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Preparation of Polycrystalline $Si_{1-x}Ge_x$ Thin Films by Ion-Beam Evaporation

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Polycrystalline silicon germanium (poly-$Si_{1-x}Ge_x$) thin films with low oxygen content have been successfully prepared without heat treatment by using an intense, pulsed ion-beam evaporation (IBE) method. From the results of transmission electron microscopy (TEM) and Raman scattering spectroscopy, the thin films were found to consist of $Si_{1-x}Ge_x$ grains with various Ge contents.
Key words: intense pulsed ion-beam evaporation, $Si_{1-x}Ge_x$ solid solution, thin film

1. INTRODUCTION

In recent years, polycrystalline silicon germanium (poly-$Si_{1-x}Ge_x$) has drawn big interests as a basic material in high performance thin film transistors (TFT) rather than poly-silicon [1]. The hole mobility of $Si_{1-x}Ge_x$ has been known to be higher than that of Si and to change with increasing Ge content (x) [2,3]. Therefore, $Si_{1-x}Ge_x$ is expected to be used in wide areas [4].

Thin films of $Si_{1-x}Ge_x$ have been mainly prepared by chemical vapor deposition (CVD), pulsed laser deposition (PLD) and sputtering methods [1,4-7]. However, to prepare the thin films of crystallized $Si_{1-x}Ge_x$ solid solution by the above methods, it is necessary to carry out heat-treatment. In contrast, the thin films of crystallized $Si_{1-x}Ge_x$ solid solution have been prepared without heat-treatment by using intense, pulsed ion-beam evaporation (IBE) method [8].

However, the distribution of Ge content in the $Si_{1-x}Ge_x$ thin films, which is an important parameter for the properties of such thin films, is still uncertain. Moreover, the oxygen contents in thin films were not measured. Thus, the variation of Ge content in the $Si_{1-x}Ge_x$ thin films, which were synthesized by the IBE method has been investigated. In addition, oxygen content in the $Si_{1-x}Ge_x$ thin films was measured. The oxygen content was attempted to be reduced by using a high-purity target.

2. EXPERIMENTAL PROCEDURE

For the preparation of $Si_{1-x}Ge_x$ thin films by IBE, two different Si-Ge bulks were used as the target. One is a commercially available Si–50at.%Ge bulk sintered by hot press (HP target). Another is made by spark plasma sintering (SPS target). The mixed powder was compacted in a graphite die at pressure of 80 MPa. Then, the powder was evacuated and heated in a spark plasma sintering apparatus at the temperature of 800 °C for 5 min. Figure 1 shows the experimental setup of the thin film deposition by the IBE method [8-10]. The thin films were prepared by using an intense, pulsed ion-beam generator ("ETIGO-II"). A voltage of 1 MV (peak) with pulse width of approximately 50 ns and current of 60 kA was applied between the cathode and the anode, which was covered by a polyethylene sheet (flashboard). The pulsed light ion beam (LIB) mainly consisted of protons [11] (approximately 75 %). The ion beam was geometrically focused on the target, which was located at the distance (d_{AT}) of 180 mm from the anode. The target was tilted by 45° to the beam axis. The ablation plasma was produced by the ion-beam irradiation on the target. The substrates were placed at the distance (d_{TS}) of 70 and 90 mm from the target. In addition, the substrate was kept at room temperature (RT). Experiments were carried out under the pressure of 26.6 mPa. Experimental conditions are presented in Table I.

The crystal structure of the thin film was identified by an X-ray diffractometer (XRD). The diffraction patterns were measured using a CuKα radiation of 1.5418 Å under the conditions

of 50 kV and 300 mA. A sample for the transmission electron microscopy (TEM) observations was prepared by a focused ion beam (FIB), where gallium (Ga) ions were accelerated at 30 kV. The surface of the thin film was covered with glue and Au thin film to keep mechanical strength and electrical conductivity. Then, the thin film was cut into a specimen with a size of $1\times1\times0.1$ mm^3. Finally, a part of the specimen was thinned by FIB into an electron-transparent film with a size of $10\times10\times0.1$ μm^3 for the TEM observations [12]. Microstructural observations were performed with a TEM operated at the acceleration voltage of 200 kV. The atomic bonds in the thin film were identified by a Raman scattering spectroscopy. The Raman scattering spectra were measured by an argon (Ar) laser of the wavelength of 514.5 nm. The composition of the thin films was identified by an X-ray photoelectron spectroscopy (XPS).

3. RESULTS AND DISCUSSION

3.1 Characteristics of $Si_{1-x}Ge_x$ thin films prepared by IBE

Figure 2 shows XRD patterns of HP target and a thin film prepared by IBE method. The thin films were synthesized on the Si substrate at d_{TS} = 70 mm. The JCPDS data of Si, Ge and germanium dioxide (GeO_2) were shown under the diffraction patterns for comparison [13-15]. As a result, HP target contained GeO_2 phase other than Si and Ge ones which was considered to be oxidized during the sintering. In contrast, since the diffraction peaks of the thin film appeared between each position attributed to Si and Ge, the thin film of $Si_{1-x}Ge_x$ solid solution was clarified to be formed without heat-treatment. However, the diffraction peaks attributed to $Si_{1-x}Ge_x$ 111, 220 and 311 had shoulders at higher angle. This fact suggested us that the thin film prepared by IBE method may be composed of the $Si_{1-x}Ge_x$ grains with various Ge content.

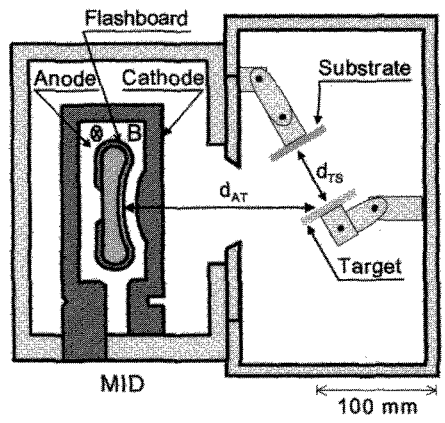

Fig. 1 Experimental setup for thin film deposition by IBE method.

Table I Experimental conditions

Si-Ge target	Si–50 at.% Ge
Substrate	Si (100), Quartz glass
d_{AT}	180 mm
d_{TS}	70, 90 mm
Number of shot	1 shot
Substrate temperature	RT
Pressure	26.6 mPa

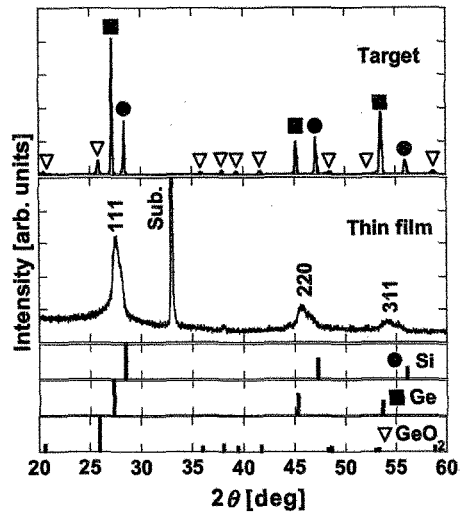

Fig. 2 XRD patterns of HP target and a thin film prepared using the target by IBE method.

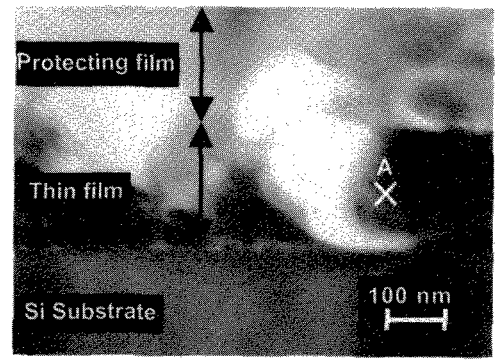

Fig. 3 BF image of cross-section of $Si_{1-x}Ge_x$ thin film.

Figure 3 shows a bright-field (BF) image of cross-section of a $Si_{1-x}Ge_x$ thin film prepared by IBE method. As seen for Fig. 3, a 100 nm thick thin film was prepared by 1 shot of IBE method. In addition, peeling was not observed at the boundary between Si substrate and the thin film.

Figure 4 shows a selected area diffraction (SAD) pattern of the $Si_{1-x}Ge_x$ thin film. The SAD pattern was obtained by irradiating electron beam having the diameter of 1 μm around the point A in Fig. 3. In Fig. 4, the diffraction spots with regular spacing are for planes of the zone axis [011] of the Si substrate. The rest was

indexed by 220, 311, 422 and 511. Such diffraction spots indicated that the $Si_{1-x}Ge_x$ thin film is polycrystalline. In addition, this result was consistent with that of Fig. 2.

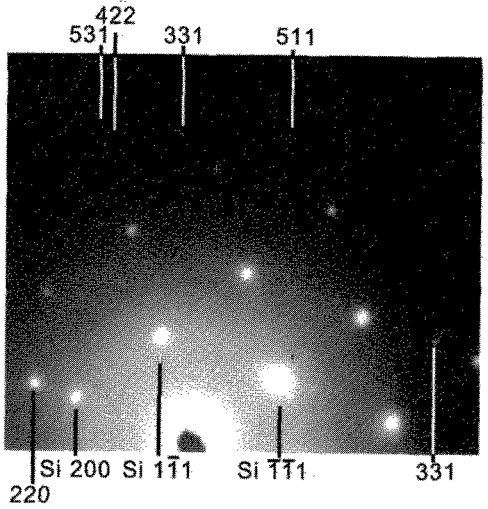

Fig. 4 SAD pattern of $Si_{1-x}Ge_x$ thin film.

Table II Lattice constant and Ge content of $Si_{1-x}Ge_x$ thin film.

	a [Å]	x
XRD	5.565	0.58
SAD	5.53±0.07	0.45±0.31

Table II shows lattice constant and Ge content with relative standard deviation of the $Si_{1-x}Ge_x$ thin film. The lattice constant of the $Si_{1-x}Ge_x$ thin film was led from the results of XRD and SAD. The average Ge content of $Si_{1-x}Ge_x$ thin film was calculated by

$$x = \left(\frac{a_{film} - a_{Si}}{a_{Ge} - a_{Si}} \right),$$

where a_{film}, a_{Si} and a_{Ge} are the lattice constant of the $Si_{1-x}Ge_x$, Si and Ge, respectively [13,14,16]. From the result of Table II, the Ge content of the thin film was clarified to be almost same as that of HP target (x = 0.5). This fact led to the conclusion that the $Si_{1-x}Ge_x$ grains in the x ranging from 0.14 to 0.76 existed in the thin film.

Figure 5 shows Raman spectrum of $Si_{1-x}Ge_x$ thin film. The spectrum exhibits three distinct peaks attributed to atomic vibrations involving Ge-Ge, Si-Ge and Si-Si bonds. The appearance of Ge-Ge and Si-Si vibrations indicates compositional distributions of this film. As the energy of the Ge-Ge, Si-Ge and Si-Si vibrations are dependent on the relative number of bonds in the film, we use the spectrum to determine the film composition based on the method by Tsang et al [17]. Using the experimental values for the phonon frequencies measured by Fig. 5, we obtain the composition x ~ 0.5, which is in good agreement with the results of XRD and SAD (see Table II).

In Fig. 2, the thin film consisted of a $Si_{1-x}Ge_x$ phase, while some GeO_2 grains exists in the HP target. This result implies that oxygen atoms may be dissolved in $Si_{1-x}Ge_x$ phase.

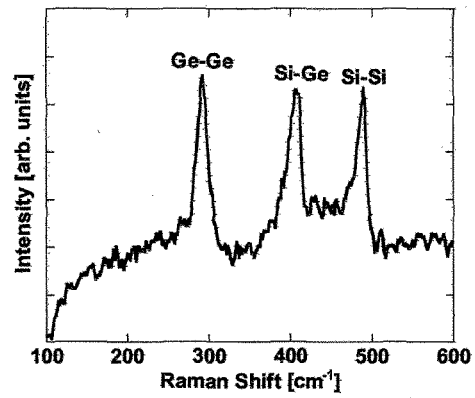

Fig. 5 Raman scattering spectrum of $Si_{1-x}Ge_x$ thin film.

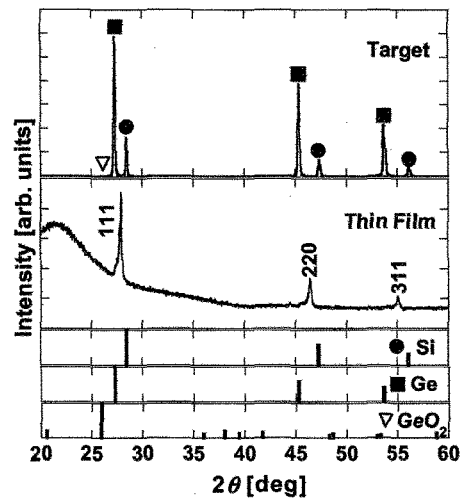

Fig. 6 XRD patterns of SPS target and a thin film using the target by IBE method.

3.2 Characteristics of $Si_{1-x}Ge_x$ thin films

Figure 6 shows XRD patterns of SPS target and a thin film prepared by IBE method. The thin film was synthesized on the quartz glass substrate at d_{TS} = 90 mm. In Fig. 6, SPS target primarily consists of Si and Ge phases, and partly a small amount of GeO_2. However, from the results of Figs. 2 and 6, the ratio of GeO_2 phase to Si and Ge in SPS target was found to be smaller than that of the HP target. Thus, the thin film prepared by SPS target is expected to have lower oxygen content. In Fig. 6, although the thin film was $Si_{1-x}Ge_x$ solid solution, the diffraction peaks attributed to $Si_{1-x}Ge_x$ 111, 220

and 311 had shoulder at lower angle. This result could be explained by the fact that the thin film prepared by SPS target was also formed by the $Si_{1-x}Ge_x$ grains with various Ge contents.

Figure 7 shows XPS spectra of the thin films prepared by IBE using (a) SPS and (b) HP targets. Each thin film was sputtered for 30 seconds with Ar ions in order to remove a surface oxide layer. As a result, in the thin film prepared by SPS target, the peak of O1s was not observed. In contrast, such a peak was observed in the thin film prepared by HP target.

In the IBE method, it was known that the composition, including oxygen content, of the thin film is almost same as that of the target [18]. The present result also confirmed the characteristics of the IBE method.

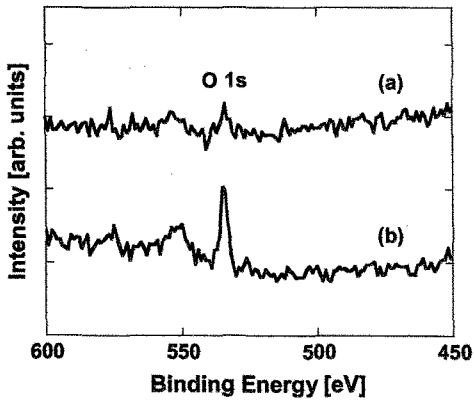

Fig. 7 XPS spectra of the thin films using (a) SPS and (b) HP targets.

4. CONCLUSIONS

From these experimental results, we have obtained the following conclusions.

1) Polycrystalline $Si_{1-x}Ge_x$ thin films with low oxygen content have been successfully prepared without heat treatment by using the IBE method.
2) The thin films prepared by the IBE method consisted of the $Si_{1-x}Ge_x$ grains having various Ge contents.

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