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Preparation of Boron–Silicon Thin Film by Pulsed Laser Deposition and Its Properties

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Boron–silicon amorphous films were prepared by pulsed laser deposition technique. Band gap was estimated from the optical absorption spectrum for the films, and it increased with increasing silicon concentration. The values and concentration dependence of the band gap are nearly the same as those measured for amorphous B–Si prepared by electron beam evaporation. Electrical (dc) conductivity of the films was two or three orders of magnitude larger than that of amorphous boron, and its temperature dependence reveals variable-range-hopping-type behavior (Mott's low). Concentration dependence of the dc conductivity is similar to that of metal-doped β-rhombohedral boron. © 2000 Academic Press

Key Words: **pulsed laser deposition; amorphous film; band gap; electrical conductivity.**

1. INTRODUCTION

Icosahedral clusters (B_{12}) and their arrangement are characteristics of boron-rich solids, whose unique properties are assumed to be characterized by those clusters (1). The cluster is two-electron deficient and has unique three centered covalent bonds as intracluster bonding (2). Electrical conductivity in both crystalline and amorphous phases is explained by hole hopping between localized states originating from the B_{12} cluster (1, 3). As a result, a change in electronic states or distortion of the cluster will lead to changes in physical properties of the boron-rich solids. We choosed the B–Si system to examine the changes, because the Si atom substitutes for the B atom in the cluster (4) and adds an electron into the electron-deficient cluster. Furthermore, boron-rich silicon borides have received attention because of their possibility to be used as thermoelectric conversion material at high temperature (5). Basic research on the B–Si system will help the material design for the application.

In the present study, we prepared B–Si thin films by pulsed laser deposition (PLD). This technique has been extensively employed for the preparation of high-quality thin films of complex multicomponent systems like high T_c copper oxide (6). The desirable features of the PLD are: (i) a highly nonequilibrium evaporation process produces an intense plasma plume and transfers the target composition into the deposited film, and (ii) a high-intensity pulsed laser easily evaporates materials with a high melting point. Thus, PLD is a suitable technique for the preparation of B–Si film, because boron has a high melting point and vapor pressures of boron and silicon are largely different.

In the present paper, we report on the preparation of B–Si film using the PLD technique. We also present the results of optical absorption and electrical conductivity, and discuss the results in terms of the existence of the cluster.

2. EXPERIMENTAL

A schematic of the PLD system is shown in Fig. 1. A stainless steel vacuum chamber was evacuated by a turbomolecular pump to a pressure of about 1×10^{-6} Torr. A frequency-doubled Nd:YAG laser (wavelength, 532 nm; pulse duration, 10 ns; repetition rate, 20 Hz) was used for ablation. The laser beam was focused on a rotating target of B–Si mounted on a target holder in the vacuum chamber. The position where the beam is focused was scanned in a radial direction of the rotating target with a swaying mirror in order to irradiate a fresh area at each laser shot. The ablated material was then deposited on a quartz glass substrate kept at a distance of 40 mm from the target surface.

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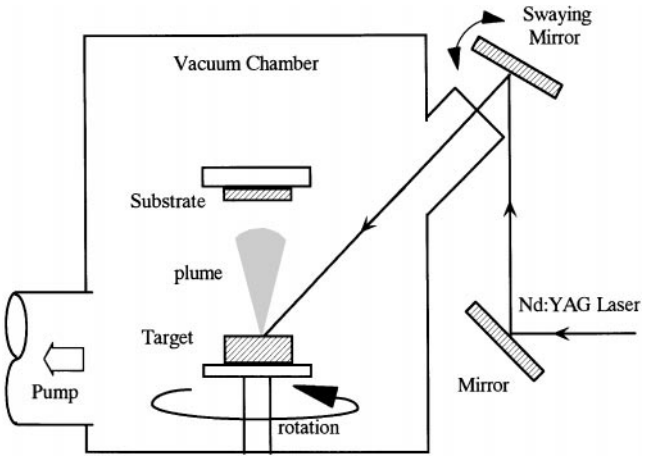

FIG. 1. Schematic diagram of the pulsed laser deposition system for B–Si thin films.

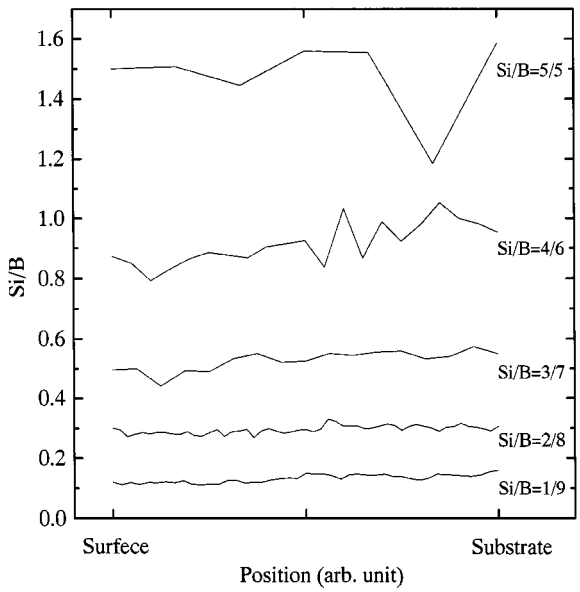

FIG. 2. Depth profiles of Si/B ratio determined by ESCA. Nominal Si/B ratios are shown beside the data.

To prepare the target, the pressed disk-shaped pellets of B–Si powder were placed on a water-cooled copper hearth and melted by arc spark in an argon atmosphere. The resultant ingot was then cut into a disk with about 20 mm in diameter and about 2 mm thick.

Surface morphology of the deposited films was observed by scanning electron microscopy (SEM). The structure of the films was determined by X-ray diffraction (XRD). Chemical compositions of the films were determined by electron spectroscopy for chemical analysis (ESCA). An optical absorption spectrum was measured by a spectrometer to obtain optical band gap and film thickness. The detailed procedure of the optical measurement has been described elsewhere (7). Temperature dependence of the dc electrical conductivity was measured by the van der Pauw method.

3. RESULTS AND DISCUSSIONS

3.1. Films Deposited by PLD

We prepared B–Si films by the PLD technique using targets with nominal Si/B atomic ratios of $\frac{1}{9}$, $\frac{2}{8}$, $\frac{3}{7}$, $\frac{4}{6}$, and $\frac{5}{5}$. With each laser shot, a plume of intense white light emission could be observed normal to the target surface. According to SEM observation of the film surface, there were many droplets at laser fluence of 1.6 J/cm^2 · pulse, and the density of the droplet decreased with decreasing laser fluence. As a result, the laser fluence of 0.8 J/cm^2 · pulse was selected for the film deposition. After 20,000 shots of laser irradiation, brown-colored films were obtained.

Figure 2 shows the depth profiles of the Si/B atomic ratios determined by ESCA measurements. Small amounts of C and O (3–5 at %) were detected in each specimen, but the concentrations of the impurities were independent of the Si/B ratio. The Si/B ratio of the films are slightly shifted toward the silicon-rich side compared to those of the target, and their average values are estimated to be 0.14, 0.30, 0.59, 0.92, and 1.50. Nevertheless, the profiles are nearly flat. XRD measurements revealed that structures of the obtained films were amorphous.

3.2. Optical Absorption

Optical absorption spectra were measured at a wavelength between 300 and 2500 nm. From the interference pattern of the spectra, film thicknesses were estimated to be approximately 3000 Å. Accordingly, deposition rate of the present PLD experiment was about 0.15 Å/pulse.

The absorption coefficient, a, was then calculated from the spectrum as a function of photon energy, hv. It is well known that photon energy dependence of a above the exponential tails is described by the following equation for many amorphous semiconductors

$$ahv = A(hv - E_{opt})^n, \qquad [1]$$

where A is a constant and E_{opt} is defined as an optical band gap. The estimated E_{opt} for the deposited films is shown in Fig. 3 (solid circles). All the data were better fitted with the exponent $n = 2$ in Eq. [1]. In Fig. 3, energy gaps of amorphous B–Si films deposited by electron beam evaporation are also shown (8) (open circles). For the latter films, data were fitted with $n = 3$ for the Si/B ratio less than 0.19, and with $n = 2$ for the others. As shown in Fig. 3, optical gaps of films prepared by both PLD and electron beam evaporation lie on a curve that increases with an increase in Si concentration. This suggests that the films prepared by the two

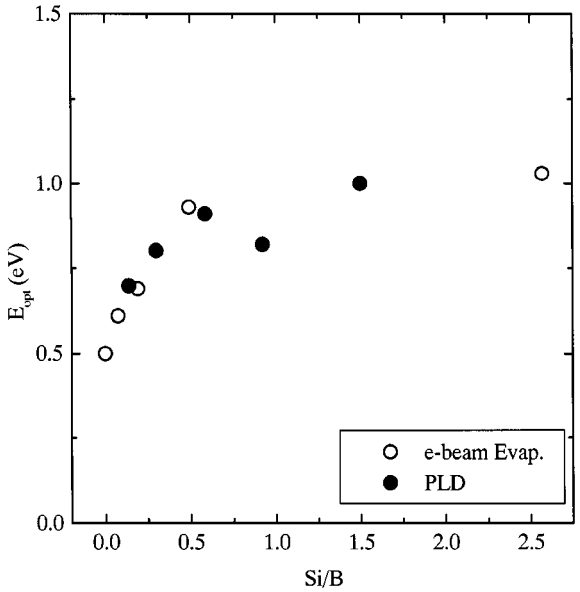

FIG. 3. Si/B ratio dependence of optical band gap for the films deposited by PLD (solid circles) and electron beam evaporation (open circles).

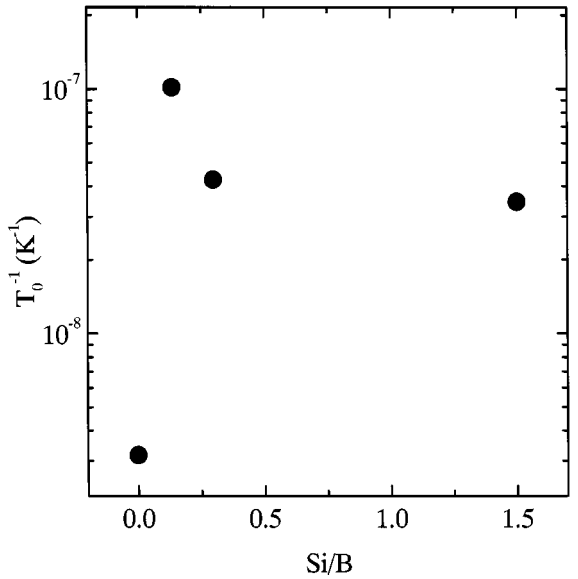

FIG. 5. Si/B ratio dependence of T_0^{-1} of the VRH formula for amorphous B–Si deposited by PLD.

methods have the same character and the change in the exponent n occurs at around Si/B = 0.17, although there is a discrepancy between exponent n for Si/B = 0.14 and that for 0.19.

3.3. DC Electrical Conductivity

Figure 4 shows the temperature dependence of dc conductivity ($\sigma(T)$) for B–Si amorphous films prepared by PLD. As shown in Fig. 4, the $\sigma(T)$ shows variable-range-hopping (VRH)-type behavior (Mott's low) rather than thermal activation-type dependence. As for the specimens with higher Si/B ratio (0.30 and 1.50), the $\sigma(T)$ deviates from the straight line at low temperature. This may be caused by the existence of another conduction path with smaller temperature dependence, but further experiments are needed to conclude. The value and temperature dependence for amorphous boron are consistent with those reported previously (9). The conductivity for amorphous B–Si is two or three orders of magnitude larger than that of amorphous boron. Such tendencies have been observed in metal-doped β-rhombohedral boron (10).

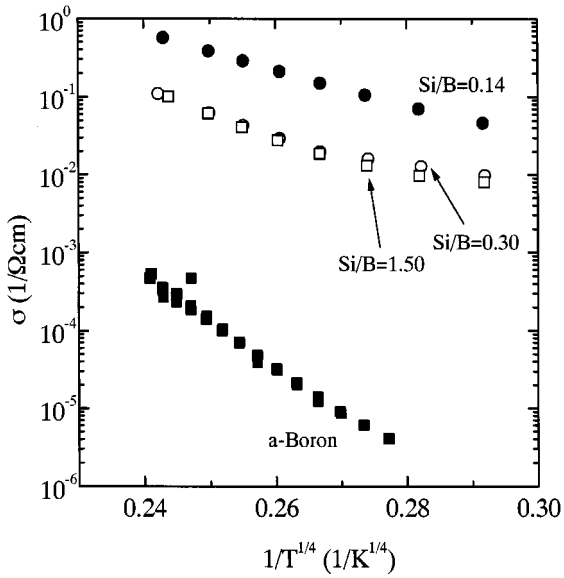

FIG. 4. Temperature dependence of dc conductivity for amorphous boron and B–Si (Si/B = 0.14, 0.30, and 1.50) films.

According to Mott's low (11) of VRH conduction, σ is expressed as

$$\sigma = \sigma_0 \exp[-(T_0/T)^{1/4}], \quad [2]$$

$$T_0 = \frac{60\alpha^3}{\pi N(E_F) k_B}, \quad [3]$$

where α^{-1} is the localization length of the wave function of the carrier and $N(E_F)$ is the density of states at the Fermi energy. Figure 5 shows the Si concentration dependence of T_0^{-1}, which is proportional to the product of $N(E_F)$ and α^{-3}. The T_0^{-1} values for amorphous B–Si, ranging from 10^{-8} to 10^{-7} (K^{-1}), are nearly equal to those for metal (Cu or Ni)-doped β-rhombohedral boron (12), in which T_0^{-1} increases with metal concentration until a certain concentration is reached and then decreases. Such a behavior in metal-doped β-rhombohedral boron was explained by

carrier doping from metal atoms to the intrinsic acceptor levels originating from B_{12} clusters.

In the case of amorphous B–Si, the situation is not simple as in β-rhombohedral boron. Structural analysis and optical measurement on amorphous B–Si suggested that the film whose structure is characterized by random packing of clusters possesses the exponent of $n = 3$ for the optical absorption spectrum, while the films characterized by tetrahedral random network possess $n = 2$ (8). According to the result, tetrahedral random network is dominant for the films prepared in the present study. In the films, however, boron-rich clusters in B–Si crystalline phases, such as M_{12} or M_{15} (M = B, Si) (13), probably exist in the network. This is because B_{12} clusters were created in the tetrahedral network of crystalline silicon by high-dose implantation of boron ion (14). It is considered that the existence of the clusters leads to the VRH-type behavior in dc conductivity.

4. CONCLUSION

Using the PLD technique, we obtained amorphous B–Si films with a flat depth profile of Si concentration. The optical absorption spectra of the films were fitted by $ahv = A(hv - E_{opt})^n$ with $n = 2$, which suggests that tetrahedral random network is dominant for the films. The result that temperature dependence of σ shows VRH-type behavior implies the existence of boron-rich clusters in the tetrahedral Si network. Further experiments are necessary to confirm the hypothesis and are now in progress.

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REFERENCES

1. R. Franz and H. Werheit, *in* "Boron-Rich Solids" (D. Emin, T. L. Aselage, A. C. Switendick, B. Morosin, and C. L. Beckel, Eds.), AIP Conf. Proc., Vol. 231, p. 29. AIP, New York, 1991.
2. M. Morosin, A. W. Mullendore, D. Emin, and G. A. Slack, *in* "Boron-Rich Solids" (D. Emin, T. L. Aselage, C. L. Beckel, I. A. Howard, and C. Wood, Eds.), AIP Conf. Proc., Vol. 140, p. 70. AIP, New York, 1986.
3. M. Takeda, K. Kimura, and K. Murayama, *J. Solid State Chem.* **133,** 201 (1997).
4. T. Lundström and H. Bolmgren, *in* "Proc. 11th International Symposium on Boron, Borides, and Related Compounds" (R. Uno and I. Higashi, Eds.), JJAP Series Vol. 10, p. 1. JJAP, Japan, 1994.
5. L. Chen, T. Goto, J. Li, and T. Hirai, *Mater. Trans. JIM* **37,** 1182 (1996).
6. O. Auciello, *in* "Handbook of Crystal Growth, Vol. 3. Thin Films and Epitaxy, Part A: Basic Techniques" (D. T. J. Hurle, Ed.), Chap. 9. Elsevier, Netherlands, 1994.
7. A. Hori, M. Takeda, H. Yamashita, and K. Kimura, *J. Phys. Soc. Jpn.* **64,** 3496 (1994).
8. H. Yamaguchi, Y. Sakairi, M. Takeda, K. Kimura, S. Tanaka, and E. Matsubara, *Trans. Mater. Res. Soc. Jpn.* **24,** 85 (1999).
9. A. A. Berezin, O. A. Golokova, M. M. Kazanin, T. Khomidov, D. N. Mirlin, A. V. Petrov, A. S. Umarov, and V. K. Zaitsev, *J. Non-Cryst. Solids* **16,** 237 (1974).
10. H. Matsuda, T. Nakayama, K. Kimura, Y. Murakami, H. Suematsu, M. Kobayashi, and I. Higashi, *Phys. Rev. B* **52,** 6102 (1995).
11. N. F. Mott and E. A. Davis, "Electronic Processes in Non-Crystalline Materials." Clarendon Press, Oxford, 1979.
12. H. Matsuda, N. Tanaka, T. Nakayama, K. Kimura, Y. Murakami, H. Suematsu, M. Kobayashi, and I. Higashi, *J. Phys. Chem. Solids* **57,** 1167 (1996).
13. A. Vlasse, G. A. Slack, M. Garbauskas, J. S. Kasper, and J. C. Viala, *J. Solid State Chem.* **63,** 31 (1986).
14. I. Mizushima, M. Watanabe, A. Murakoshi, M. Hotta, M. Kashiwagi, and M. Yoshiki, *Appl. Phys. Lett.* **63,** 373 (1993).