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Equilibrium surface segregation enthalpy of Ge in concentrated amorphous SiGe alloys

J. Nyéki[a,b], C. Girardeaux[a,*], G. Erdélyi[b], A. Rolland[a], J. Bernardini[a]

[a]Laboratoire Matériaux et Microélectronique de Provence, Faculté des Sciences de St Jérôme, CNRS-UMR 6137, case 142, 13397 Marseille Cédex 20, France

[b]Departement of Solid State Physics, University of Debrecen, P.O. Box 2, H-4010 Debrecen, Hungary

Abstract

Auger electron spectroscopy technique was used to study surface segregation of Ge in concentrated amorphous $Si_{1-x}Ge_x$ thin film alloys. The alloys (with Ge bulk concentrations in the range of 18–58 at.%) were prepared by dc magnetron sputtering and annealed in a UHV chamber in the temperature range of 653–673 K. The surface equilibrium data ($X_{s(Ge)}$ versus $X_{b(Ge)}$) were determined from segregation kinetics. We show that (i) the experimental data can be interpreted using McLean–Langmuir isotherms with a segregation enthalpy $\Delta H_{(exp)}$ equals to 5.3 ± 0.5 kJ mol^{-1}and (ii) the estimated segregation enthalpy is lower than the theoretical one calculated in crystalline alloys neglecting the alloying and the size effects.
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1. Introduction

Numerous works reported that, during the growth of epitaxial Si/Ge layers, the control of Ge concentration is difficult due to the preferential surface segregation of Ge [1–3]. The driving force of germanium surface segregation in Si–Ge system is due to the difference in the surface tension of the elements [4,5] and the difference in size between Ge and Si atoms favours also the phenomenon (the atomic radius of these elements are the following $r_{Ge} = 0.137$ nm and $r_{Si} = 0.132$ nm). However, the changes of surface composition with temperature have been studied only in few works [6,7] and to our knowledge only one experimental work is devoted to the study of equilibrium segregation of Ge in SiGe alloys [8], which can be described in terms of phase transformation and characterized by a segregation enthalpy.

In this paper, we present an AES study of Ge surface segregation kinetics in a series of concentrated homogeneous amorphous $Si_{1-x}Ge_x$ thin films in the temperature range of 653–673 K (amorphous Ge crystallizes at about 693 K [9]). The main difficulty of this study was to determine equilibrium data ($X_{s(Ge)}$ versus $X_{b(Ge)}$) from AES kinetics results (i.e. the variations of the peak-to-peak heights of Si and Ge Auger signals versus time). Firstly, since the Ge (1147 eV) peak is not sensitive to the composition of the topmost layer the Si (92 eV) was used to follow the variation of composition

* Corresponding author. Fax: +33-4912-88775.
E-mail address: girarde@l2mp.u-3mrs.fr (C. Girardeaux).

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in the surface layer. Secondly, because of the high bulk concentration of the segregating specie (Ge) in the alloys, the estimation of the atomic fraction of Ge in the first layer needs a modelisation. Thirdly, long annealing is necessary to restore homogeneity of the alloy after segregation (i.e. to estimate the bulk Ge concentration near the segregated layer).

2. Materials and techniques

In order to study the composition dependence of segregation, amorphous $Si_{1-x}Ge_x$ thin film alloys with different concentrations of Ge (in the range of 18–58 at.%) were prepared. The general experimental set-up as described in previous work [8] is the following: the samples (thickness of 20 nm) were prepared by dc magnetron sputtering onto a SiO_2 substrate (size of 8 mm × 8 mm) at room temperature using a Si target covered by Ge pieces (base pressure in the equipment: 5×10^{-7} Pa, argon pressure during sputtering: 5×10^{-3} Pa, distance between the substrate and the target: 3.5 cm, applied power and tension: 69 W and 537 V dc, respectively, time of sputtering: 60 s). The samples were mounted in a conventional UHV chamber equipped with a CMA (Riber, OPC 105) and the surface was cleaned in situ by repeated cycles of low energy argon ion bombardment at room temperature until no carbon and oxygen could be detected. Then the specimen was heated by a graphite furnace controlled by an Eurotherm (902P) regulator, the temperature was monitored by a Pt–PtRh thermocouple fixed on the surface of the sample. The derived Auger peaks of germanium (Ge_{LMM} (1147 eV)), silicon (Si_{LVV} (92 eV)) and carbon (C_{KLL} (272 eV)) were recorded as a function of annealing time.

3. AES results

Annealing of the samples are performed at 653 K ($X_{b(Ge)}$: 0.18, 0.37, 0.55) and 673 K ($X_{b(Ge)}$: 0.51, 0.58) to avoid crystallisation of the alloys. Typical variations of Si, Ge, and C Auger signals (peak-to-peak height) versus time during annealing are the following:

1. the decrease of the Si (92 eV) peak-to-peak height is important in all experiments while the variation of the Ge (1147 eV) peak-to-peak height is not significant;
2. at the end of the kinetics (for annealing time long enough) constant values of the Si (92 eV) peak are obtained (note that for the alloys having nearly the same initial composition, the observed variations are reproducible);
3. the carbon signal remains constant and negligible during the process.

The typical variation of Si, Ge and C Auger signals during annealing at 653 K, and the AES spectra obtained before and after annealing are presented in Fig. 1.

The low value of the Si (92 eV) transition Inelastic Mean Free Path (IMFP) (0.47 nm on the basis of Seah and Dench formalism [10]), allowed us to analyse a maximum in-depth of about 3–4 atomic layers. Thus, the attenuation of the silicon peak indicates a local exchange between Ge and Si atoms in the uppermost layers: Ge atoms replace the Si surface atoms to minimize the surface free energy in agreement with theoretical predictions [4,5]. In contrary, the Ge (1147 eV) peak was not sensitive to the Ge surface segregation. This can be explained considering (i) the high value of the IMFP of Ge (1147 eV) transition (1.68 nm on the basis of Seah and Dench formalism [10]) (ii) the high initial Ge concentrations in our alloys (indeed in binary alloys with total mutual solubilities a low level of segregation was expected). As the carbon signal remains constant and negligible during the process, we suppose that, in all experiments the carbon does not play an important role in the Ge segregation process (surface site competition between Ge and C atoms, indeed, could occur only for sufficiently high carbon coverage).

The evidence of Ge surface segregation in Si–Ge amorphous thin film alloys is in agreement with the previous results in crystalline alloys and theoretical predictions. On the basis of the monolayer model [10], the calculated theoretical transmission factor giving the fraction of the Si (92 eV) signal transmitted through a complete Ge (1 1 1) layer is 0.51. Taking the ratio of the normalized Si (92 eV) intensities at the end and at the beginning of the experiments, we calculated the transmission factor (ω) of the Si (92 eV) signal: in the 0.64–0.82 range for all experiments. As these values are higher than the theoretical one, we have obtained experimental segregated germanium quantities at saturation lower than a complete Ge monolayer.

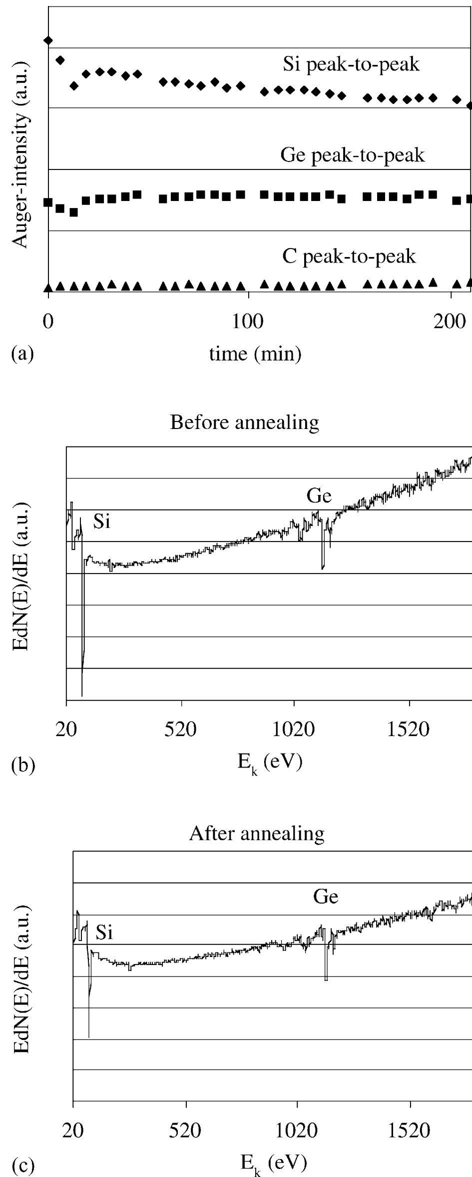

Fig. 1. (a) Typical variation of Si, Ge and C Auger signals during annealing. (b) Auger survey-scan before annealing. (c) Auger survey-scan after annealing.

4. Determination of surface equilibrium data at 653–673 K

To estimate equilibrium data, we assumed the existence of a local equilibrium during the kinetics process [12]. It means that the surface and the bulk (near the surface) concentrations follows the equilibrium isotherm during Ge segregation.

A depletion (due to the local exchange between Si superficial atoms and Ge bulk atoms from the underlying layers) was expected in the bulk layers near the surface at the beginning of the process. Assuming that the annealing time was long enough to restore the composition of the initial homogeneous alloy in the underlying region, the saturation of the superficial layer was completed: equilibrium $X_{b(Ge)}$ concentration with the segregated phase is the initial concentration of germanium in the alloy.

The equilibrium atomic fraction of Ge in the surface layer ($X_{s(Ge)}$) was estimated from the measured Auger peak-to-peak intensities from each experiment (end of the experiment corresponding to the saturation of the superficial layer). However, the determination of surface composition from the Auger data for alloys with high concentration of segregating component is more difficult than for dilute solid solutions and thus a method was developed and detailed in previous work [13].

To summarize, we estimate the atomic fraction of a component in the first layer of an inhomogeneous binary alloy, assuming that the surface layer has different composition than the bulk. Considering a semi-infinite sample of a $Si_{1-x}Ge_x$ alloy, in which several Ge atoms segregated on the surface, the surface layer is a $Si_{1-x}Ge_x$ layer with different composition than the bulk composition. We can define the so-called sensitivity factor q in the following way:

$$q = \frac{I_{Ge}/I_{Ge,\infty}}{I_{Si}/I_{Si,\infty}} = \frac{X_{s(Ge)}'(1-\beta_{Ge}) + X_{s(Ge)}\beta_{Ge}}{1 - X_{s(Ge)}'(1-\beta_{Si}) - X_{s(Ge)}\beta_{Si}}, \quad (1)$$

where I_∞ is the intensity coming from the bulk specimen, β the attenuation factor, $X_{s(Ge)}$ the atomic fraction of Ge in the first layer of a homogeneous $Si_{1-x}Ge_x$ and $X_{s(Ge)}'$ the atomic fraction of Ge in the segregated layer. According to reference [11] the values of the attenuation factor for Ge (1147 eV) and Si (92 eV) are respectively, $\beta_{Ge} = 0.82$ and $\beta_{Si} = 0.51$.

In these conditions, the atomic fraction of Ge in the segregated layer is expressed as:

$$X_{s(Ge)}' = \frac{q[(1-\beta_{Si}) + (1-X_{s(Ge)})\beta_{Si}] - X_{s(Ge)}\beta_{Ge}}{(1-\beta_{Ge}) + q(1-\beta_{Si})}. \quad (2)$$

The values of $X_{s(Ge)}$ in the surface layer in equilibrium with $X_{b(Ge)}$ in the underlying layers at saturation have been determined from Eq. (2).

5. Comparison between experimental and theoretical Ge surface segregation isotherms

The obtained experimental equilibrium data $X_{s(Ge)}$ versus $X_{b(Ge)}$ at 653 and 673 K are reported in Table 1. and plotted in Fig. 2. As the Si–Ge system is almost ideal, we have fitted our data obtained for different bulk concentrations using a McLean–Langmuir type isotherm:

$$X_{s(Ge)} = \frac{X_{b(Ge)}K(T)}{1 + (K(T) - 1)X_{b(Ge)}}. \quad (3)$$

From Eq. (3), we have determined the experimental segregation coefficient (taking it as a fitting parameter):

Table 1
$X_{b(Ge)}$ and $X_{s(Ge)}$ (sat) are the bulk and surface (at saturation) atomic fraction of Ge, respectively, ω is the calculated transmission coefficient of the Si (92 eV) signal through the segregated layer in each experiment and T the annealing temperature

$X_{b(Ge)}$	$X_{s(Ge)}$ (sat)	ω	T (K)
0.18	0.40	0.71	653
0.37	0.55	0.78	653
0.55	0.80	0.74	653
0.58	0.70	0.82	673
0.51	0.81	0.64	673

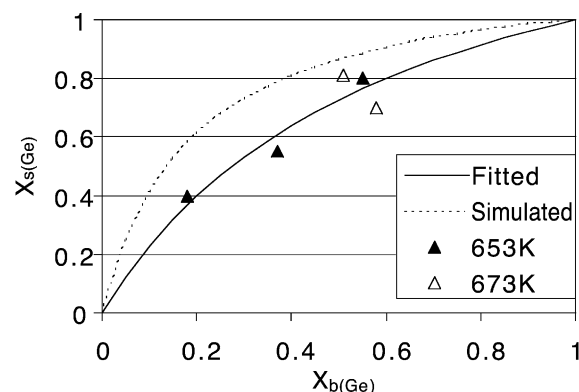

Fig. 2. Experimental results at the temperature range of 653–673 K and the fitted McLean isotherm marked with continuous line. The simulated McLean isotherm is also plotted with dashed line.

$K^{exp}(653\,K) = 2.6 \pm 0.3$. Then, supposing Arrhenius-type temperature dependence for the segregation factor, we have estimate the experimental segregation energy: $\Delta H_s^{exp} = 5.3 \pm 0.5$ kJ mol^{-1} (where the error given is the error of fitting).

Theoretically, the segregation energy of crystalline alloys can be determined from the binding energies of the components, the number of the free bonds of a surface atom and the size difference [4,5]. As previously noted, the Si–Ge system is almost ideal and the difference between the radii of the atoms is less than 4%. Thus, we assume that the segregation energy depends only on the relative surface energies of the two components and can be expressed as:

$$\Delta H_s^{theo} = -\frac{1}{n_0}(\sigma_B - \sigma_A) \quad (4)$$

where n_0 is the number of surface atoms per unit area, σ_{Si} and σ_{Ge} are the surface energies of the two components ($\sigma_{Ge} = 0.62$ J m^{-2} for Ge and $\sigma_{Si} = 0.735$ J m^{-2} for Si at the melting points of the elements). Taking $n_0 = 7.2 \times 10^{14}$ at cm^{-2} (the number of surface atoms per unit area corresponding to the Ge(1 1 1) plane) we obtained the theoretical segregation energy: $\Delta H_s^{theo} = 9.6$ kJ mol^{-1}.

In Fig. 2, we have plotted the fitted experimental and the simulated McLean isotherms and one can see that the surface segregated Ge quantities in amorphous alloys are lower than the theoretical ones. Presence of a substantial concentration of dangling bonds and defects in the superficial layers of amorphous semiconductor alloys reduces the segregation level by comparison to what happens with crystalline surfaces. Moreover, numerous factors have been neglected in the calculation of ΔH_S^{theo}: size effects and the use of crystalline surface energy data will increase the segregation energy while the neglected temperature dependence of the surface energies will decrease this value. Thus, we estimate that a qualitative agreement was obtained between experimental and theoretical germanium segregation isotherms and this provides a convincing support to conclude that segregation phenomena taking place in crystalline and amorphous $Si_{1-x}Ge_x$ thin film alloys are comparable (assuming that relaxation in amorphous state does not induce significantly changes in surface structures).

6. Conclusion

We have studied by AES the segregation of germanium in series of amorphous $Si_{1-x}Ge_x$ thin film alloys at 653 and 673 K and the main results of this work are the following:

1. The variation of Auger signals during annealing indicates a local exchange between Ge and Si atoms in the uppermost layers: Ge atoms replace the Si surface atoms to minimize the surface free energy as observed in crystalline alloys. For annealing time long enough, equilibrium data have been determined and an experimental segregation isotherm was obtained. It was found that the germanium surface coverage is always much lower than a complete Ge monolayer.
2. The experimental segregation energy ($\Delta H_S^{exp} = 5.3 \pm 0.5\,kJ\,mol^{-1}$) has been determined using McLean–Langmuir formalism and a theoretical segregation energy was calculated: $\Delta H_S^{theo} = 9.6\,kJ\,mol^{-1}$ assuming that germanium segregation is only related to the difference in the surface tensions of the elements (i.e. size and chemical effects are negligible). The lower value of the experimental segregation energy was explained by the presence of a substantial concentration of defects in the surface layers of amorphous semiconductor alloys compared to crystalline state. Thus, the qualitative agreement observed between these segregation energies provides a convincing support to conclude that segregation of Ge in amorphous $Si_{1-x}Ge_x$ thin film alloys can be compared to that in crystalline alloys.

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