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Density measurement of amorphous Si_xGe_{1-x} alloys

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The atomic density of amorphous Si_xGe_{1-x} alloys ($x = 1$, 0.85, 0.67, 0.50, 0.20 and 0) has been measured. Mono-crystalline Si_xGe_{1-x} layers were implanted with 1.50–2.75 MeV Si^{2+} and Ge^{2+} ions to produce the amorphous material. Using surface profilometry and RBS/channeling, it was found that amorphous alloys are less dense than the crystalline alloys, and that Vegard's law underestimates the a-Si_xGe_{1-x} density.

1. Introduction

Ion implantation of Si_xGe_{1-x} alloys has recently attracted interest because of its potential application in electronic and optoelectronic device processing. It can also be used to produce amorphous layers of high purity. This enables one to study fundamental properties of amorphous Si_xGe_{1-x} alloys, such as its atomic density. Silicon and germanium form a completely miscible system, with the same type of chemical bonding (fourfold coordinated covalent) as in the pure elements. It is known that a-Si is less dense than c-Si [1] and that the density of crystalline Si_xGe_{1-x} alloys deviates slightly from that predicted by Vegard's law [2], (Vegard's law states that the lattice parameters of alloys varies linearly with composition). We have found that Si_xGe_{1-x} alloys are less dense in their amorphous form than in their crystalline form.

2. Experimental

The samples used in this work consisted of 2–3 μm thick Si_xGe_{1-x} layers with a Si concentration $x = 0.85$, 0.66, 0.48 and 0.24 deposited epitaxially on silicon substrates. The molecular beam epitaxy (MBE) depositions, courtesy of the National Research Council of Canada (NRCC), were carried out with the substrates held at 500°C. In addition, we have investigated pure Si and Ge samples. High energy ion bombardment with Si^{2+} and Ge^{2+} ions to different doses (see Table 1), was used to produce amorphous regions. During the implantations, a raster scan was used to achieve later-ally homogeneous implantations, the beam current on target was around 100 nA. The samples were clamped to a copper block which was held at liquid nitrogen temperature, and the pressure during all the bombardments was typically less than 10^{-6} Torr. A steel mask was clamped on the sample to produce alternating amorphous/crystalline Si_xGe_{1-x} regions. In one case, a mixed silicon and germanium implantion was used, so as not to change the stoichiometry of the alloy. For the other alloys, only silicon bombardments were performed, which led to a change in stoichiometry less than 1%.

Under the implantation conditions described above, the material will amorphize. In fact, the dose used (see Table 1) exceeds the threshold for amorphization by about a factor of 5. For some samples, Raman spectroscopy was used to confirm that the layers had amorphized all the way up to the surface.

A cross-sectional view of a sample after implantation is shown schematically in Fig. 1. The step height h and interface depth $d + h$ were determined by surface profilometry and channeling, respectively. The ratio of

Table 1
Implantation parameters

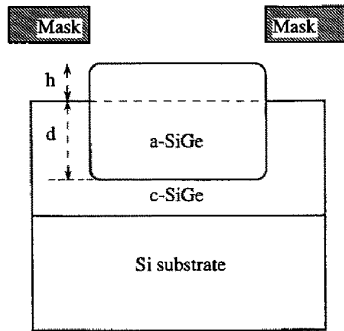| Samples	Energy [MeV]	Dose [atoms/cm^2]
Si	2.00	5×10^{15} Si^{2+}
Si$_{0.85}$Ge$_{0.15}$	2.00	5×10^{15} Si^{2+}
		5×10^{15} Ge^{2+}
Si$_{0.66}$Ge$_{0.34}$	2.00	5×10^{16} Si^{2+}
Si$_{0.48}$Ge$_{0.52}$	2.00	6×10^{16} Si^{2+}
Si$_{0.24}$Ge$_{0.76}$	2.75	4×10^{16} Si^{2+}
Ge	2.50	6×10^{15} Ge^{2+}

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Fig. 1. Sketch of the sample after implantation, indicating: d: the original thickness of the amorphized Si_xGe_{1-x} before implantation. h: step height.

the crystalline and amorphous densities is then calculated from

$$\frac{\delta_c}{\delta_a} = 1 + \frac{h}{d}. \tag{1}$$

The expansion upon amorphization is thought to be due to a change in the atomic density rather than to porosity. Porous material may result when large doses of noble gases are implanted [3] or when very high beam currents and elevated target temperatures are used [4]. In our samples, porosity has been avoided by using low current, cooling to LN_2 temperature, and self-implantation.

A Dektak 3030ST instrument was used to carry out the surface profilometry. Each scan of 4 mm covered 3 periods of alternating amorphous/crystalline Si_xGe_{1-x} regions. The traces were treated mathematically by fitting a polynomial function so as to compensate for the initial curvature of the sample.

Channeling/Rutherford backscattering spectrometry (C/RBS) analysis using a 3.0 MeV ^{4}He beam, backscattered over 157.5°, was utilized to determine the position of the amorphous/crystalline interface. The areal density of the amorphous zone was calculated using the stopping power of the Si_xGe_{1-x} alloys, deduced from Bragg's rule [5]. For Ge, the Ziegler stopping power [6] was used, and for Si the stopping power given by Santry and Werner [7,8]. The depth d (see Fig. 1), corresponding to the distance between the original surface and the amorphous crystalline interface, was then obtained by dividing the measured areal density by the atomic density of the crystalline Si_xGe_{1-x} alloy.

3. Results and discussion

Fig. 2 shows the aligned and non-aligned backscattering spectra for the $Si_{0.85}Ge_{0.15}$ sample. The surface

channels for Si and Ge are indicated in the figure. The sharp decrease in the yield of backscattered particles around channel 250 corresponds to the interface between the $Si_{0.85}Ge_{0.15}$ layer and the Si substrate. The channeled spectrum (taken in the $\langle 100 \rangle$ direction), coincides almost completely with the random one. However, a decreased yield in the channeled spectrum can be observed in the channel range 220 to 320. The transition region between reduced and non-reduced channeled yield, indicated with an arrow, identifies the position of the interface separating the amorphized $Si_{0.85}Ge_{0.15}$ alloy and the underlying undamaged c-$Si_{0.85}Ge_{0.15}$.

The position of this interface is consistent with an amorphous $Si_{0.85}Ge_{0.15}$ areal density of $(1.09 \pm 0.10) \times 10^{19}$ atom/cm^2. The error is mainly due to the uncertainty in the stopping power. Taking into account the estimated amount of sputtered [9] and added material, this would correspond to an equivalent c-$Si_{0.85}Ge_{0.15}$ thickness (d in Fig. 1) of 2.21 ± 0.10 μm. The amorphous/crystalline position has been measured for all samples and the results are listed in Table 2.

Fig. 3 shows the surface profile of the same sample. The elevated regions correspond to the amorphous zones. The average step height, determined from 12 steps, was found to be 50 ± 2 nm. The ratio of amorphous and crystalline densities can now be determined from the RBS and profilometry results using Eq. (1). For this particular alloy, it is found to be $1.0217 \pm$
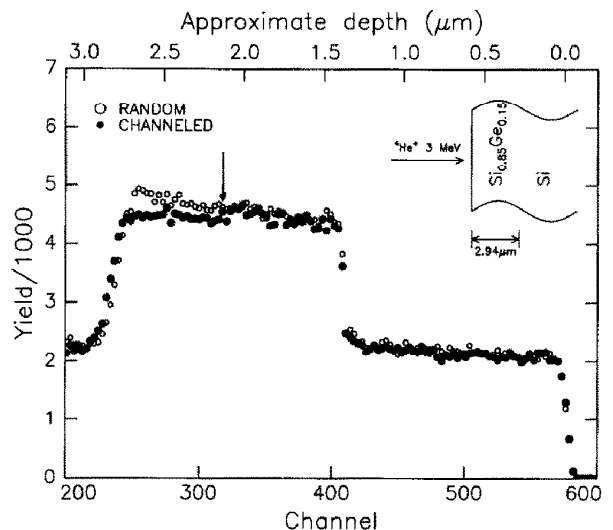

Fig. 2. Channeled and random RBS spectra for amorphous $Si_{0.85}Ge_{0.15}$ alloy. Full circles: $\langle 100 \rangle$ channeled; open circles: random spectrum. The depth scale is based on a surface approximation calculation, and for backscattering from Ge only.

Table 2
List of all experimental results

Samples	Crystalline density δ_c [a] [g/cm^3]	d [nm]	h [nm]	Net material added [nm]	δ_c / δ_a	Amorphous density [g/cm^3]
Si	2.327	2380 ± 100	40 ± 2	0.9	1.0164 ± 0.0010	2.289
Si$_{0.85}$Ge$_{0.15}$	2.842	2210 ± 100	50 ± 2	2	1.0217 ± 0.0010	2.781
Si$_{0.66}$Ge$_{0.34}$	3.457	2230 ± 100	57 ± 4	12	1.020 ± 0.002	3.389
Si$_{0.48}$Ge$_{0.52}$	4.009	2190 ± 100	46 ± 4	13	1.015 ± 0.002	3.949
Si$_{0.24}$Ge$_{0.76}$	4.694	2630 ± 100	53 ± 3	9	1.0167 ± 0.0010	4.617
Ge	5.326	1780 ± 100	28 ± 2	− 0.3	1.0158 ± 0.0015	5.243

[a] ref. [2].

0.0010. Again, the results for all the alloys are listed in Table 2. Examining the results, it is seen that both the alloys and the pure elements expand upon amorphization.

In order to evaluate these expansions, we have plotted in Fig. 4 the deviations in density from Vegard's law for amorphous and crystalline Si$_x$Ge$_{1-x}$. It should be noted that Vegard's law has been evaluated separately for crystalline and amorphous alloys; shown in the figure is the difference between the measured density and that predicted by the corresponding Vegard-curve. It is now seen that both amorphous and crystalline Si$_x$Ge$_{1-x}$ alloys are less dense than predicted by Vegard's law. The magnitude of the difference appear to be smaller for the amorphous than for the crystalline alloys.

For the crystalline alloys, it has been suggested that the deviations from Vegard's law are due to the difference in compressibility of Si and Ge [10]. The amorphous solids are expected to be softer than the corresponding crystals. Indeed, calculations of the elastic properties of a continuous random network model, based on the Keating potential, showed that the bulk modulus of a-Ge is 3% less than that of c-Ge [11]. A similar calculation showed that a-Si is softer than c-Si [12].

If the softening upon amorphization would be the same in Si and Ge, the deviation from Vegard's law would be the same for the amorphous and crystalline alloys. We observe, however, that of the four alloys measured, three have a density that is much closer to Vegard's law than that of the corresponding crystalline alloy. This would seem to indicate that the softening upon amorphization is larger in Si than in Ge.
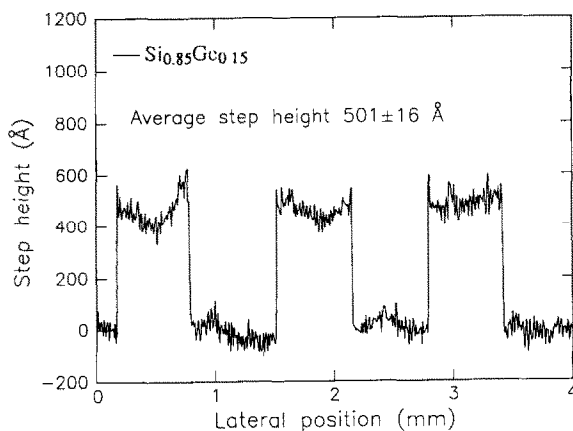

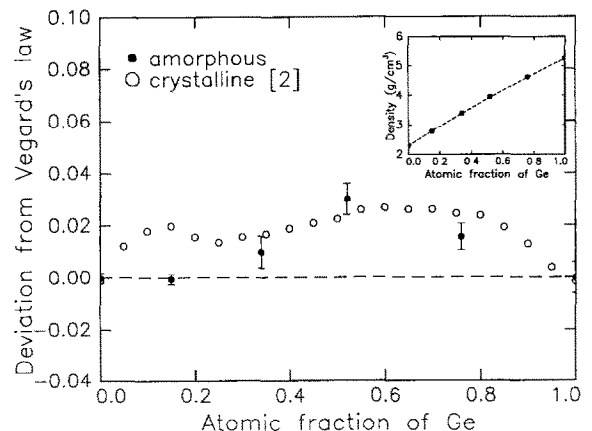Fig. 3. Dektak profile of Si$_{0.85}$Ge$_{0.15}$ alloy, after masked implantation.

Fig. 4. Difference between measured density and density predicted by Vegard's law for both crystalline and amorphous Si$_x$Ge$_{1-x}$ alloys. The density according to Vegard's law has been calculated separately for the amorphous (full circles) and crystalline (open circles) alloys. Inset: measured a-Si$_x$Ge$_{1-x}$ densities (points) and density according to Vegard's law (dashed line) on an absolute scale.

4. Conclusion

In conclusion, we have measured densities of amorphous Si_xGe_{1-x} alloys, and we have found that amorphous alloys are less dense than the crystalline alloys. The differences range from 1.5% for $Si_{0.66}Ge_{0.34}$ to 2.2% for $Si_{0.85}Ge_{0.15}$. It has been found that Vegard's law underestimates both the amorphous and the crystalline Si_xGe_{1-x} density.

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