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Preparation and Properties of Boron Thin Films

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Boron thin films were prepared by plasma assisted chemical vapor deposition. The source gas was boron trichloride (BCl_3). Ring patterns of transmission electron beam diffraction indicated that films were polycrystalline α-rhombohedral boron. Optical absorption edge was estimated from absorption spectrum. The absorption edge was about 1.05 eV for the films deposited at 700°C and was increased to about 1.4 eV as the deposition temperature increased to higher than 800°C. The Hall mobility was 10^{-4}–10^{-1} cm^2/Vs and the carrier concentration was 10^{16}–10^{18} cm^{-3}. All films showed *p*-type conduction. The piezoresistive gauge factor was about 10. © 1997 Academic Press

1. INTRODUCTION

Boron is known as one of elemental semiconductors. Some papers have described fundamental properties such as resistivity (1, 2), optical properties (2), thermoelectric properties (1, 3), and mechanical properties (4). Shirai and coworkers (5) have reported preparation and characterization of hydrogenated amorphous boron film. Cirri and coworkers (6) fabricated boron thermistors. Instead of these early efforts, boron still seems to be one of the least understood materials among the elemental semiconductors. The difficulty in preparing high quality films seems to be the main reason that few papers have been written, as compared to the amount of literature on other elemental semiconductors such as Ge, Si, or Se. Another reason seems to be that boron is thought to be unsuitable for use in electronic devices except for thermistors.

In this work, boron films were deposited by plasma assisted chemical vapor deposition of boron trichloride (BCl_3). From the application point of view, it is desirable to prepare a high quality film at as low a substrate temperature as possible. Plasma assistance is one of the effective methods of lowering the deposition temperature.

Films were characterized by ESCA, transmission electron beam diffraction, and Hall measurement. Piezoresistive characteristics were measured by conventional cantilever method.

2. PREPARATION

Boron thin films were prepared by plasma assisted chemical vapor deposition. The source gas was boron trichloride (BCl_3). Boron trichloride is safer and cheaper than diborane (B_2H_6). Figure 1 shows the schematic representation of deposition chamber. The chamber was made from a quartz tube with an inner diameter of 38 mm.The BCl_3 was kept to 0°C by dipping the container in iced water. The flow rate of BCl_3 was controlled with a mass flow controller. Deposition conditions are listed in Table 1.

A silicon wafer or a quartz glass plate was used as the substrate. The substrate was heated with a resistance furnace. The substrate temperature was measured by a CC thermocouple attached between the quartz reactor and the furnace as shown in Fig. 1. The RF power of 13.56 MHz was supplied by a coil. With this setup, the glow discharge spread into the furnace, and the source gas was ionized effectively.

Boron films were deposited at 700–1000°C for 60 min. Figure 2 shows the deposition rate under the conditions listed on Table 1. The deposition rate increased followed by saturation as the substrate temperature was increased. At low temperature, the surface reaction determined the deposition rate, and at higher temperatures, the deposition rate seemed to be controlled by the transport of the source material to the substrate surface.

3. CHARACTERIZATION

The films were characterized by ESCA, transmission electron beam diffraction, optical absorption, and electrical measurement.

Chemical compositions. The chemical properties were characterized by ESCA measurement. Figure 3 shows a typical ESCA spectrum of a boron film deposited at 900°C.

Small amounts of carbon and oxygen were detected by the ESCA measurement. These impurities seemed to be doped from residual gases and surface contamination because the peaks corresponding to these elements decreased as the etching time was increased. After etching of 5 min, the

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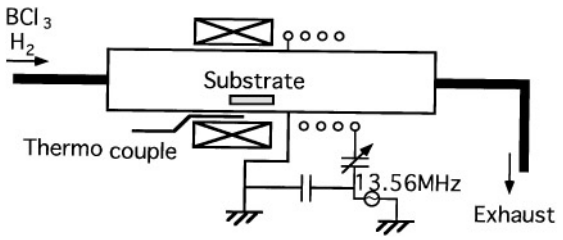

FIG. 1. Schematic representation of the deposition chamber.

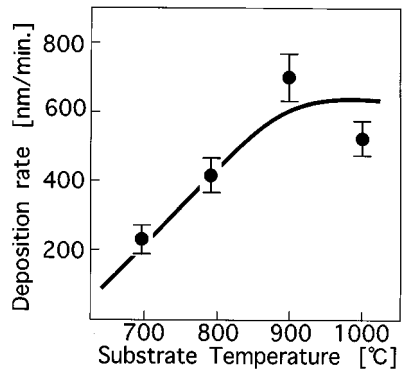

FIG. 2. Deposition rate of boron films.

ratio of C/B and O/B was about 0.12 and 0.06, respectively. Nakamura (7) also reported about boron films deposited by pyrolysis of decaborane and detected oxygen and carbon localized near the surface of the boron film by ESCA measurement. Their concentrations were almost half of our data.

Crystal structure. The structure of the film was characterized by transmission electron beam diffraction. Figure 4 shows a typical diffraction pattern of a boron film deposited at 900°C on quartz glass. Ring patterns indicated that films were polycrystalline α-rhombohedral boron. The pattern was rather diffuse. The data suggested that the samples were partly amorphous and partly polycrystalline with the α-rhombohedral structure. Patterns obtained for the films deposited at lower temperature were even more diffuse.

Electrical properties. The electrical properties were estimated by Hall measurement. Few papers have been reported about electrical properties of polycrystalline boron films (2, 7). Figure 5 shows the carrier concentration and Hall mobility of polycrystalline boron films measured by Van der Pauw method at room temperature. The Hall mobility was found to be 10^{-4}–10^{-1} cm^2/Vs and the carrier concentration derived was 10^{16}–10^{18} cm^{-3}. All films showed *p*-type conduction. High substrate temperature resulted in high mobility. The higher the rate of crystallization, the higher the mobility in the film. The mobility in crystalline boron is obviously higher than that in amorphous boron. Figure 6 shows the temperature dependence of resistivity. The resistivity depends almost linearly on the reciprocal temperature $(1/T)$ as shown in Fig. 6. The activation energy was 0.35–0.45 eV. Shaw and his co-workers (1) reported the T^{-1} dependence with multiple activation energies (0.25–0.79 eV). Nakamura (7) and Prudenziati (2) reported $T^{-1/4}$ dependence for amorphous boron films. They also estimated the activation energy from T^{-1} dependence in the high temperature range, and the values were 1.07 and 0.46 eV, respectively. These results suggested that the crystalline part in the boron film determined the temperature dependence of the resistivity shown in Fig. 6.

Absorption edge. Optical transmission spectrum was measured by a monochromator. Absorption coefficient α was determined from the transmission spectrum. The value of $(\alpha hv)^{1/2}$ was plotted against the photon energy *hv*. Fundamental absorption edge was determined by extrapolating

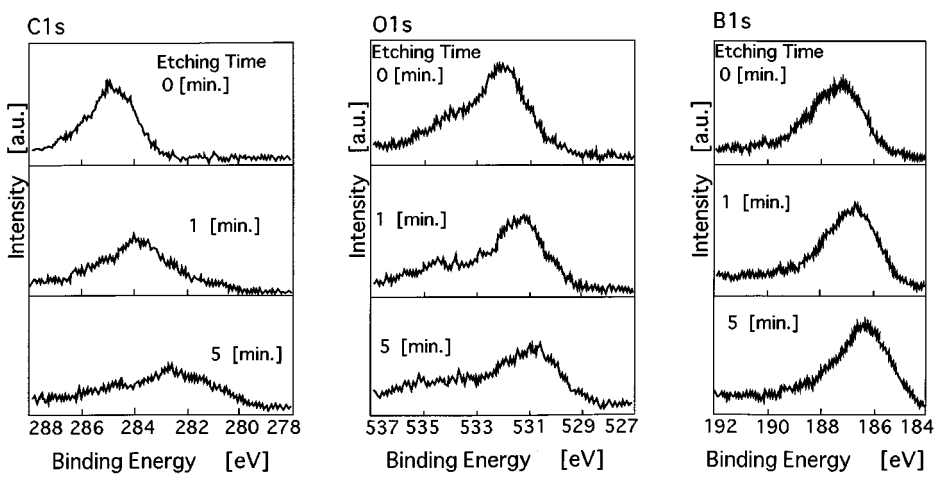

FIG. 3. ESCA spectrum of O1s, C1s, and B1s in the boron film.

TABLE 1
Deposition Conditions

Condition	Value
RF power	40 W, 13.56 MHz
Deposition temperature	700–1000°C
Flow rate of dilution gas (H_2)	3×10^{-5}–7×10^{-5} m^3/s
Flow rate of source gas (BCl_3)	8×10^{-6}–3×10^{-5} m^3/s
Total pressure	120–310 Pa

the linear portion to zero. Figure 7 shows the relation between deposition temperature and absorption edge. The absorption edge changed from 1.05 to 1.4 eV. The films deposited at low temperature (700–800°C) showed the absorption edge of about 1.05 eV, which corresponds to the energy gap of amorphous boron (7). Higher deposition temperature resulted in higher absorption edge. The absorption edge of the films deposited at temperatures higher than 850°C is comparable to the value of crystalline boron (7, 8). The sample deposited at lower temperature seemed to consist mainly of amorphous boron. The fraction of crystallized portion increased in the film, as the deposition temperature was increased. The films seemed to be almost polycrystalline when they were deposited at temperatures above 850°C. These results correspond to the electron beam diffraction. The films deposited at lower temperature show diffused ring patterns. The higher deposition temperature resulted in a less diffuse ring pattern, although diffuse rings were observed in some of the diffraction patterns of the samples deposited at 900°C also.

Piezoresistive characteristics. Piezoresistive characteristics were measured by conventional cantilever method. The strain was estimated from the deformation of the cantilever, and the resistance of the boron film was measured by a digital multimeter. Figure 8 shows the relation between the resistance change ($\Delta R/R$) and strain in the film. The compressive strain resulted in an increase in the resistance.

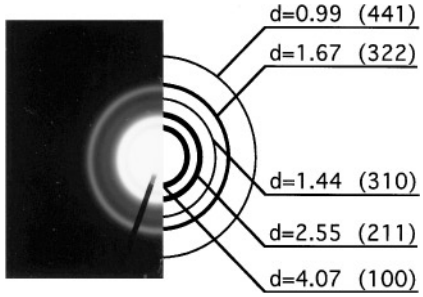

FIG. 4. Transmission electron beam diffraction pattern of a boron film deposited at 900°C.

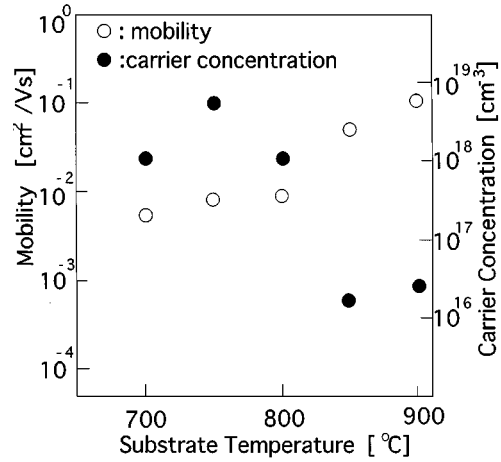

FIG. 5. The Hall mobility and carrier concentration as a function of deposition temperature.

The resistance changed linearly to the strain. The gauge factor is defined as the ratio of change in resistance ($\Delta R/R$) to strain and is the most important parameter for the application of thin film to strain gauge. The value of gauge factor was estimated from the result in Fig. 8 and was about 10 for the film deposited at 900°C. This value was almost the same as that of a polycrystalline Si gauge element of the commercially available pressure sensor.

The gauge factor of the film deposited at 900°C is higher than that of the film deposited at 700°C. The electron beam diffraction showed that the film deposited at 900°C contained much more crystalline grains than that deposited at 700°C. Therefore the crystallization of the film seemed to increase the gauge factor.

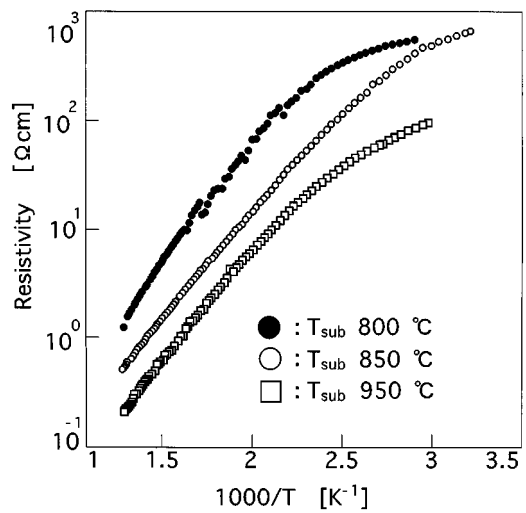

FIG. 6. Temperature dependence of the resistivity of boron films.

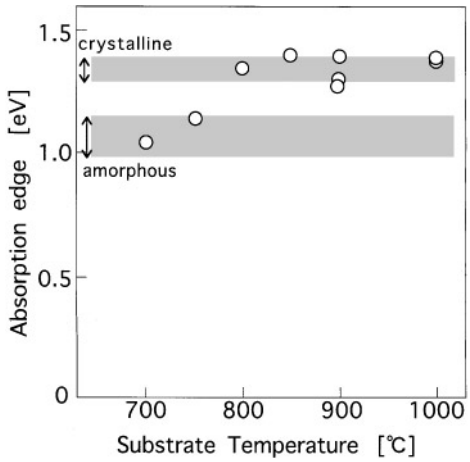

FIG. 7. Optical absorption edge of boron films determined from $(\alpha hv)^{1/2}$ vs hv plot.

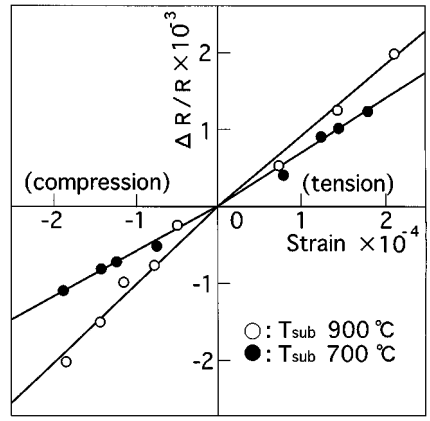

FIG. 8. Piezoresistive characteristics of boron films.

4. CONCLUSION

Boron films were deposited by plasma assisted chemical vapor deposition of BCl_3. Films were amorphous or polycrystalline α-rhombohedral boron. Major impurities were carbon and oxygen, which were localized at the surface of boron film. The films were almost amorphous when they were deposited at temperatures lower than 800°C. Polycrystalline structure was observed by means of electron beam diffraction in the films deposited at higher temperatures ($T > 850$°C). The gauge factor was about 10 for the film deposited at 900°C. Higher deposition temperature resulted in higher gauge factors. The gauge factor of 10 was of the same order of magnitude as that found for polycrystalline Si gauge element of the commercially available pressure sensor. At this stage, boron can be used only for thermistor devices. To find another application of boron, it is important to establish a technology to produce high quality films.

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