Sb surface segregation during epitaxial growth of SiGe heterostructures: The effects of Ge composition and biaxial stress

A. Portavoce,[1,2] I. Berbezier,[1,*] P. Gas,[2] and A. Ronda[1]
[1]*CRMC2-CNRS, Campus de Luminy, Case 913, 13288 Marseille Cedex 9, France*
[2]*L2MP-CNRS, Fac. des Sciences St. Jérôme, Case 142, 13397 Marseille Cedex 13, France*
(Received 2 January 2003; revised manuscript received 17 July 2003; published 15 April 2004)

Antimony is the most widely used *n*-type dopant for Si molecular-beam epitaxy (MBE). However, because of surface segregation during growth, the control of doping profiles remains difficult. The case of $Si/Si_{1-x}Ge_x$ heterostructures is complicated by the existence of stresses, which may affect both the thermodynamics and kinetics of segregation. In this study, we analyze the segregation of Sb resulting from the MBE growth of $Si_{1-x}Ge_x/Si(100)$ heterostructures using secondary ion mass spectrometry as a function of (i) growth temperature ($200\,°C \leqslant T° \leqslant 550\,°C$), (ii) germanium content ($0 \leqslant x \leqslant 0.2$), and (iii) stresses (compressively strained and relaxed layers). We show that Sb segregation: (i) increases with temperature, (ii) increases with Ge content in biaxially compressed layers, (iii) decreases with Ge content in relaxed layers. The temperature variation indicates that Sb surface segregation during growth is kinetically controlled. The contrasting behaviors observed as a function of Ge content in stressed and relaxed layers can thus be explained by a decrease of the segregation enthalpy induced by Ge addition and an increase of near-surface diffusion in stressed layers.

DOI: 10.1103/PhysRevB.69.155414 PACS number(s): 68.35.Dv, 68.55.Ln, 68.65.Fg, 66.30.Jt

I. INTRODUCTION

The permanent size reduction and increasing complexity of microelectronic structures is accompanied by drastic requirements on doping. This is the case of ultrashallow junction formation and of locally doped nanostructures such as quantum well wires or dots.[1] For example the new generation of Si/Si_xGe_{1-x}-based microelectronics and optoelectronic devices, e.g., velocity modulation transistor, resonant tunneling diode, single electron transistor, require accurate control of dopant profiles in both *p*- and *n*-type material.[2–4] In order to control and possibly predict dopant incorporation during the growth of Si/Si_xGe_{1-x} heterostructures a correct understanding of redistribution mechanisms: diffusion, segregation, and desorption phenomena, is necessary. There exist several difficulties. The first one is that redistribution during growth is a dynamic process, which combines thermodynamics (driving force) and kinetics (exchange rate). A second one is that the addition of Ge to Si in $Si/Si_{1-x}Ge_x$ heterostructures has two consequences: (i) an "intrinsic" alloying effect and (ii) a stress effect due to the $Si/Si_{1-x}Ge_x$ lattice mismatch.

The goal of this paper is to discriminate the respective role of thermodynamics and kinetics and the respective influence of "stress" and "chemistry." Attention is focused on surface segregation which is recognized as the main limiting factor in dopant incorporation. Other redistribution mechanisms such as desorption[5] and diffusion[6,7] are the subject of other publications. The dopant selected is Sb, which is the most widely used *n*-type dopant for Si molecular beam epitaxy (MBE) growth.

II. EXPERIMENT

In order to distinguish the effect of stress from that of Ge concentration, we analyzed the Sb distribution profiles resulting from the growth of strained and relaxed $Si/Si_{1-x}Ge_x$ heterostructures (with $0 \leqslant x \leqslant 0.2$). $Si/Si_{1-x}Ge_x$ structures were grown in a Riber MBE system with a residual pressure typically $\sim 10^{-11}$ Torr. Silicon was evaporated using an electron gun. Germanium and antimony were evaporated from effusion Knudsen cells. Phosphorous-doped Si(100) wafers of nominal orientation (misorientation $<0.1°$) were used as substrates. They were first cleaned and protected by an oxide layer using a standard chemical process. After introduction into the growth chamber, a 900 °C annealing was performed to dissociate the surface oxide. A 50-nm-thick Si buffer layer was then grown on the substrates at 750 °C to achieve a reproducible initial Si surface; its quality was checked by the reflected high-energy electron diffraction intensity of the (2×1) reconstruction.

Three sets of $Si_{1-x}Ge_x$ structures were grown. The first set (type 1), was used to check the influence of temperature and Ge concentration. These structures, sketched in Fig. 1,

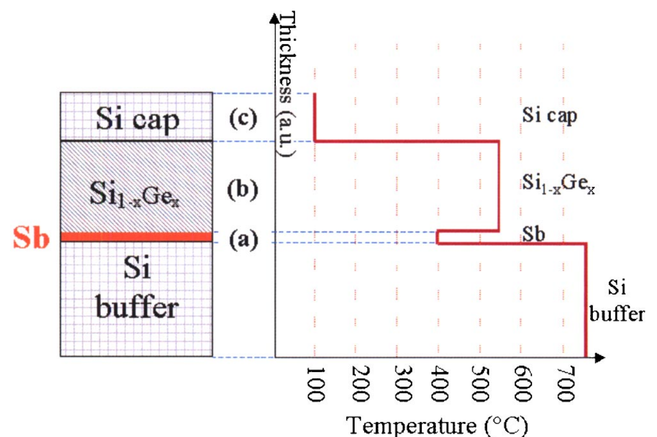


FIG. 1. (Color online) Schematic representation of type-1 structures used for the analysis of Sb segregation with growth temperature.

 ©2004 The American Physical Society

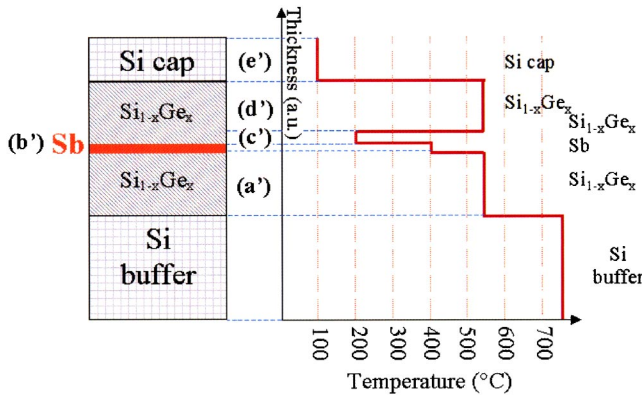


FIG. 2. (Color online) Schematic representation of type-2 structures used for the analysis of Sb segregation with both Ge content and induced compressive stress. All the $Si_{1-x}Ge_x$ layers have the same composition.

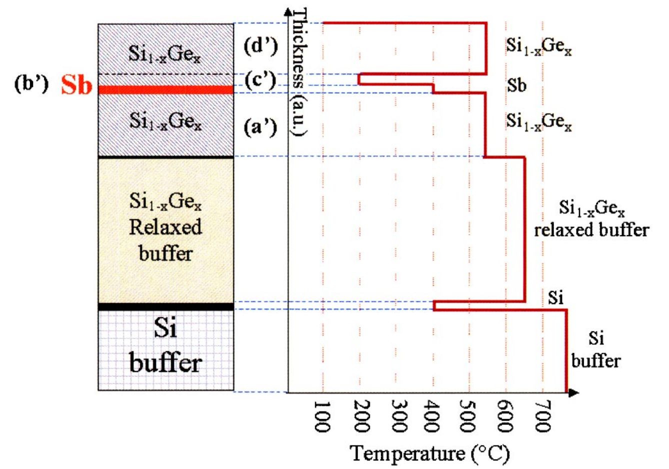


FIG. 3. (Color online) Schematic representation of type-3 structures used for the analysis of Sb segregation with Ge content in relaxed layers. All the $Si_{1-x}Ge_x$ layers have the same composition.

consist of (a) an Sb half monolayer (coverage $\theta\sim3\times10^{14}$ at/cm^2) deposited at 400 °C, (b) a 50-nm $Si_{1-x}Ge_x$ layer (with $x=0$, 0.1, and 0.2) grown at 350, 450, and 550 °C, and (c) a 20-nm Si layer deposited at $T<200$ °C in order to encapsulate the Sb fraction which has moved towards the surface during growth.

The second and third sets of structures (type 2 and 3, respectively) were used to separate the influence of Ge concentration and the influence of stress. Type-2 structures (Fig. 2) consist of four layers: (a') a 50-nm $Si_{1-x}Ge_x$ layer deposited at 550 °C (with $x=0$, 0.09, and 0.18), (b') an Sb half monolayer deposited at 400 °C, (c') a 6-nm $Si_{1-x}Ge_x$ layer deposited at 200 °C, (d') a 45-nm $Si_{1-x}Ge_x$ layer deposited at 550 °C, (e') a 20-nm Si cap grown at $T<200$ °C. In this case, the $Si_{1-x}Ge_x$ layers are fully compressively stressed on the substrate, they all have the same composition.

Type-3 structures (Fig. 3), consist of layers (a'), (b'), (c'), and (d') deposited on a $Si_{1-x}Ge_x$ relaxed buffer (with $x_{\mathrm{buffer}}=x_{\mathrm{structure}}$). In that case the $Si_{1-x}Ge_x$ layers were relaxed. The relaxed buffer was obtained by using the low-temperature compliant layer process.[8,9] This technique allows the glide of the majority of the threading dislocations in the low-temperature Si layer. It involves depositing 700 nm $Si_{1-x}Ge_x$ grown at 650 °C with a fixed composition (x) on a 50-nm Si layer grown at 400 °C. The concentration of dislocations in these $Si_{1-x}Ge_x$ buffers was measured by atomic force microscopy and transmission electron microscopy (plan view), and was found lower than 10^5 cm^{-2} (see Fig. 4, for instance). X-ray diffraction measurements confirmed that the level of relaxation was in all cases larger than 95%.

In type-2 and -3 structures, layer (c') was grown at an unusually low temperature (200 °C) in order to bury as much as possible the Sb distribution. Its crystallographic quality was restored before deposition of layer (d') by a 5-min anneal, at 750 °C for the strained structures and at 600 °C for the relaxed ones to limit dislocations propagation, respectively. If one looks at a typical Sb distributions in such structures (Fig. 5), one can discern two Sb peaks: one corresponds to the fraction incorporated after growth of layer (c'), the other to the fraction of Sb segregated during growth of layer (c') and which then floated to the growing surface during the growth of layer (d').

The Sb concentration versus depth profiles were measured by secondary ion mass spectrometry (SIMS) using a Cameca IMS4F operated at 8 Kev with O_2^+ primary ions. The Ge concentration was checked by RBS.

III. RESULTS

A. Influence of temperature

Figure 6 shows the Sb redistribution profiles obtained by SIMS in pure Si layers grown at 350, 450, and 550 °C (type 1). At 350 °C two peaks are observed, one in the vicinity of the surface which corresponds to the Sb quantity segregated during growth (Q_{seg}) and one at ~65 nm corresponding to the incorporated Sb quantity (Q_{inc}). An increase in temperature results in a decrease of the incorporated quantity and an increase of the segregated one. This indicates that in this temperature regime ($350\leq T$(°C)≤550 °C) segregation in-

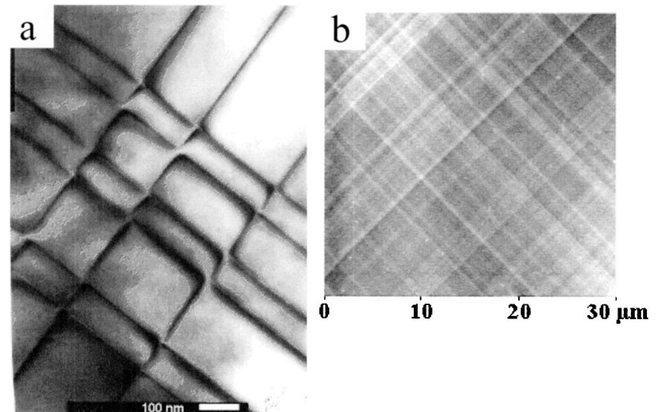


FIG. 4. (Color online) Dislocations density of 8×10^4 disloc/cm^2 and 5×10^4 disloc/cm^2 are measured on TEM plan view image of a $Si_{0.91}Ge_{0.09}$ layer tensily strained on $Si_{0.81}Ge_{0.19}$ relaxed buffer layer (a) and AFM image of $Si_{0.91}Ge_{0.09}$ relaxed buffer layer (b), respectively.

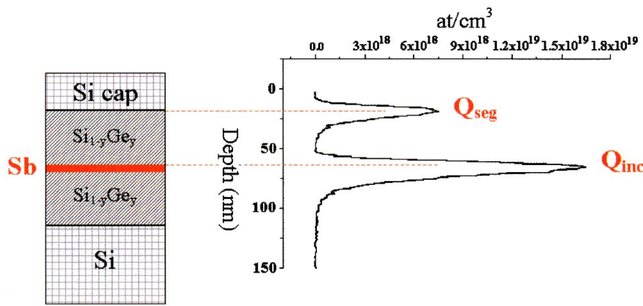


FIG. 5. (Color online) Correspondence between the layer structure and the SIMS profile: example of a typical type-2 structure (for $Si_{0.81}Ge_{0.19}$ compressively stressed).

creases with temperature. The same behavior is observed for the growth of $Si_{0.9}Ge_{0.1}$ and $Si_{0.8}Ge_{0.2}$ layers.

B. Influence of Ge content: combined effect of chemistry and stress

Figure 7(a) shows the Sb redistribution profiles obtained in Si, $Si_{0.9}Ge_{0.1}$, and $Si_{0.8}Ge_{0.2}$ layers grown at 350 °C on Si(100). One notices that the incorporated quantity decreases with increasing Ge content. This is very clear on Fig. 7(b) which gives the incorporation coefficient ($r = Q_{inc}/\theta$) at 350 °C as a function of Ge content. In order to calculate this coefficient, the two peaks have been fitted using SIMS profile simulation, they were deconvoluted and integrated.

C. Influence of biaxial strain

Figure 8(a) shows the Sb redistribution profile obtained in $Si_{0.82}Ge_{0.18}$ layers (type 2 and 3). A very large quantity of Sb is now incorporated. This quantity results from the incorporation of Sb during the growth of layer (c') at 200 °C. The surface peak corresponds to the quantity of Sb initially segregated at 200 °C and then redistributed at the surface during the growth of layer (d') at 550 °C. The comparison of the Sb redistribution obtained in a $Si_{0.82}Ge_{0.18}$ layer compressively strained (grown on Si) and relaxed (grown on a $Si_{0.82}Ge_{0.18}$ buffer) is presented. The incorporated quantity is significantly higher in the relaxed layer. One has to notice that Mashita *et al.* have shown a similar behavior for In in InGaAs.[10]

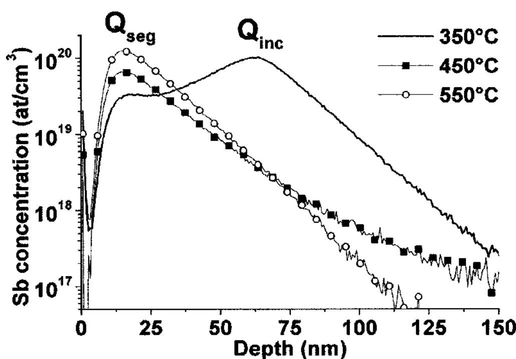
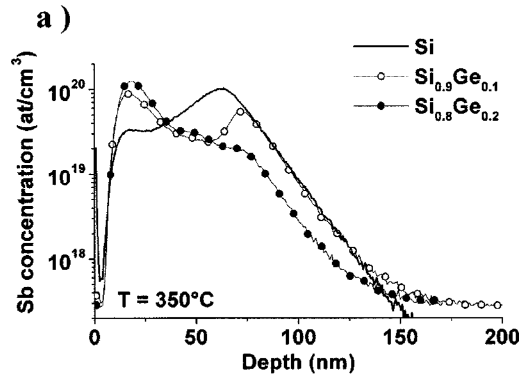


FIG. 6. Sb redistribution profiles in Si epitaxial layers on Si(100) grown, respectively, at 350, 450, and 550 °C (type 1). Q_{inc} corresponds to the Sb incorporated quantity and Q_{seg} to the segregated quantity.



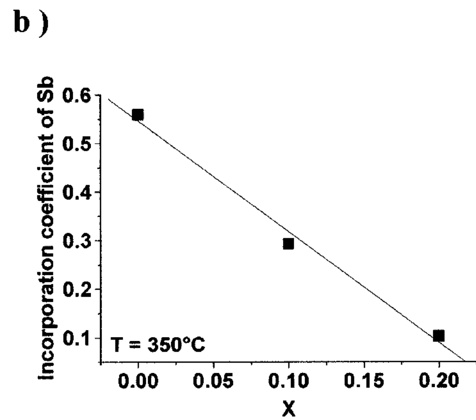


FIG. 7. (a) Sb redistribution profiles in $Si_{1-x}Ge_x$ layers (type 1) with different Ge compositions ($x = 0, 0.1, 0.2$) grown at 350 °C in epitaxy on Si(100). (b) Variation of the incorporation coefficient of Sb ($r_{inc} = Q_{inc}/\theta$) as a function of the Ge content (x) in $Si_{1-x}Ge_x$ layers grown in epitaxy on Si(100).

The results obtained are summarized in Fig. 8(b) where the Sb incorporation coefficient at 200 °C is plotted as a function of Ge content in strained and relaxed layers. θ cannot be deduced from the SIMS profiles for layers with $x > 0$ due to the desorption of Sb during the deposition of layer (d').[5] For the calculation of r on Fig. 8(b), θ was chosen equal to the value measured by SIMS in Si. The error bars on Fig. 8(b) correspond to the maximum error on the measurement of θ using the SIMS spectra performed in $Si_{1-x}Ge_x$ layers grown at 350 °C (no desorption of Sb) and in Si.

In strained layers the incorporation coefficient decreases with increasing Ge content. Consequently, it can be deduced that the combined effects of Ge composition and induced compressive stress is to increase Sb segregation.

In relaxed layers, the incorporation coefficient is larger for $Si_{1-x}Ge_x$ than for pure Si. It reaches a value close to ~ 1 (full incorporation) as soon as $x = 0.09$. The further evolution with Ge concentration cannot be analyzed at this low temperature. However one can infer that the intrinsic effect of Ge addition is a decrease of Sb segregation.

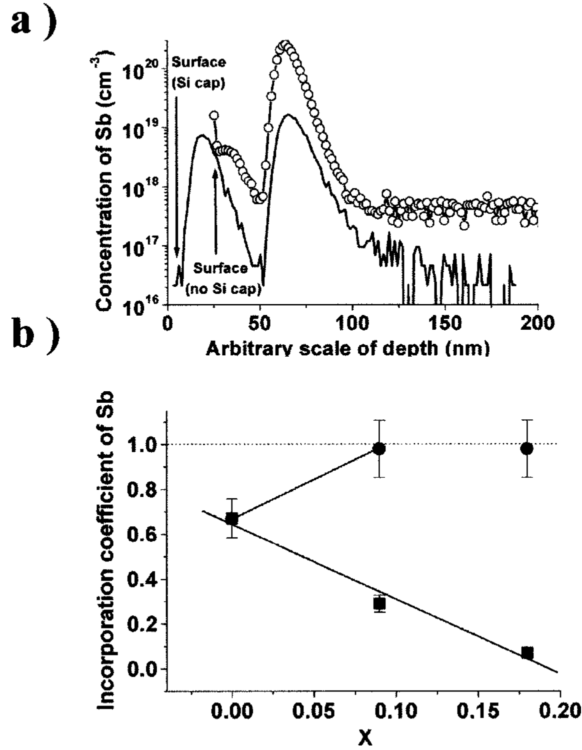


FIG. 8. (a) Comparison of the Sb concentration profiles obtained from a compressively strained (−) (type 2) and relaxed (○) (type 3) $Si_{0.82}Ge_{0.18}$ layer. The profiles are superimposed by referring to the position of the incorporated Sb peak and not the free surface (since the Si surface cap was only deposited on the strained layer). (b) Variation of the incorporation coefficient of Sb ($r_{inc}=Q_{inc}/\theta$) at 200 °C as a function of the Ge content (x) in relaxed (●) and compressively strained (■) $Si_{1-x}Ge_x$ layers.

IV. INTERPRETATION

This analysis shows that during the growth of $Si/Si_{1-x}Ge_x$ heterostructures, Sb segregation increases with temperature in the 350–550 °C temperature range. Moreover, at 200 °C the Sb segregation: (i) increases with Ge content in compressively stressed layers, (ii) decreases with Ge content in unstressed layers, and (iii) increases with compressive stress at constant Ge composition. Thus, it appears that the variation of the segregation of Sb with Ge composition (x) in stressed layers results from the combination of two opposite effects: a decrease due to Ge addition, an increase due to compressive stress.

In order to understand these results, one has to consider the flux of Sb segregating to the surface during growth. This flux is proportional to the product of the Sb kinetic mobility close to the surface (related to the activation energy for diffusion: E_{diff}) and the thermodynamic driving force for segregation (related to the enthalpy of segregation: E_{seg}). One has to remark that these two components follow an opposite behavior versus the temperature: the mobility increases with the temperature, even though the surface segregation driving force decreases as the temperature increases (E_{diff} and E_{seg} have opposite sign). This situation has been modeled by several groups on the basis of direct atomic exchange between surface and subsurface layers.[11–14] At high growth temperature, and neglecting desorption, the segregation is determined by E_{seg}, the equilibrium energy difference between surface and bulk. At lower temperatures, the segregation is kinetically limited and dominated by the E_{diff} term. These models predict that in the range of temperatures used in our experiments, the segregation is kinetically limited, which is in agreement with our experimental results showing an increase of segregation as the temperature increases. The variations of the Sb segregation with Ge composition and stress should thus be analyzed on the basis of this kinetic limitation. Providing that an analogy is made between the variations of the kinetic term in the vicinity of the surface and that observed in the volume, we can deduce the modifications of the activation energy for diffusion with Ge composition and stress from experimental data available in the literature. These data show that (i) the Sb lattice diffusion coefficient increases with Ge content for compressively stressed $Si_{1-x}Ge_x$ layers [for epitaxy on (100)Si],[6,7,15,16] (ii) this increase is due to the additive effects of Ge composition and compressive biaxial stress.[6,7,17] If we now assume, that the segregation enthalpy (E_{seg}) is constant, such variations of diffusion should lead to an increase of Sb segregation with Ge composition, both in relaxed and compressed layers. This agrees with the results obtained in compressed layers but not in relaxed layers. In that last case, Sb segregation decreases with Ge addition which implies that the Sb segregation enthalpy should decrease with Ge addition.

This is consistent with the characteristics of the Sb-Si-Ge ternary system. If one analyzes the three main components of equilibrium surface segregation[18] (parameters affecting E_{seg}), namely, (i) the difference in surface energy between solute (Sb) and solvent ($Si_{1-x}Ge_x$), (ii) the difference in atomic size,[19] (iii) the tendency towards phase separation (mixing energy), one finds the following.

(i) Ge has a lower surface energy than Si; its addition will decrease the alloy surface energy and thus the tendency for Sb to segregate. Moreover, Ge segregates on Si (Refs. 20, 21) which should amplify this phenomenon.

(ii) Ge has a larger atomic size; its addition increases the alloy lattice parameter and thus decreases the steric effect.

(iii) Sb-Ge interactions are repulsive,[22] which means that there should not be any synergetic effect between Ge and Sb surface segregation.

Consequently, the behavior of Sb segregation in relaxed layers leads to the conclusion that the variation of Ge concentration has a more effective influence on the energy of segregation (E_{seg}) than on the energy of diffusion (E_{diff}). In the case of stressed layers, the magnitude of the decrease of E_{diff} due to the increase of Ge concentration is expected to be more important than in relaxed layers due to the addition of the stress effect to the composition effect. The behavior of E_{seg} is less obvious and two scenarios can be considered. Considering that the minimization of the surface energy is the main driving force for surface segregation, one expects that E_{seg} still decreases as the Ge concentration increases in stressed layers. In this case, the increase of the Sb segregation during growth is attributed to the decrease of E_{diff} and the stress effect is found having a more effective influence on E_{diff} than on E_{seg}. The second scenario consists in consider-

ing that the driving force for surface segregation in stressed layers is the minimization of the strain energy of the total system. In this case, one can expect E_{seg} increasing with Ge composition and the increase of the Sb surface segregation is attributed to both an increase of the mobility and an increase of the thermodynamic driving force for segregation. One has to notice that the surface energy minimization is generally expected being the predominant driving force for surface segregation, which would favor the first scenario.

V. CONCLUSION

We have studied the surface segregation of Sb during the growth of $Si_{1-x}Ge_x$ heterostructures on Si(100) as a function of growth temperature ($200\,°C \leqslant T° \leqslant 550\,°C$), germanium content ($0 \leqslant x \leqslant 0.2$), and stresses (compressively strained and relaxed layers).

We show that Sb surface segregation: (i) increases with temperature, (ii) increases with Ge concentration for epitaxial layers on Si (combined effect of Ge composition and compressive stress), and (iii) decreases with Ge concentration in relaxed layers.

We analyze these variations on the basis of a kinetic limitation of Sb segregation, which is well illustrated by the temperature dependence. The contrasting behaviors observed as a function of Ge content in stressed and relaxed layers can thus be explained by an increase of diffusion in stressed layers combined with a decrease of the segregation energy due to Ge addition.

ACKNOWLEDGMENTS

It is a real pleasure to thank J. S. Christensen, A. Yu. Kuznetsov, and B. G. Svensson (KTH Stockhom) for their support and help with the SIMS experiments. We also thank G. Treglia (CRMC2) for discussions on the kinetics of segregation, R. Ghez, F. M. d'Heurle (IBM-Yorktown), C. Girardeaux, and D. Mangelinck (L2MP) for comments and critical readings of the manuscript. The EC projects SiGeNet (Grant No. IHP-RTN-99-1) and FORUM FIB (Grant No. IST-2000-29574) are acknowledged for financial support.

*Email address: berbezier@crmc2.univ-mrs.fr

[1] International Technology Roadmap for Semiconductors—2001, URL http://public.itrs.net/files/2001 itrs

[2] D. J. Paul, Thin Solid Films **321**, 172 (1998).

[3] U. König, M. Zeuner, G. Hock, T. Hackbarth, M. Gluck, T. Ostermann, and M. Saxarra, Solid State Electron. **43**, 1383 (1999).

[4] E. Kasper, G. Reitemann, in *Future Trends in Microelectronics*, edited by S. Luryi, J. Xu, and A. Zaslavsky (Wiley, New York, 1999), p. 125.

[5] A. Portavoce, F. Bassani, A. Ronda, and I. Berbezier, Surf. Sci. **519**, 185 (2002).

[6] A. Portavoce, Ph.D. Thesis, University Aix-Marseille, 2002.

[7] A. Portavoce *et al.* (unpublished).

[8] Y. H. Luo, J. Wan, R. L. Forrest, J. L. Liu, G. Jin, M. S. Goorsky, and K. L. Wang, Appl. Phys. Lett. **78**, 454 (2001).

[9] Y. H. Luo, J. Wan, R. L. Forrest, J. L. Liu, M. S. Goorsky, and K. L. Wang, J. Appl. Phys. **89**, 8279 (2001).

[10] M. Mashita, Y. Hiyama, K. Arai, B.-H. Koo, and T. Yao, Jpn. J. Appl. Phys. **39**, 4435 (2000).

[11] H. Jorke, Surf. Sci. **193**, 569 (1988).

[12] S. A. Barnett and J. E. Greene, Surf. Sci. **151**, 67 (1985).

[13] S. Fukatsu, K. Fujita, H. Yaguchi, Y. Shiraki, and R. Ito, Surf. Sci. **267**, 79 (1992).

[14] K. Kimura, Y. Endoh, M. Mannami, H.-J. Gossmann, G. H. Gilmer, and L. C. Feldman, Appl. Phys. Lett. **69**, 67 (1996).

[15] A. Yu. Kuznetsov, J. Cardenas, D. C. Schmidt, and B. G. Svensson, Phys. Rev. B **59**, 7274 (1999).

[16] A. Nylandsted Larsen and P. Kringhøj, Appl. Phys. Lett. **68**, 2684 (1996).

[17] P. Kringhøj, A. Nylandsted Larsen, and S. Yu. Shirayev, Phys. Rev. Lett. **76**, 3372 (1996).

[18] G. Tréglia, B. Legrand, F. Ducastelle, A. Saùl, C. Gallis, I. Meunier, C. Mottet, and A. Senhaji, Comput. Mater. Sci. **15**, 196 (1999).

[19] G. Pindoria, R. A. A. Kubiak, S. M. Newstead, and D. P. Woodruff, Surf. Sci. **234**, 17 (1990).

[20] G. G. Jernigan, P. E. Thompson, and C. L. Silvestre, Surf. Sci. **380**, 417 (1997).

[21] Y.-J. Zheng, A. M. Lam, and J. R. Engstrom, Appl. Phys. Lett. **75**, 817 (1999).

[22] W. W. Scott Jr., *Binary Alloy Phase Diagrams*, edited by T. B. Massalski, H. Okamoto, P. R. Subramanian, and L. Kacprzak (ASM International, Materials Park, OH, 1990).