase epitaxy growth process to reduce Ge outdiffusion from the Ge substrate

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A barrier based on GaAs for controlling the Ge out diffusion has been developed by metalorganic vapor phase epitaxy. It is based on a thin GaAs layer (50 nm) grown at a low temperature (≈500 °C) on top of a predeposition layer, showing that GaAs prevents the Ge diffusing when it is grown at a low temperature. Additionally, two different predeposition monolayers have been compared, concluding that when the Ga is deposited first, the diffusions across the GaAs/Ge heterointerface decrease. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2901029]

The growth of III-V materials on Ge substrates has been very relevant since 1980s.[1] Different technology challenges appear when growing GaAs on Ge such as antiphase domains (APDs), misfit dislocations, Ge out diffusion, or Ga and As interdiffusion. When Ge diffuses into the GaAs layer, it acts as a *n* type dopant. This fact is very relevant for different electronic devices, such as solar cells,[2] especially for the *n*-on-*p* configuration, which is most commonly used nowadays, since the Ge can compensate the *p*-type GaAs layer—which is the closest active layer to the Ge substrate—or even change its polarity. Additionally, the effect of cross diffusion (As and Ga into the Ge) through the interface can form uncontrolled *p*/*n* junctions, spoiling the performance of electronic devices.[3] In a previous work, AlAs has been proposed as a diffusion barrier for Ge.[4] This solution has a disadvantage that high Al concentration layers can be highly resistive when grown by metalorganic vapor phase epitaxy (MOVPE) as a result of oxygen contamination.

Another way to decrease the Ge outdiffusion is by growing the active layers at a low temperature. This solution is not always viable since for some epitaxial techniques such as MOVPE, the optimum temperature range to achieve high quality GaAs layers is between 600 and 650 °C.[5] Consequently, it is important to develop a growth routine that stops the Ge outdiffusion even when the solar cell structure is grown at high temperatures.

Accordingly, in this paper a GaAs barrier layer has been designed to minimize the Ge outdiffusion from the Ge substrate. This layer is grown in two steps: firstly, a monolayer is deposited in order to homogenize the Ge surface [As monolayer -(AsML)-or a double monolayer based on a Ga monolayer followed by an As monolayer–(GaML+AsML –)]. As a second step, a GaAs layer of 50 nm is grown at a low temperature (≈475 °C) with a V/III ratio of 4 and a growth rate of 1 μm/h.

Since the arsenic shows a self-terminating tendency on Ge at a growth temperature higher than 350 °C,[6] for any AsH_3 exposure time, an As monolayer is formed. On the other hand, the gallium tends to form clusters and, consequently, a precise Ga flux is required in order to form a monolayer. This has been carried out by the optimization of the TEGa exposure time by using atomic force microscopy (AFM) measurements. Additionally, this GaAs layer grown at low temperature using a double predeposition monolayer (GaML+AsML) has been used as a nucleation layer to achieve APD-free GaAs on Ge substrates.[7]

In order to evaluate the Ge out diffusion, a 1000 nm *p*-type GaAs control layer grown at a high temperature (625 °C) on a Ge substrate using three different routines has been analyzed. In Table I, the characteristics of the three samples are summarized in order to simplify the presentation of the results. In sample 1, the GaAs control layer has been grown straightforwardly on the Ge substrate (“without any diffusion barrier”). In samples 2 and 3, a GaAs diffusion barrier has been grown between the Ge substrate and the control GaAs layer in order to check its influence as a germanium stop layer (“routine with diffusion barrier”). The difference between samples 2 and 3 is basically the type of predeposition monolayer used; GaML+AsML for sample 2 and AsML for sample 3. MOVPE growths have been carried out in a 2 in. AIX200 horizontal reactor system using TBAs and TEGa as metalorganic sources for As and Ga, respectively. Ge wafers, *p* type, 150 μm thick, (100) 6° off toward (111) have been used as substrates. The samples have been analyzed by means of secondary ion mass spectroscopy (SIMS), photoluminescence (PL) and electrochemical capacity–voltage (ECV) measurement. Firstly, the convenience of using GaAs grown at low temperature as a diffusion barrier for Ge has been verified by means of SIMS and PL (samples 1 and 2). Secondly, the influence of the type of the predeposition monolayer (GaML+AsML or AsML)

TABLE I. Characteristics of the three samples analyzed.

Sample	Diffusion barrier[a]	GaAs Control layer	SIMS	PL	ECV
1	Non	1000 nm	Fig. 1	Fig. 2	
2	With double predeposition monolayer (GaML+AsML)	1000 nm	Figs. 1 and 4	Fig. 2	Fig. 3
3	With As ML	1000 nm	Fig. 4		Fig. 3

[a]The diffusion barrier is a 50 nm GaAs layer grown at 475 °C. V/III=4.

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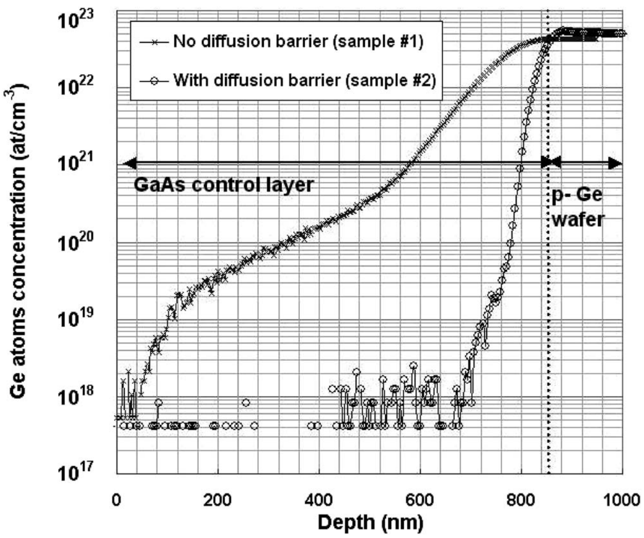

FIG. 1. SIMS profiles of Ge atom concentration for the GaAs control layer grown at high temperature on a Ge substrate with and without the GaAs diffusion barrier.

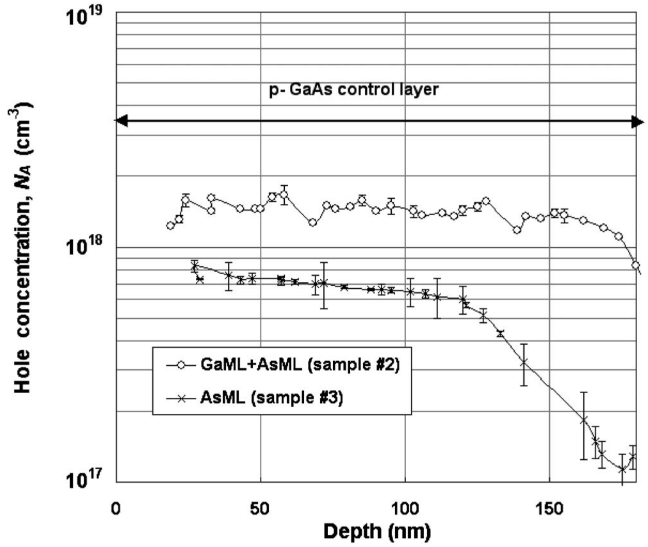

FIG. 3. ECV profiles for the GaAs control layer grown at high temperature on a Ge substrate with the GaAs diffusion barrier with a double predeposition layer (GaML+AsML) and with a As predeposition monolayer (AsML).

has been analyzed by means of ECV and SIMS (samples 2 and 3).

In Fig. 1, the SIMS profiles of Ge atomic concentration for the GaAs control layer grown at 625 °C on a Ge substrate without barrier layer (sample 1) and using a GaAs barrier layer with double predeposition monolayer (sample 2) are presented. As can be seen, the SIMS curves show that without any diffusion barrier, the Ge atoms penetrate more than 800 nm into the GaAs control layer (sample 1), while when using the GaAs diffusion barrier (sample 2), the Ge atoms diffuse less than 100 nm.

In Fig. 2, the PL spectra of the two GaAs control layers (samples 1 and 2) are presented. Analyzing the spectra for sample 1, it can be seen that an emission at 1.48 eV appears (peak A in Fig. 2), which is related to Ge transition in GaAs.[8] This energy level is not detected when the GaAs barrier is introduced (sample 2). On the other hand, for sample 2, an emission at 1.49 eV can be measured (peak B in Fig. 2),

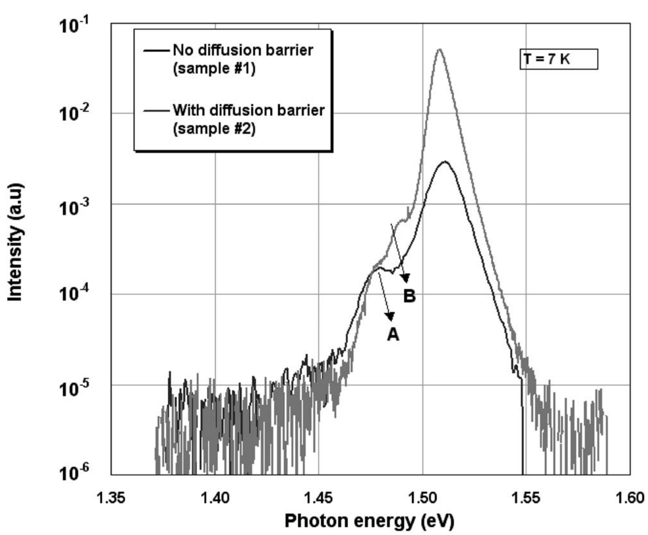

FIG. 2. PL spectra from 1.3 to 1.7 eV for the GaAs control layer grown at high temperature on a Ge substrate with and without the GaAs diffusion barrier.

which is related to carbon transition as a result of the low temperature growth of the diffusion barrier.

Consequently, from SIMS and PL measurements, it is shown that a thin GaAs layer grown at low temperature acts as a barrier for Ge outdiffusion.

This result can be explained by the fact that Ge diffuses into GaAs via Ga vacancies left by the outdiffusion of Ga atoms into the Ge substrate. The density of Ga vacancies increases as the growth rate decreases and as the growth temperature increases.[9] Consequently, as T_G decreases, the formation of Ga vacancies also decreases, diminishing the Ge outdiffusion. Additionally, the segregation of Ge atoms at the interface during the growth of the GaAs initial layers is another important mechanism for Ge outdiffusion.[4] This effect is directly related to the growth temperature of the initial layers,[10] being less important as the growth temperature decreases. As result of the reduction of the growth temperature, the formation of gallium vacancies as well as the germanium segregation decreases. These two factors imply a significant diminution of Ge outdiffusion. Consequently, GaAs grown at low temperature acts as a barrier layer for Ge outdiffusion.

Once the validity of a GaAs layer grown at low temperature as a barrier layer for Ge has been shown, the two predeposition monolayers used (samples 2 and 3) have been compared. Since the layers are very thin, ECV has been chosen in order to verify the doping level of the control layer (see Fig. 3). As it can be observed, when a double predeposition monolayer of GaML+AsML (sample 2) is used, the GaAs layer doping remains almost constant, while when an As ML is used, the GaAs layer presents a compensation profile as result of the Ge outdiffusion.

Consequently, the use of a GaML first probably causes a reduction in Ga vacancies that prevents the Ge outdiffusion. This could be related to the existence of APDs.

As it was mentioned before, the routine based on a double predeposition monolayer (GaML+AsML) generates APD-free GaAs, while when only an AsML is used, the existence of APDs has been measured by AFM.[7] The presence of APDs forces the dislocations in the interface GaAs/Ge to go into the epilayer running along their boundaries.[11] Since

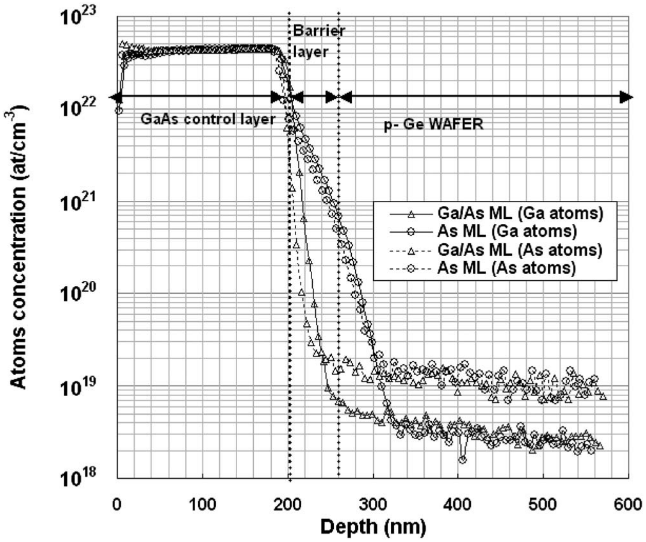

FIG. 4. SIMS profiles of As and Ga atom concentration for the Ge substrate with the GaAs diffusion barrier with a double predeposition layer (GaML +AsML) and with a As predeposition monolayer (AsML).

one of the mechanisms for the formation of V_{Ga} is the existence of dislocations,[12] it can be concluded that the existence of APDs favors cross diffusions through interface as a result of the formation of V_{Ga}.

Additionally, this result is coherent with the As and Ga diffusion in the Ge substrate depending on the type of monolayer used (Fig. 4). As can be seen, when a GaML is used, the Ga and As hardly diffuse in the Ge substrate, while when an AsML is chosen, a typical diffusion profile for both Ga and As is measured. These results show that when a GaML is grown on the Ge substrate, it prevents the cross diffusions more efficiently than when an AsML is chosen.

To summarize, a diffusion barrier for Ge based on GaAs grown at low temperature is proposed and verified. Additionally, this diffusion barrier acts as nucleation layer to grow APD-free GaAs on Ge.

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