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Abstract

The segregation and incorporation coefficients of antimony (Sb) in $Si_{1-x}Ge_x$ buried doped layers were investigated simultaneously using specific temperature sequences. We first showed an exponential kinetic evolution of Sb surface segregation in Si. In contrast such an evolution could not be observed in $Si_{1-x}Ge_x$ because of the Sb thermal desorption, at growth temperatures of 550°C. We also showed an increased surface segregation increasing with the partial Ge concentration in $Si_{1-x}Ge_x$ alloys, which was explained by a decrease of the kinetic barrier for Sb atoms mobility. It was, therefore, possible to determine the growth conditions to obtain a $Si_{1-x}Ge_x$ doped layer with a controlled incorporation level and a negligible surface segregation obtained by the thermal desorption of the Sb surface coverage. Finally, using Sb surfactant mediated growth, we found Ge dots with lateral sizes reduced by a factor of 2.8 and density multiplied by a factor of four as compared to dots directly deposited on Si(001).

Keywords: Surfactant mediated growth; Sb surface segregation; Doping; Quantum dots; Ge; Molecular beam epitaxy; Morphology

1. Introduction

The new generation of microelectronic or optoelectronic devices (velocity modulation transistor, resonant tunnelling diode, single electron transistor, etc.) require p- or n-type doped active channels (Si or SiGe) with a high level of dopant distribution control (both concentration and concentration variations). The growth of such structures presents problems particularly when selective doping of layers < 50 nm in width is needed. For example, the most widely used n-type dopant in Si molecular beam epitaxy (MBE), Sb, is characterised by severe surface segregation and/or desorption at the usual MBE growth temperature ($>$ 500°C) that drastically reduces its incorporation. Further difficulties are also raised during the growth of optoelectronic structures based on low dimensional active regions (small Ge dots for instance) for which the presence of impurities, surfaces and interfaces induce non-radiative recombination paths that lead to scattering limiting life-time.

For such zero-dimensional structures, difficulties related to the growth of nanometer sized crystals (< 10 nm) should also be overcome. Indeed, Ge dots grown in the Stranski–Krastanov mode have typical sizes of 50–100 nm in diameter [1,2]. Approaches in solving the above growth problems involve complex processes using patterned substrates [3,4], pre-patterned SiGe template layers [5], or C-doped Ge dots [6]. Even if reduced lateral sizes can be achieved by such processes, efficient radiative recombination generated by carrier localisation in low dimensional structures is far from being realised and effort should be afforded to reduce the size of these structures.

In this context, we have used the adsorption of

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sub-monolayer coverages of Sb impurities with two different goals: first to modify the growth mechanism of Ge dots using the surfactant effect of Sb, and secondly, to obtain n-type δ-doped structures. In spite of extensive research, the physical mechanism by which a surfactant modifies the Ge/Si growth mode remains unresolved. As a kinetic driving force for this effect, the reduction of the surface diffusion [7,8] and the change of the step edge energy barrier [9–11] have been reported. However, thermodynamic driving forces such as changes of the surface free energy [12,13], of the equilibrium shape [14] and of the defect energy (which induces strain relaxation [15]) would also play a role. A temperature transition from kinetic to thermodynamic dependent behaviour was also evidenced in [16]. Schematically, the Ge/Sb/Si growth at low temperature proceeds by the formation of an atomic scale micro-roughness (which consists of a very high density of two-dimensional islands). Up to a thickness of 8 ML Ge, the surface formed small micropyramids (with lateral length of approx. 10 nm). Further deposition leads to a rapid coalescence of islands accompanied by the generation of defects at the edges of these islands.

In this paper, we present experimental results obtained using depth profiles concentration analysis to determine the surface coverage and the dopant incorporation simultaneously from an investigation of Sb segregation kinetics during $Si_{1-x}Ge_x$ MBE growth. It is shown that both experimental doping conditions and segregation values can be deduced from these set of experiments. Depth concentration measurements reveal that surface segregation increases with the Ge concentration in the alloy in contrast with thermodynamic predictions. Consequently, the kinetic barrier for atomic motion play an important role in surface segregation. Moreover Sb desorption is also shown to increase with the Ge concentrations. In the end, a Sb surfactant mediated growth technique is applied to realise Ge dots with reduced lateral sizes and increased density.

2. Experimental

All the structures were grown in a Riber MBE system with a base pressure typically $< 10^{-11}$ torr. Floating zone silicon was evaporated thermally from an electron beam evaporator. Ge and Sb were evaporated from effusion Knudsen cells. Phosphorous doped Si(001) wafers of nominal orientation (miscut $< 0.5°$) were ex-situ cleaned and protected by an oxide layer as a final step. The subsequent in-situ cleaning, consisting of thermal desorption of the oxide layer at a temperature of approximately 900°C, was realised. A 50-nm thick Si buffer layer was systematically grown to achieve reproducible surface whose cleanliness is qualitatively

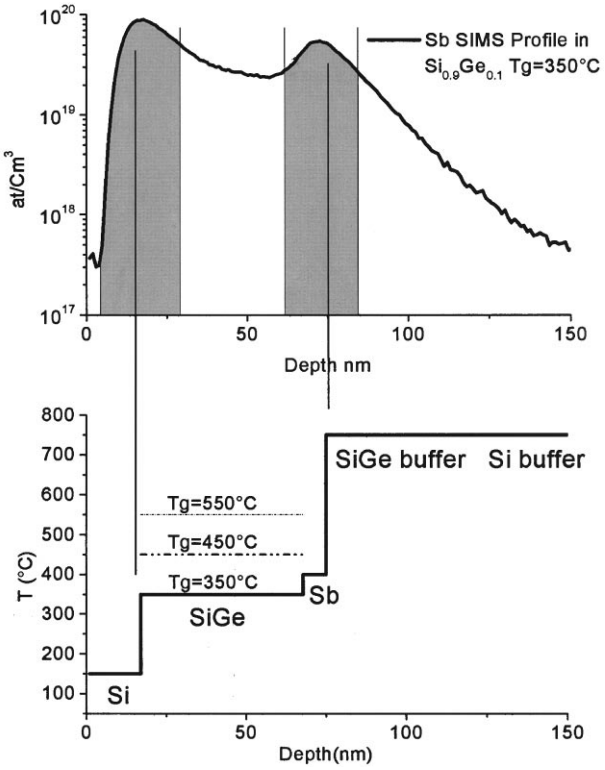

Fig. 1. Temperature sequences during growth.

checked by the (2×1) reconstruction streaks intensity in the RHEED pattern.

The dopant concentration profiles were measured from secondary-ion mass spectrometry (SIMS) using a Cameca IMS3F operated at 10 keV with Cs^+ primary ions.

The growth procedure producing Sb doped layers buried below an undoped $Si_{1-x}Ge_x$ layer (see for instance the Sb depth profile of Fig. 1 upper part) consisted of temperature programmed sequences, schematically represented in Fig. 1. After a deposition of 0.44 ML of Sb at 400°C, $Si_{1-x}Ge_x$ layers (with x varying between 0 and 0.2) were grown at constant temperature values T_G between 350° and 550°C. At the end of this sequence, the sample was immediately cooled to ambient temperature (lower than 200°C) and covered by an amorphous Si layer (approximately 20-nm thick), aimed at trapping the surface-segregated dopant atoms.

3. Results

Fig. 2a shows the evolution of the Sb (SIMS) profiles in a pure Si layer grown at different temperatures (T_G). At low temperature (350°C) two peaks can be observed: one (N_{seg}) relates to surface segregated atoms and the other (N_{inc}) relates to incorporated atoms. As the growth temperature increases, N_{inc} vanishes at the expense of N_{seg}. The surface segregation coefficient (r_{seg}), which can be defined as the fraction of the

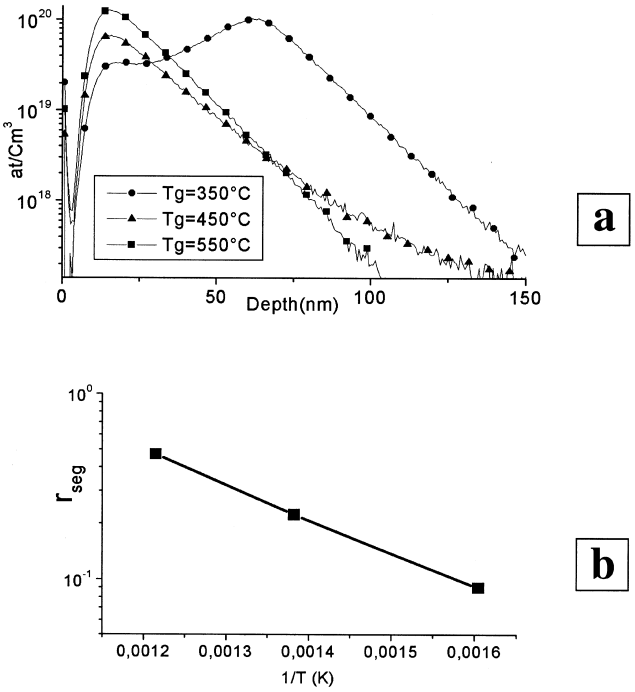

Fig. 2. (a) SIMS profiles of Sb in Si: $T_G = 350$, 450 and 550°C. (b) Sb surface segregation coefficient (r_{seg}) measured in Si.

integrated area of the surface peak (N_{seg}) over the total pre-deposited impurity atoms ($r_{seg} = N_{seg}/N_{tot}$), varies exponentially vs. the inverse growth temperature with $E_{activation} = 0.36$ eV (Fig. 2b). At 550°C, a Sb sheet concentration of ~ 0.4 ML was determined by integrating the area of the peak. This value is in good agreement with the pre-deposited Sb coverage (~ 0.44 ML). It confirms the negligible Sb desorption from Si(001) at this temperature.

A similar set of experiments have been performed for the growth of $Si_{1-x}Ge_x$ on Sb/Si (001).

A first interesting feature concerns the thermal desorption of Sb atoms from $Si_{0.9}Ge_{0.1}$ and $Si_{0.8}Ge_{0.2}$ (Fig. 3) surfaces, which occurs at 550°C, in contrast to the negligible desorption observed from the Si surface. Similar results have been found by Falkenber et al. [17]. This phenomenon can be attributed to the lower heat of sublimation of Ge leading to lower Sb–Ge bond breaking energy in comparison to Sb–Si. In addition calculations [18] have shown that each Sb–Si bond is approximately 0.1 eV stronger than each Sb–Ge bond.

From SIMS profiles, we also measured the incorporation coefficient (r_{inc}), which is determined as the fraction of the integrated area of the (N_{inc}) peak over the total pre-deposited impurity atoms. The Ge composition dependence of r_{inc} and r_{seg} is presented in Fig. 4. A surprising feature is that Sb atoms incorporation and segregation, respectively, decreases and increases with increasing Ge concentration. Similar results have been

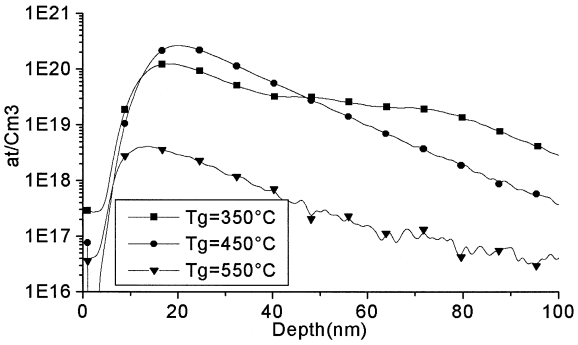

Fig. 3. Sb segregation in $Si_{0.8}Ge_{0.2}$. SIMS profiles for $T_G = 350$, 450 and 500°C.

reported by Fujita et al. [19], in contrast to results obtained for B atoms that are preferably incorporated in $Si_{1-x}Ge_x$ layers [20,21].

The driving force for Sb segregation is still a matter of debate since contradictory results have been obtained (both experimentally and theoretically). Discrepancies between Sb and B dopant atoms segregation/incorporation was mainly attributed to their different atomic sizes [21]. Concerning the B behaviour, it was established that the reduced B surface segregation in SiGe alloys is due to the partial compensation by Ge atoms with larger atomic sizes of the tensile strain induced by the smaller size of B atoms. Another explanation based on differences in the bond breaking energy of B–Si, Si–Si and Sb–Si has been given by Ushio et al. [22] by density functional calculations (without taking into account the strain). The lowering of the barrier energy at the numerous step edges induced by Sb during growth is also invoked [23–25].

In order to model Sb surface segregation during the growth of Si and $Si_{1-x}Ge_x$ layers during MBE experiments, calculations using a two-state atomic exchange model were performed and will be detailed elsewhere. Briefly, segregation is mainly driven by two contributions: an activation barrier for dopant atoms motion and an energetic term including chemical (alloying),

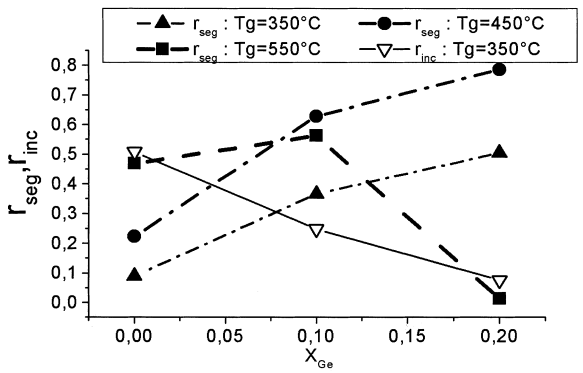

Fig. 4. Sb surface segregation (r_{seg}) and incorporation (r_{inc}) coefficients in $Si_{1-x}Ge_x$.

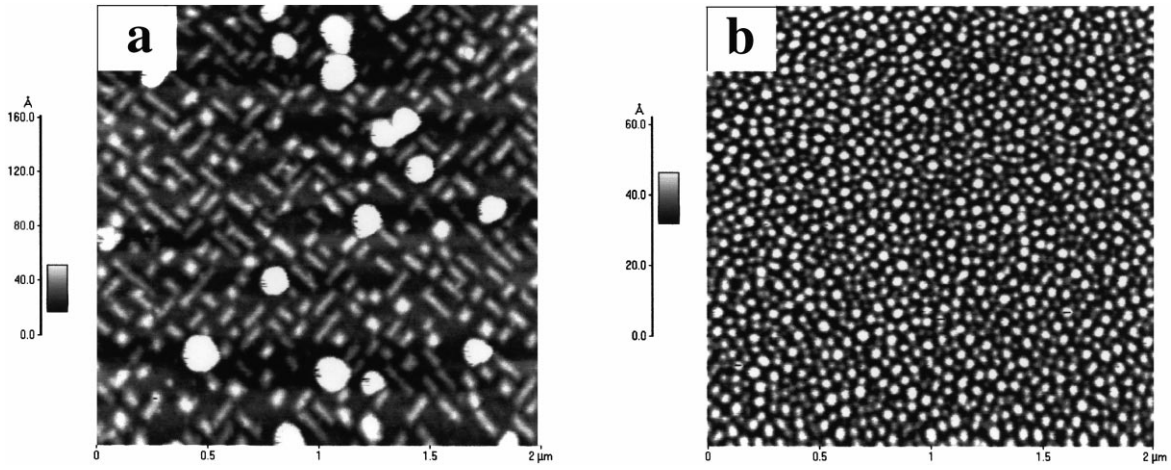

Fig. 5. AFM images 2×2 μm. Growth of 8 ML of Ge (a) on Si(100) surface, (b) on 1 ML Sb pre-deposited on Si(100) surface.

size effects and surface free energy. In such a model, the energetic contribution is not favourable at an increased surface segregation with increasing Ge ratios in $Si_{1-x}Ge_x$. In addition, by fitting our experimental results, we found that the kinetic activation barrier predominantly controls the evolution of Sb segregation in the overall range of temperature even if the physical meaning of this term has not been clarified up to now.

In a more technological view, the results show that highly doped $Si_{1-x}Ge_x$ structures ($N_{inc} \sim 10^{19}$ at/cm^3) can be realised at temperatures of approximately 350°C. Surface segregated atoms could then be removed easily by a flash-off treatment of the sample at temperatures of approximately 750°C, as shown in [26]. Following this procedure, it was then possible to grow Ge dots by Sb-surfactant mediated growth on Si(001). We then used a growth sequence consisting of the pre-deposition of 1 ML Sb on Si(001) at 400°C, followed by 13 ML Ge growth at 550°C. As a comparison, the Ge dots obtained without the surfactant are also presented in Fig. 5. While in the latter case, the bimodal size distribution of dots is observed (with mean lateral sizes ~ 55 nm and ~ 100 nm for elongated hut clusters and domes respectively), we clearly notice an increased dots density (multiplied by a factor of 10) and a reduced lateral size (mean size approx. 30 nm) with the surfactant.

4. Conclusion

SIMS profiles analyses were performed to determine the incorporation and segregation coefficients as a function of temperature and Ge concentration in $Si_{1-x}Ge_x$. A first interesting result is the enhanced thermal desorption induced by increasing Ge concentration. Moreover, in contrast to other doping impurities (B, As), Sb surface segregation (bulk incorporation) in $Si_{1-x}Ge_x$ alloys increases (and, respectively, decreases) with the Ge concentration. We suggest that lower kinetic barrier for Sb atoms motion in $Si_{1-x}Ge_x$ can be invoked to explain this behaviour. Finally, we have shown that it is possible to drastically change the growth mode of the Ge dots on Si(001) by using Sb surfactant mediated growth. Highly packed Ge dots (4.5×10^{11} clusters/cm^2) of very small size ($\varnothing \sim 30$ nm) were obtained by this process.

Acknowledgements

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