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Effects of Ion Beam Mixing on the Formation of SiGe Nanocrystals by Ion Implantation*

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Abstract–Nanocrystals of SiGe alloy have been formed inside a SiO_2 matrix by the ion implantation technique. It is demonstrated that the sequence of implantation of Si and Ge ions affects the nanocrystal formation significantly. This is explained by the ion-beam mixing effect during sequential implantation. The size distributions of the SiGe nanocrystals can also be controlled by annealing conditions.

I. Introduction

Semiconductor nanocrystals, exhibiting new electronic and optical properties, are attractive materials due to their potential applications in optoelectronics. The ion implantation technique has been used to synthesize nanocrystals of a variety of semiconductor materials, such as Si, Ge, III-V and II-VI semiconductors [1-11]. Our studies on the elemental and compound semiconductor nanocrystals show that the size distribution of these nanocrystals can be controlled by the implantation dose and thermal annealing temperature. To form nanocrystals of alloy semiconductors, it requires that two different elements to be implanted inside the host matrix. This paper presents our study of SiGe nanocrystals formed in SiO_2 by the ion implantation technique. For materials consisting of more than one element, the sequence of implantation for each constituent species becomes an important issue [12].

II. Experimental

SiGe semiconductor nanocrystals were formed by implantation of Si and Ge ions into a SiO_2 layer on (100) silicon and subsequent thermal annealing. A typical SiO_2 layer was ~ 0.75 μm thick, formed by thermally oxidizing a (100) Si wafer. The samples used in this paper were heavily implanted with equal doses, 3×10^{17} cm^{-2}, of Si and Ge at room temperature (RT), unless specified otherwise. The implant energies, 215 keV for Si and 500 keV for Ge, were chosen to overlap the peak concentrations in the middle of the oxide layer. Samples were annealed isochronally for 1 h under Ar + 4%H_2 ambient at atmospheric pressure. The annealing temperatures varied from 900°C to 1100°C.

The nanocrystalline structures were investigated by transmission electron microscopy (TEM) and X-ray diffraction. All the TEM specimens were prepared in cross sections since the concentration distribution from ion implantation is a function of depth. Depth profiles of implanted Ge ions were examined by Rutherford backscattering spectrometry (RBS) using a 2.3 MeV He^{2+} beam.

III. Results and Discussions

A cross-sectional TEM image, from a sample implanted with Ge at RT and Si at 500°C and then annealed at 1000°C for 1 h, is shown in Fig. 1. A high density of SiGe particles precipitates during annealing for this high dose sample. Similar to the Ge nanocrystals [5], these SiGe nanocrystals are randomly oriented and near-spherical in shape in the amorphous SiO_2 matrix. The sizes of the SiGe nanocrystals are in the range of 2 – 20 nm. The X-ray diffraction measurement, shown in Fig. 1, confirms the formation of SiGe alloy.

When the sample, implanted with Ge and then Si, was annealed at 1100°C that is near to the melting temperature of the SiGe alloy, the SiGe precipitates grow to much larger sizes. Fig. 2 shows that the large precipitates extend up to a

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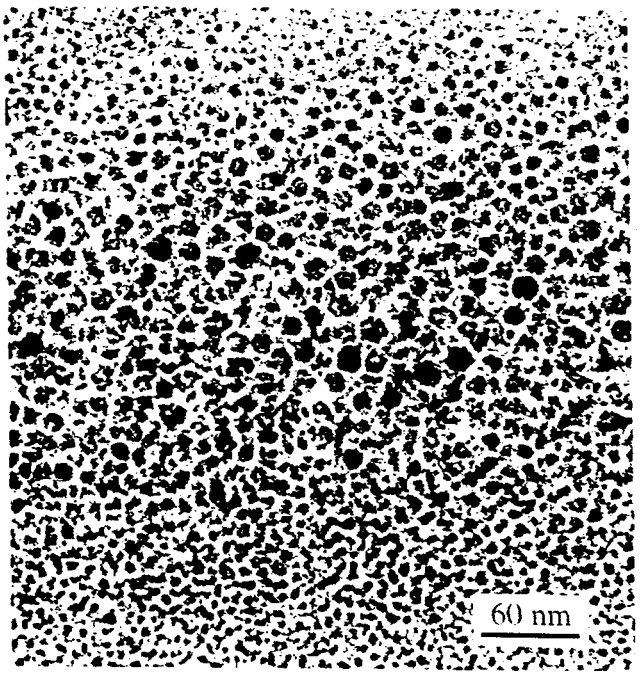
few tens of nanometers in size. In the middle of the implanted region, where the concentration is the highest, it appears that coalescence of the particles has occurred. In this region, the SiGe precipitates are usually not spherical in shape. A high-resolution TEM image in Fig. 3 shows a precipitate with faceted surfaces/interfaces, mostly {111} and {100} lattice planes. When the sequence of implantation of Si and Ge is reversed, the precipitates of SiGe alloy are much bigger after annealing under the same condition, as shown in Fig. 4. The



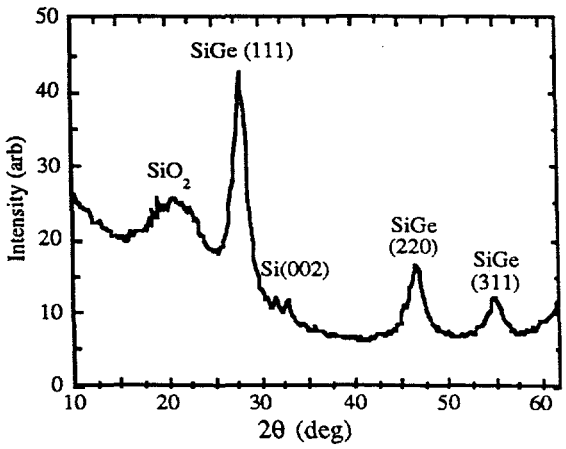


Fig. 1. Cross-sectional TEM image and X-ray diffraction spectrum from a sample implanted with Ge (RT) and Si (500°C) and annealed at 1000°C/1h.

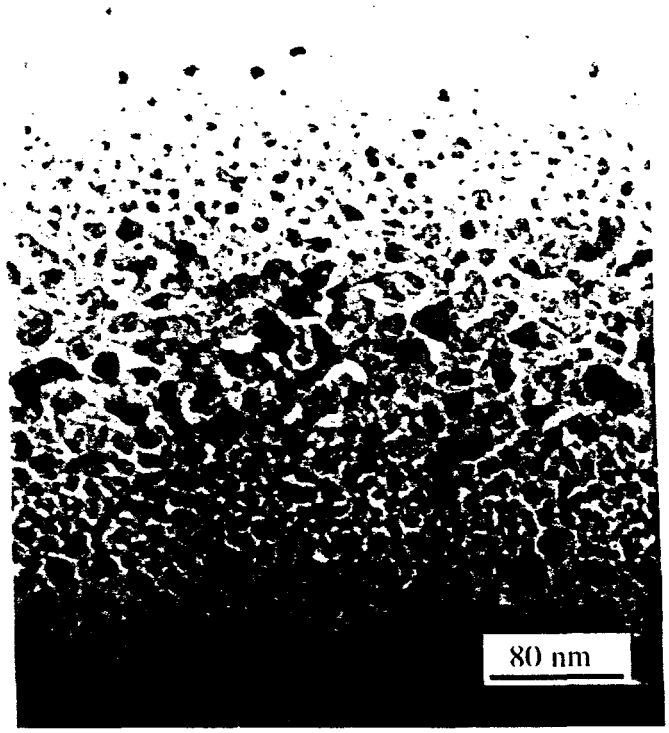


Fig. 2. Cross-sectional TEM image of a sample implanted with Ge and Si and annealed at 1100°C.

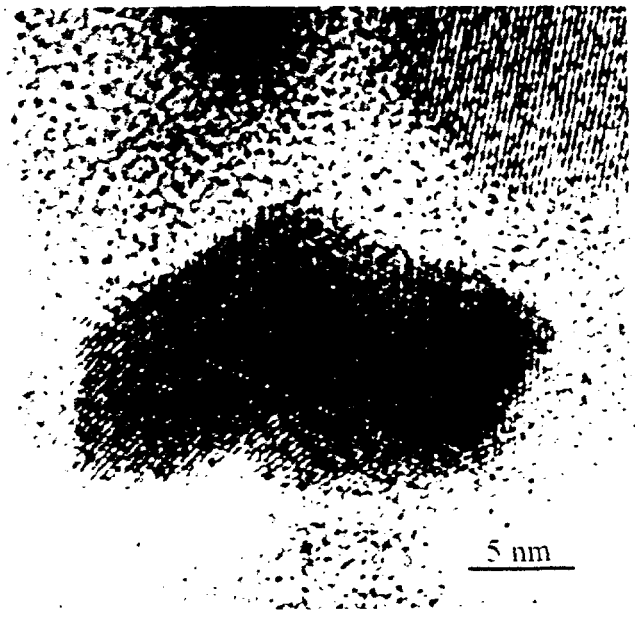


Fig. 3. A high-resolution TEM image showing a faceted precipitate.

large precipitates are about a few hundreds of nanometers. Coarsening of SiGe particles is much more significant in this sample implanted with Si first and then Ge.

RBS measurements have been used to obtain Ge concentration-depth profiles. Fig. 5 shows the Ge profiles for two pairs of samples, one implanted with Ge first and then Si and the other implanted with Si first and then Ge, before and after annealing at 1100°C. At the as-implanted stage, the Ge profile for the sample implanted with Ge first is broader than that for the sample implanted with Si first. The broadening of the Ge profile can be explained by the ion-beam mixing effect which occurs when Si ions are implanted after the Ge implantation. After annealing at 1100°C, sharpening of the Ge peak is very prominent for the sample implanted with Si first. There is also some sharpening of the Ge profile for the sample implanted with Ge first. These RBS results are consistent with the TEM observation that the SiGe precipitates are much bigger in the sample implanted with Si first after annealing at 1100°C. X-ray diffraction peak width measurements also shows larger precipitate sizes in samples where Si is implanted before Ge. The concentration of the SiGe alloy precipitated would vary from the targeted $Si_{0.5}Ge_{0.5}$ with different Ge concentration profiles. The center region in the sample implanted with Si first is more likely to be Ge rich, and thus the alloy would have a lower melting point. This helps to explain why the SiGe precipitates in the center of the implanted region, which is Ge-rich for the sample implanted with Si first, are much bigger than those in the sample implanted with Ge first. Our previous study has revealed that Ge nanocrystals can grow much bigger in SiO_2 matrix than Si nanocrystals under similar thermal annealing conditions [5]. In the upper and lower regions in the sample implanted with Ge first (see Fig. 2), the SiGe precipitates are Ge rich (since the center region is Si rich) with near spherical shape. The particles in the upper and lower regions in the sample implanted with Si first (see Fig. 4) are considered to be Si rich and are much smaller in size.

Small SiGe nanocrystals can be formed when the sample is annealed at lower temperatures. Fig. 6 shows a cross-

Fig. 4. Cross-sectional TEM image of a sample implanted with Si and Ge and annealed at 1100°C.

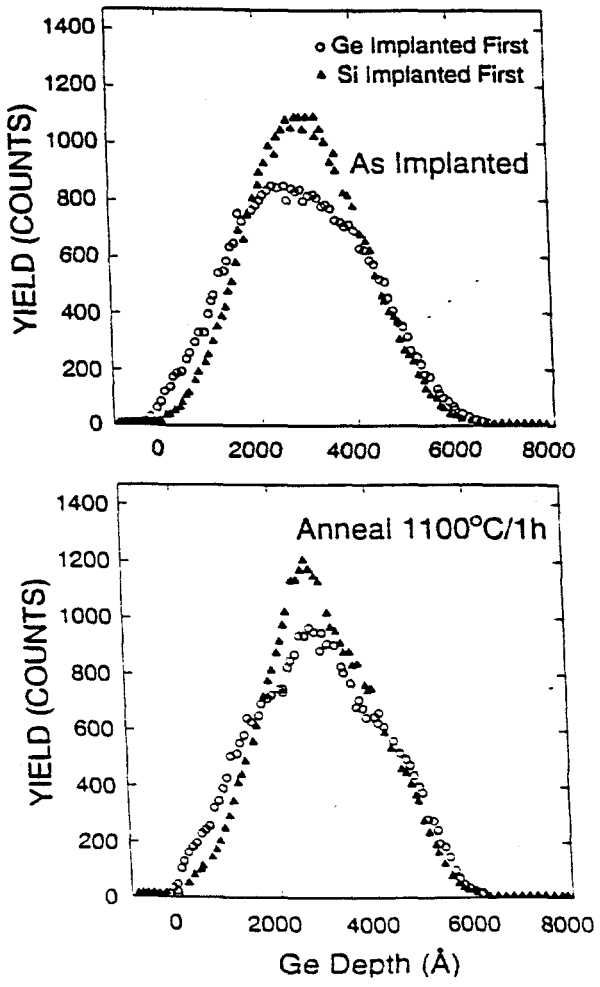


Fig. 5. Ge concentration-depth profiles measured by RBS from samples implanted with Si and Ge with different implantation sequences in the as implanted stage and after annealing at 1100°C.

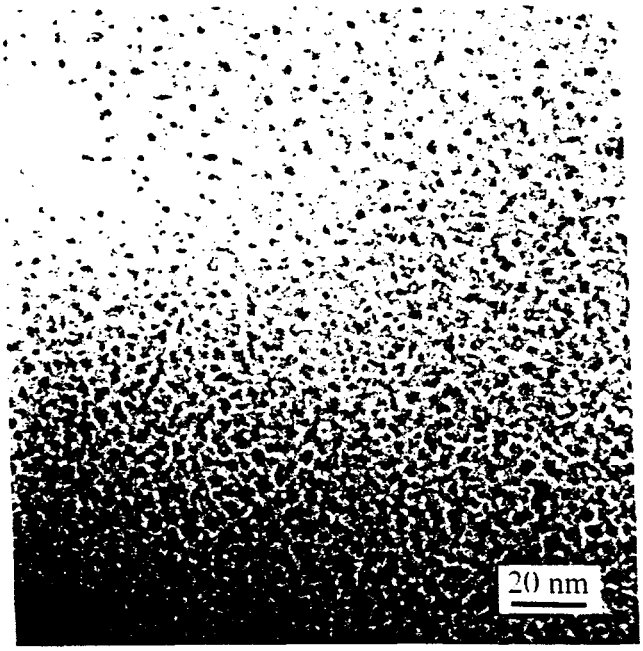


Fig. 6. Cross-sectional TEM image of a sample implanted with Ge and Si and annealed at 900°C.

sectional TEM image from a sample implanted with Ge and Si and annealed at 900°C for 1 h. These SiGe nanocrystals are ~ 2 nm in size, which is the size desired for strong quantum confinement effect [13].

The exact amounts of deviation from the targeted alloy composition for SiGe nanocrystals need to be further investigated. However, X-ray diffraction measurements from the samples containing large-size SiGe precipitates indicate that the precipitates are close to $Si_{0.5}Ge_{0.5}$. The samples studied in this paper have been implanted with Ge and Si at RT except that shown in Fig. 1. Further investigation of implantation at elevated temperatures is under progress. Nucleation of nanocrystals is expected when a sample is heated during ion implantation, which could change the concentration-profile redistribution, therefore, assist the control of alloy concentration. Remarkable differences in the nanocrystal formation due to the change of implantation sequences have also been observed in the formation of GaAs nanocrystals. Details about the formation of GaAs nanocrystals can be found in [12], where the very different diffusion behaviors of Ga and As inside SiO_2 have been illustrated.

IV. Conclusions

Nanocrystals of SiGe alloy have been formed inside SiO_2 matrices by the sequential ion implantation technique. The implantation sequence of Si and Ge ions is demonstrated to affect the nanocrystal formation substantially. The microstructure of these SiGe nanocrystals has been studied by TEM and X-ray diffraction. RBS measurements of the Ge concentration-depth profiles reveal the broadening of Ge profiles when Si ions are implanted after the Ge implantation due to the ion-beam mixing effect. This effect could alter the alloy composition when the implantation sequence is reversed. When the heavily implanted samples were annealed at a temperature about the melting temperature of the alloy, the sizes of the largest SiGe precipitates formed are about a few hundreds of nanometers in the sample implanted with Si first, about a few tens of nanometers in the sample implanted with Ge first. Very small SiGe nanocrystals, ~ 2 nm, are formed in the sample annealed at 900°C. Results regarding the effect of implantation sequence on the formation of GaAs nanocrystals can be found elsewhere [12].

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