Transactions of the Materials Research Society of Japan 28 [2] 425-428 (2003)

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

Hisayuki Suematsu, Takehiko Honzawa, Makoto Hirai, Tsuneo Suzuki, Weihua Jiang and Kiyoshi Yatsui
Extreme Energy-Density Research Institute, Nagaoka University of Technology, Nagaoka, Niigata 940-2188, Japan
Fax: 81-258-47-9890, e-mail: suematsu@nagaokaut.ac.jp

Compositionally gradient $Si_{1-x}Ge_x$ thin films were prepared by ion beam evaporation. A pulsed ion (75% proton) beam with energy of 1 MeV (peak), current of 60 kA and pulse width of 50 ns was irradiated on a Si-Ge hybrid target, which consisted of sintered Si and Ge plates. Thin films prepared on stainless steel substrates were investigated by X-ray diffraction and energy dispersive X-ray spectroscopy and were found out to be compositionally gradient $Si_{1-x}Ge_x$ thin films. From this result, we concluded that a new method to prepare compositionally gradient material thin films was successfully developed.

Key words: ion-beam evaporation, compositionally gradient thin films, $Si_{1-x}Ge_x$, ablation plasma

1. INTRODUCTION

Various novel functions, i.e. high-T_c superconductivity[1], giant magneto resistance[2], co-existence of high thermopower and low resistivity[3], have recently been discovered. During the investigations, many samples with various compositions had to be synthesized. In particular, synthesis of low melting point compounds needs heat treatments at low temperatures, which require long-term heating or well mixed, fine grained raw materials to enhance atomic diffusion. Such process is time consuming and other quick processes are needed to be developed.

A novel, quick synthesis method of "combinatorial chemistry", which had originally been developed in synthesis of organic materials, was imported to the synthesis of inorganic materials[4,5]. In this method, various vapors were sprayed on a substrate through masks to form chips with different compositions. In other words, the chips on the substrate are nothing but a compositionally gradient thin film. Not only for quick synthesis of various compounds but also for development of functionally gradient materials, preparation of compositionally gradient thin films is required. However, in the reported methods, the masks have to be precisely controlled so that the apparatus becomes complex and expensive. Thus, other simple, quick methods to prepare compositionally gradient thin films have to be developed.

Ion-beam evaporation (IBE) has been known as a novel thin film preparation method[6,7]. By irradiation of an intense, pulsed ion beam on a target, high temperature, high-density plasma was formed and was deposited on substrates. Utilizing this plasma, this method enables us to prepare thin films with an instantaneous deposition rate of a few mm/s. If we could irradiate a hybrid target consisting of two or more different compound plates simultaneously, ablation plasma formed from the plates are injected toward a substrate. Around the interface between the two plasma, constituent species in the plasma may be mixed. Thus, it is expected that some parts of the substrate may be coated by a compositionally gradient thin film.

In the present study, a Si-Ge hybrid target was irradiated by the pulsed ion beam and preparation of compositionally gradient Si-Ge thin films were attempted. The prepared thin films were characterized with an X-ray diffractometer (XRD), a scanning electron microscope (SEM) and an energy dispersive X-ray analyzer (EDX).

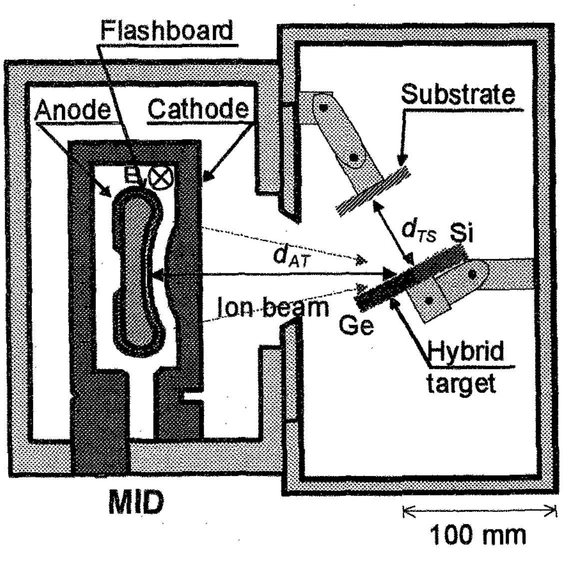

Fig. 1 Schematic diagram of ion-beam diode and thin film preparation chambers for production of compositionally gradient $Si_{1-x}Ge_x$ thin films.

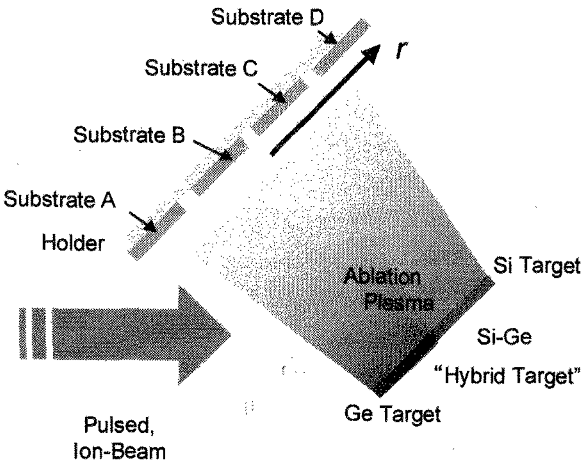

Fig. 2 Schematic diagram of position of Substrates A – D for preparation of compositionally gradient $Si_{1-x}Ge_x$ thin film.

2. EXPERIMENTAL PROCEDURE

For preparation of compositionally gradient $Si_{1-x}Ge_x$ thin films, a hybrid target consisting of Si and Ge sintered plates was irradiated by a pulsed ion beam. The ion beam was produced by a pulsed power generator, "ETIGO-II"[7]. The operating conditions for the ion-beam evaporation is accelerating voltage of 1 MV (peak), current of 60 kA and pulse width of 50 ns.

Schematic diagram of ion-beam diode and thin film preparation chambers are shown in Fig. 1. The ion-beam diode used was a magnetically insulated diode, where the motion of electrons was insulated by the transverse magnetic field. Using a polyethylene sheet as a flashboard anode, the ion species were mostly protons more than 75 %, which was diagnosed with an energy spectrometer. The Si-Ge hybrid target was placed from 200 mm from the anode. By irradiating the pulsed ion beam on the Si-Ge hybrid target, high-density ablation plasma was formed. Time evolution of the plasma was recorded on an emulsion film with a high-speed camera. Exposure time of each photograph was 100 ns and inter-frame interval was 15 μs.

Substrates were placed on a substrate holder, which was located 80 mm from the hybrid target. Four stainless steel substrates with size of 15 x 15 x 0.5 mm were attached on the substrate holder. Positions of the four substrates (Substrates A-D) and definition of distance from the plasma center (r) are shown in Fig. 2. The substrates were kept at room temperature. Thin films were deposited on Substrates A-D.

Phases in the thin films were identified by XRD (Cu$K\alpha$ radiation) operated at 50 kV and 300 mA. Composition of the thin films was measured by EDX equipped on SEM operated at acceleration voltage of 10 kV. By using this voltage, range of the incident electron was comparable to the thickness of the thin film (300 nm). Thus, intensity of characteristic X-ray from the substrate became almost the same as that of background of the spectra. Composition of the thin films was determined by $\phi(\rho, z)$ method[8] using a Cliff-Lorimer factor obtained from a spectrum for a standard Si-50at%Ge bulk.

3. RESULTS AND DISCUSSION

Irradiation of the pulsed ion beam on the Si-Ge hybrid target generated ablation plasma from the target. High-speed photographs of the ablation plasma are shown in Fig. 3. First, plasma was formed from the surface of Ge at 15 μs after the irradiation. Then, plasma from the surface of Si was generated at 30 μs after the irradiation. On the other hand, since space

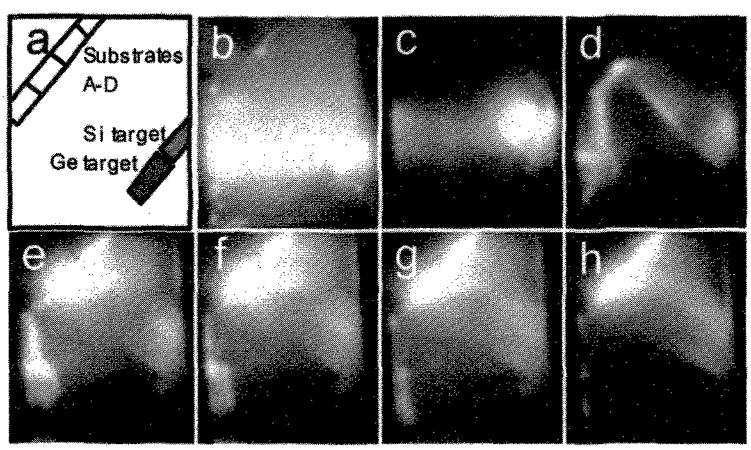

Fig. 3 (a): schematic diagram of Si and Ge targets and Substrates A-D, (b)-(h): high-speed photographs of ablation plasma from the Si-Ge hybrid target.

around Substrates A-D continued to glow up to 90 μs after the irradiation, plasma existed around Substrates A-D for 90 μs. These photographs indicate that plasma might have been mixed during the period on Substrates A-D and compositionally gradient thin films may be deposited.

Patterns of XRD for thin films on Substrates A-D are shown in Fig. 4. In the thin films on Substrates A and B, only a peak is seen in each pattern. This peak position coincides with diffraction angle of the 111 reflection for Ge. In the thin film on Substrate C, two peaks appear in the pattern. These peaks are located between diffraction angles of the 111 reflections for Ge and Si. In the thin film on Substrate D, only a peak exists in the pattern, the position is same as that of the 111 reflection of Si.

Composition of some portion of the thin films has been determined by EDX and is shown in Fig. 5. The thin films on Substrates A and D are almost pure Ge and Si, respectively. These results are in agreement with those of XRD (Fig. 4). Furthermore, composition of thin films on Substrates B and C varies with *r*.

In Figs. 4 and 5, it is easily seen that thin film on Substrate A is purely Ge, while thin film on Substrate D consists of Si. Since Substrates A and D are facing to Ge and Si plates in the Si-Ge hybrid target (Fig. 2), it is obvious that the compositions of thin films on Substrates A and D are same as that of the nearest plate. Furthermore, in high-speed photographs of the ablation plasma (Fig. 3), the species of plasma seem to fly almost

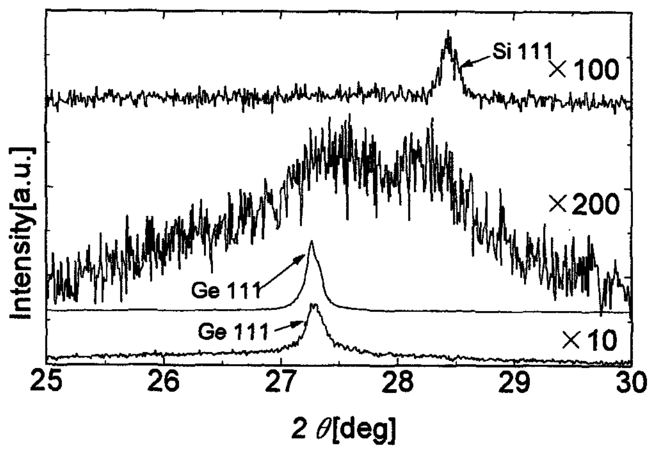

Fig. 4 XRD patterns for $Si_{1-x}Ge_x$ thin film on Substrates A-D.

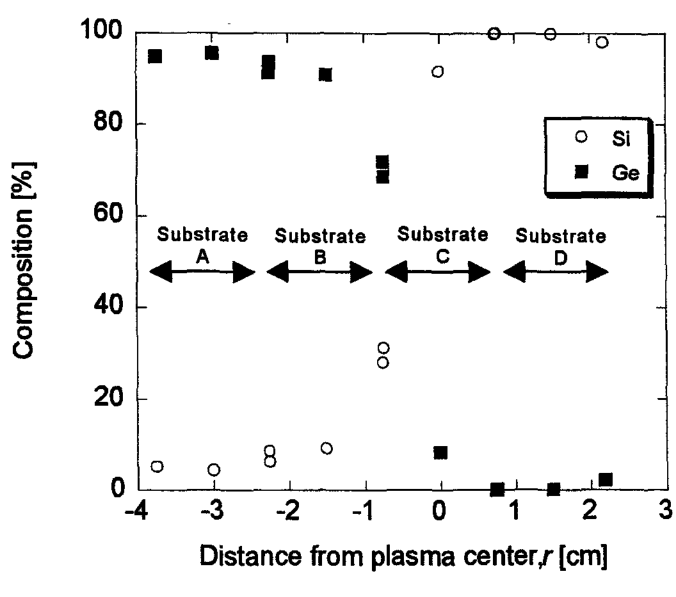

Fig. 5 Composition variation in $Si_{1-x}Ge_x$ thin films measured by EDX. Positions of Substrates A-D are also shown.

perpendicular to the hybrid target. This result also supports that the results of the compositional analysis. From these results, we conclude that compositionally gradient Si-Ge thin films were prepared by IBE.

4. CONCLUSION

Compositionally gradient Si-Ge thin films were deposited by irradiating pulsed ion beam on a Si-Ge hybrid target. We successfully developed a method to prepare compositionally gradient thin films to seek novel materials.

ACKNOWLEDGEMENTS

This work was partly supported by New Energy Development Organization, Grant-in-Aide for Scientific Research and the 21st Century COE Program of Ministry of Education, Culture, Sports, Science and Technology, Japan.

REFERENCES

[1] J. G. Bednorz and K. A. Muller, *Z. Phys. B* **64**, 189-193 (1986).
[2] Y.Moritomo, A.Asamitsu, H.Kuwahara and Y.Tokura, *Nature* **380**, 141-144 (1996).
[3] I. Terasaki, Y. Sasago and K. Uchinokura, *Phys. Rev. B* **56**, R12685-12687 (1997).
[4] X.-D. Xiang, X. Sun, G. Briceno, Y. Lou, K.-A. Wang, H. Chang, W. G. Wallace-Freedman, S.-W. Chen and P. G. Schultz, *Science* **368**, 1738-1740 (1995).
[5] H. Koinuma, *Solid State Ionics* **108**, 1-4 (1998).
[6] Y. Shimotori, M. Yokoyama, H. Isobe, S. Harada, K. Masugata and K. Yatsui, *J. Appl. Phys.* **63**, 968-970 (1988).
[7] K. Yatsui, *Laser and Particle Beams* **7**, 733-741 (1989).
[8] D. B. Williams and C. B. Carter, "Transmission Electron Microscopy, Spectroscopy IV", Plenum Press, New York (1996) pp.599-600.

(Received December 21, 2002; Accepted March 26, 2003)