JOURNAL OF SOLID STATE CHEMISTRY **133,** 269–272 (1997)
ARTICLE NO. SC977454

Preparation and Electrical Properties of Boron and Boron Phosphide Films Obtained by Gas Source Molecular Beam Deposition

Y. Kumasiro, T. Yokoyama, T. Sakamoto, and T. Fujita

Facility of Engineering, Yokohama National University, 156 Tokiwadai, Hodogaya, Yokohama, 240 Japan

Received April 14, 1997; accepted April 28, 1997

Boron and boron phosphide films were prepared by gas source molecular beam deposition on sapphire crystal at various substrate temperatures up to 800°C using cracked B_2H_6 (2% in H_2) at 300°C and cracked PH_3 (20% in H_2) at 900°C. The substrate temperatures and gas flow rates of the reactant gases determined the film growth. The boron films with amorphous structure are *p* type. Increasing growth times lead to increasing mobilities and decreasing carrier concentrations. Boron phosphide film with maximum P/B ratio is obtained at a substrate temperature of 600°C, below and above which they become phosphorus deficient due to insufficient supply of phosphorus and thermal desorption of the phosphorus as P_2, respectively, but they are all *n* type conductors due to phosphorus vacancies. © 1997 Acadamic Press

INTRODUCTION

Boron and boron phosphide are wide gap refractory semiconductors and have potential applications in electronic devices used in extreme environments, such as solid-state neutron detection utilizing a large cross section of 10. For this purpose, high purity material is required.

Among various crystal growth techniques, chemical vapor deposition (CVD) is the most popular. The problem with CVD lies in a fairly high carrier concentration and a low electric resistivity due to autodoping of silicon deposited on a silicon substrate (1)

In contrast, physical vapor deposition (PVD) is a low temperature and nonequilibrium growth, so high purity specimens result. Molecular beam epitaxy (MBE) has the potential to produce both low-temperature growth and high-purity film. We prepared boron subphosphide films by molecular beam deposition (MBD) (2), evaporating boron with an electron beam gun and producings P_2 molecular flux by cracking phosphine (0.8–1 sccm) on the substrate under a vacuum of $\sim 5 \times 10^{-5}$ Torr (2), which was the upper limit of operation of the electron beam gun. Then the high incident frequency of boron over phosphorus produced a film with composition $B_{12}P_2$, far from BP.

Gas-source molecular beam epitaxy (GS-MBE) has recently been shown to offer potential advantages over solid-source MBE for the growth of refractory GaN (3) and SiC (4, 5) and to avoid high throughput. GS-MBE allows one to control the flow rates of reactant gases so that stoichiometric films are obtainable.

The present paper describes the preparation and the electrical properties of boron and boron phosphide film obtained by GS-MBD for the first time.

EXPERIMENTAL

Growth experiments were carried out in a ultra-high-vacuum chamber designed for gas-source molecular beam deposition (Fig. 1), which was modified by MBD apparatus (Eiko Engineering, EV-10). Instead of an electron beam gun, a diborane gas cell was used. Source gases of diborane (2% in H_2) and phosphine (20% in H_2) entered the chamber through variable leak valves and were each cracked in the cells 25 cm from the substrate. The gas supply was monitored by a quadruple mass spectrometer. Before the experiment, the chamber was evacuated to below 2×10^{-9} Torr and then the substrate temperature was lowered to the growth temperature to confirm radical hydrogen and a small amount of nitrogen determined by the mass spectrometer under a vacuum of 2×10^{-9} Torr. The growth experiment was performed with cracked B_2H_6 at 300°C and cracked PH_3 at 900°C under a vacuum of 5×10^{-4} Torr.

The films were deposited on a single sapphire crystal at gas flow rates of 1–5 sccm and growth temperatures of 30–800°C. The film thickness was determined by a quartz oscillator.

The crystal structure of the films was studied by reflection high-energy electron diffraction (RHEED) and X-ray diffraction techniques. The composition of the boron phosphide films was determined by X-ray photoelectron spectroscopy (XPS). The electrical properties were measured by the van der Pauw method. Ohmic contacts were made by

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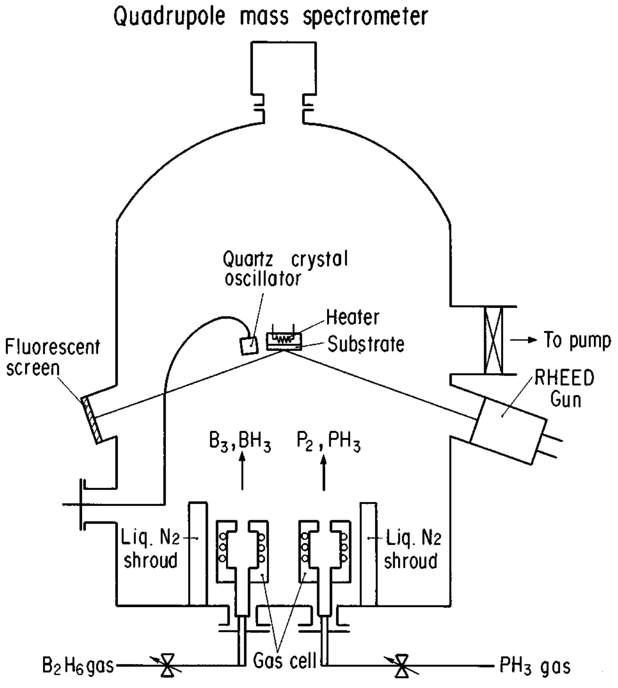

FIG. 1. Schematic illustration of gas-source molecular beam deposition for boron and boron phosphide.

evaporating Al, subsequently annealed in argon at 400°C for 1 h.

RESULTS AND DISCUSSION

A. Boron Film

Mass spectrometry indicated the peaks H_2, B_2H_x ($x = 0$–9), BH_x ($x = 0$–7), and B_3H_x ($x = 0$–4) from cracked diborane. The main peaks of BH_x and B_2H_x consisted of BH_3 and B_2H_6, respectively. The films were grown at substrate temperatures higher than 600°C. They grew rapidly between 700 and 800°C, which is consistent with results from mass spectrographic analysis showing that increasing the substrate temperature above 600°C enhanced the cracking of the B_2H_6 gases (6). The peak height of B_3 at 800°C indicates that B_3 is main precursor of film growth. Figure 2 shows the temperature dependence of the deposition rate, which increases with an activation energy of 42.2 kcal/mol. This agrees with 39 kcal/mol for the deposition of boron by pyrolysis of decaborane in the molecular flow region (7).

The thickness of the boron film increases at diborane gas flow rates of 1–3 sccm at a growth temperature of 800°C. Above 4–5 sccm the film becomes inhomogeneous with many porosities in the film. They are probably due to the generation of new reactant gases of the substrate in the case of insufficient film growth. Gas flow rates of 3 sccm allowed the highest growth rates of homogeneous films with thicknesses increasing linearly with time. X-ray diffraction patterns indicate that films grown for 10 and 20 h are amorphous boron but those grown for 50 h showed α-rhombohedral structure. According to SEM observation the particle size of the film increases with time.

TABLE 1
Electrical Properties of Boron Films Grown at 800°C

Growth time (h)	Resistivity ($\Omega \cdot$cm)	Hole concentration (cm^{-3})	Hole mobility ($cm^2/V \cdot s$)
10	1.7×10^4	1.6×10^{13}	18.1
20	1.8×10^4	8.8×10^{12}	31.2

The electrical properties of these films are listed in the Table 1. All the films are *p* type. Increasing growth time leads to increasing mobility and decreasing carrier concentration with the consequence of improvement in the film quality. These films have lower carrier concentrations and higher mobilities than those obtained by the SSMBD process (2), which is assumed to be due to the higher purity of the starting materials. The electrical properties of the present films are in good agreement with those of our amorphous boron films deposited by CVD on the same substrate materials. Therefore the present data are assumed to reveal the intrinsic properties of amorphous boron films. Unfortunately we could not measure the electrical properties of films obtained at growth times of 50 h because these films cracked.

B. Boron Phosphide Film

The growth experiments on boron phosphide films were performed under optimum gas flow rates of 3 sccm for B_2H_6. According to previous SSMBD processes (2) the $\sim 10^{-4}$ Torr vacuum used corresponds to flow rates of 5 sccm for PH_3.

The number of diborane and phosphine molecules impinging on the substrate surface, *S*, is determined by gas dynamics (7, 8) according to

$$S = P(M_w/2\pi RT_g)^{1/2} = 5.8 \times 10^{-2} P(M_w/T_g)^{1/2} \ (g/cm^2), \quad [1]$$

where P is the gas partial pressure in Torr, M_w the molecular weight, R the gas constant, and T_g the gas temperature. Using Avogadoro's number, the number of impingement molecules, v, is

$$v = 3.5 \times 10^{22} P(M_w/T_g)^{1/2} \ (molecules/cm^2 \cdot s). \quad [2]$$

When the total pressure of 5.0×10^{-4} Torr, phosphine concentration of 20%, and diborane concentration of 2% are substituted into Eq. [2], in the cases of diborane and phosphine, $\nu_{B_2H_6} = 2.9 \times 10^{16}$ moleculer/cm$^2 \cdot$ s, and $\nu_{PH_3} = 3.7 \times 10^{17}$ molecule/cm$^2 \cdot$ s are obtained, leading to the incident frequency ratio $\nu_{PH_3}/\nu_{B_2H_6} = 12.8$.

The temperature dependence of the deposition rate of boron phosphide film differs from that of boron (Fig. 2). The deposition rate increases with increasing temperature up to 600 K and then tends to saturate. This behavior is similar to that of boron nitride formed by the pyrolysis of decaborane and ammonia in the molecular flow region (8). For $T_S \leq 600$°C, the activation energy is 10.3 kcal/mol. This is comparable to the activation energy of 6.3 kcal/mol below 850°C for the B–N reaction determined by Nakamura (8) in the reaction rate of nitrogen with boron in the production of boron nitride. Thus our activation energy of 10.3 kcal/mol is probable.

Mass spectrometry of cracked PH_3 at 900°C contained PH_x ($x = 0$–4) and P_2. The peak for P began to appear at a substrate temperature of 400°C and increased up to 800°C. The deposition of boron phosphide film was performed by involving the simultaneous presence of both boron precursors, such as B_2H_6, BH_3, and B_3, and phosphorus precursors, such as PH_3, PH_2, PH, P, and P_2, on the substrate.

At $T_S \geq 400$°C, hydrogen is desorbed from the adsorbed overlayer, leaving phosphorus on the surface (6), but phosphorus atoms cannot stay on the substrate surface without bonding boron atoms or desorbing from the growing surface.

The growth rate is controlled by kinetics, which encompasses mass transport of the reactants onto the growing surface and reactions occurring both in the gas phases and on the surface, including the nature and motion of surface steps.

At high temperatures the growth rate is independent of temperature (Fig. 2). Since $\nu_{PH_3}/\nu_{B_2H_6}$ is larger than unity, the growth rate in this regime is controlled by mass transport of boron species through the vapor to the growth interface (9).

At $T_S > 600$°C the deposition rate is determined by the boron flux (9, 10). The incident phosphorus atoms could adsorb onto the growing surface to form a migration state so that P atoms can be incorporated into the crystal (10). Without the complicated chemical reaction parameters, the incorporation probability is controlled by the effective concentration of P atoms in the migration state (10). The small activation energy in this regime would come from the effect of the different temperature on the lifetime and chemical reaction constant on P (10).

The peak energies of B 1*s* in the XPS spectra (Fig. 3) shift to lower energies compared with those of the film grown at 600°C. This corresponds to the decreasing content of phosphorus atoms in the film. The composition of boron phosphide films grown at various substrate temperatures are shown in Fig. 4. The boron phosphide film with maximum P/B ratio is obtained at a substrate temperature of 600°C.

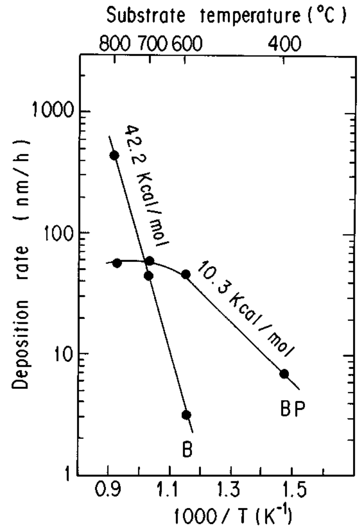

FIG. 2. Deposition rate of boron and boron phosphide vs reciprocal substrate temperature.

The behavior shown in Fig. 4 is qualitatively consistent with the following experimental facts (6). The phosphorus coverage increases at increasing substrate temperature and attains a maximum at about 550°C, above which it is thermally desorbed as P_2 to reduce the phosphorus coverage.

Thus the boron phosphide film grown at 600°C would correspond to the optimum supply of boron and phosphorus sources to establish a maximum P/B ratio. Figure 2 suggests that boron phosphide film with maximum P/B ratio would grow at a low deposition rate of boron and with a high supply of phosphorus. Thus the growth rate and incident frequency ratio of $\nu_{PH_3}/\nu_{B_2H_6}$ for the present born phosphide are lower than those of other semiconductor compounds by one order of magnitude.

We could not evaluate the crystal quality by X-ray diffraction and RHEED because of the insufficient thickness of the films (40 to 580 nm). However, boron phosphide films

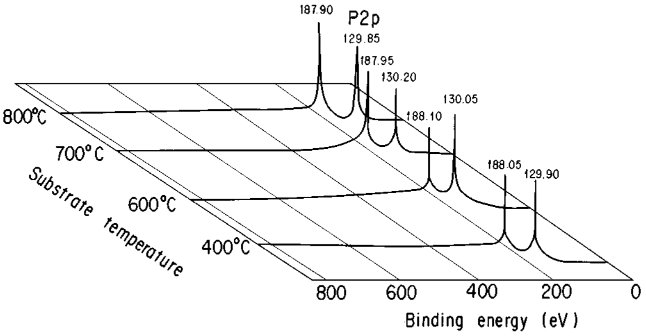

FIG. 3. XPS spectra of films grown at various substrate temperatures.

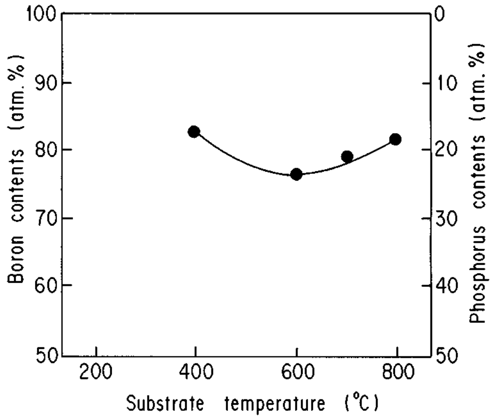

FIG. 4. Composition of boron phosphide vs substrate temperature.

on Si (100) planes obtained by the same method yield single crystalline and amorphous patterns at substrate temperatures of 800 and 600°C, respectively. Considering the melting points of the substrate materials, we assume the present boron phosphide films to be amorphous.

Electrical properties of boron phosphide films are shown in Table 2. We could not measure the electrical properties of the film prepared at 400°C because of the insufficient thickness. These films are *n*-type conductors due to phosphorus vacancies. The boron phosphide film grown at 600°C has the highest mobility. The electrical resistivity is the highest ever known. The results for a CVD BP single crystal film on a sapphire single crystal grown at 1000°C (11) and a single crystal wafer (1) grown on Si(100) at 950°C are also shown in Table 2. The CVD BP specimens contain autodoped oxygen and silicon, respectively. Thus the present boron phosphide grown at 600°C would be of the highest purity. The electron concentration of the boron phosphide films grown at 700 and 800°C increases and the mobility decreases in comparison with that grown at 600°C, which would be increasing phosphorus vacancies.

CONCLUSION

We have prepared highest purity boron and boron phosphide films on a sapphire single crystal by gas-source molecular beam deposition for the first time. Amorphous boron films give intrinsic electrical properties. Boron phosphide film with maximum P/B ratio would grow under a low deposition rate of boron and with high supply of phosphorus, with the incident ratio $\nu_{PH_3}/\nu_{B_2H_6}$ of 12.8, and would give the highest electrical resistivity with electron mobility of 170 cm^2/V · s.

TABLE 2

Electrical Properties of Boron Phosphide Films Grown by GS-MBD in Comparison with Those Grown by CVD (1, 11)

Substrate tempeature (°C)	Resistivity (Ω · cm)	Electron concentration (cm^{-3})	Electron mobility (cm^2/V · s)
600	4.0×10^4	6.0×10^{10}	170
700	1.2×10^4	4.2×10^{11}	80
800	1.0×10^4	1.6×10^{12}	26
950 (1)	0.15	3.7×10^{17}	120
1000 (11)	3.1×10^{-2}	4.8×10^{18}	37.7

ACKNOWLEDGMENTS

The authors thank Dr. K. Nakamura for valuable discussion. This work was supported by Kato Scientific Foundation.

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