Contents lists available at SciVerse ScienceDirect





Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Thin film growth of boron nitride on α -Al₂O₃ (0 0 1) substrates by reactive sputtering

Atsushi Anzai^a, Fumitaka Nishiyama^b, Shoji Yamanaka^a, Kei Inumaru^{a,*}

^a Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan ^b Technical Center, Hiroshima University, Higashi-Hiroshima 739-8527, Japan

ARTICLE INFO

Article history: Received 10 August 2011 Received in revised form 23 August 2011 Accepted 9 September 2011 Available online 16 September 2011

Keywords: A. Nitride B. Sputtering C. X-ray diffraction D. Crystal structure

ABSTRACT

Boron nitride thin films were grown on α -Al₂O₃ (0 0 1) substrates by reactive magnetron sputtering. Infrared attenuated total reflection (ATR) spectra of the films gave an intense signal associated with inplane B-N stretching TO mode of short range ordered structure of BN hexagonal sheets. X-ray diffraction for the film prepared at a low working pressure (ca. 1×10^{-3} Torr) gave a diffraction peak at slightly lower angle than that corresponding to crystal plane *h*-BN (0 0 2). It is notable that crystal thickness calculated from X-ray peak linewidth (45 nm) was close to film thickness (53 nm), revealing well developed sheet stacking along the direction perpendicular to the substrate surface. When the substrates of MgO (0 0 1) and Si (0 0 1) were used, the short-range ordered structure of *h*-BN sheet was formed but the films gave no X-ray diffraction. The film showed optical band gap of 5.9 eV, being close to that for bulk crystalline *h*-BN.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

An increasing interest in the chemical and physical properties of nitrides has recently accelerated studies of the binary and ternary nitrides [1–15]. Nitrides are categorized into several groups such as "interstitial nitrides", "ionic nitrides" and "covalent nitrides" [16]. Many transition metal binary nitrides are often categorized as interstitial nitrides [16], in which it is considered that the nitrogen atoms occupy interstitial sites between the atoms of the parent metals. These nitrides show a wide variety of physical properties: for example 3d transition metal nitrides have been shown to exhibit antiferromagnetism (MnN [7,8], CrN [9–11], FeN [12]), Pauli paramagnetism [13] (CoN), ferromagnetism [14] (Cr_{0.5}Ti_{0.5}N) and superconductivity [15] (TiN, VN).

Covalent nitrides include silicon nitride, carbon nitride, and boron nitride (BN). They are usually electronically insulating or semiconducting. BN adopts crystal structures similar to those of elemental carbon, because BN is isoelectronic to Carbon. Cubic boron nitride (*c*-BN) adopts zinc blende structure, which corresponds to diamond structure of carbon. Since *c*-BN is a very hard material, many studies are devoted to synthesize *c*-BN coatings for cutting tools. *c*-BN is also promising as a wide band gap semiconductor and power electronic devices [16]. Another polymorph of BN is a hexagonal structure, *h*-BN. This structure consists of BN layers which resemble the sheets of graphite and the sheets are stacking to form a sequence of B-N-B-N \cdots along the *c* axis, as shown in Fig. 1. *h*-BN is attracting much attention as an optical material. Recently synthesis of single crystal of *h*-BN was reported. The crystal was demonstrated to be promising as ultraviolet illuminator [17].

BN thin films have been prepared by various methods. Chemical Vapor Deposition (CVD) is a useful method to synthesize highly covalent compounds, because chemical reactions to form covalent bonds can be controlled by selecting appropriate source volatile materials and deposition conditions [18,19]. Physical deposition techniques have been also reported for preparation of BN films: They include methods such as sputtering [20], ion beam-assisted deposition [21], and pulsed laser deposition [22]. Many researchers report formation of *c*-BN-like structure prepared by sputtering [20–26]. Formation of *h*-BN-like structure has been also reported by many authors but, there are only a few reports of the evidence for crystalline *h*-BN formation (i.e., X-ray diffraction). Noreika et al. [27] and Tanaka et al. [28] reported the formation of microcrystalline *h*-BN by reactive sputtering. X-ray diffraction of the samples in these studies were very broad due to the microcrystallinity and the cell parameters of *h*-BN were determined by electron diffraction.

Here we report formation of BN films having short range ordered structure of *h*-BN by reactive magnetron sputtering under nitrogen gas using elemental boron target. Contrary to the reports on the formation of microcrystalline *h*-BN by reactive sputtering mentioned above, in the present study, the crystal thickness calculated from X-ray peak linewidth (45 nm) was close to film

^{*} Corresponding author. Tel.: +81 82 424 7741; fax: +81 82 424 5494. *E-mail address:* inumaru@hiroshima-u.ac.jp (K. Inumaru).

^{0025-5408/\$ –} see front matter © 2011 Elsevier Ltd. All rights reserved. doi:10.1016/j.materresbull.2011.09.006



Fig. 1. Crystal structure of h-BN.

thickness (53 nm), revealing well developed stacking of the BN sheets along the direction perpendicular to the substrate surface. IR ATR spectroscopy, X-ray diffraction, X-ray photoelectron spectroscopy, and UV–Vis absorption spectroscopy were applied for the characterization of the films.

2. Experimental

2.1. Materials

Elemental B powder (purity 99%) was purchased from High Purity Chemical Co. (Tokyo) and was pressed into a disk to use as the target of sputtering. $-Al_2O_3$ (0 0 1), MgO (0 0 1) and Si (0 0 1) were used as substrates. The substrates were ultrasonically washed with anhydrous methanol in prior to use. N₂ gas (99.9999%) and Ar gas (99.9999%) were obtained from Nippon Sanso Co. Bulk *h*-BN (purity 99.5%) as a reference sample was obtained from Denki Kagaku Kogyo (Tokyo).

2.2. Synthesis of hexagonal boron nitride films on $\alpha\text{-Al}_2\text{O}_3$ and other substrates

The vacuum system (base pressure 5×10^{-8} Torr) was equipped with a magnetron sputtering gun (Model A315-ua, AJA international, MA, USA). The gun was operated in RF mode (13.56 MHz, 50 W). A mixed gas of Ar and N₂ was fed to the sputtering gun and 50 W of RF power was applied. The gas feeding rates, working pressure, and other conditions for samples prepared in this study were listed in Table 1. The typical synthetic conditions were as follows: Working pressure ~1 × 10⁻³ Torr, gas feeding rate, Ar 2 cm³ min⁻¹, N₂ 15 cm³ min⁻¹, deposition time ca. 9 h. The substrates were heated to 823 K during the deposition of all films. The film thicknesses were measured using an atomic force microscope (AFM, Nanoscope D-3100, Digital Instruments, USA)

 Table 1

 Deposition condition and properties of thin films synthesized in this study.

operated in tapping mode. The values for the films prepared under the conditions were ca. 50 nm. In order to determine the accurate film thickness of Film A, we analyzed boron in the film by using ¹¹B(p, α) ⁸Be nuclear reaction [29]. The acceleration energy was 650 keV per proton, and the accumulation was carried out up to 50 µC of the incident beam charge. The result was 1.45×10^{17} B atom cm⁻², which corresponds to a thickness of 53 nm.

2.3. X-ray diffraction analysis of the crystalline nitride phases

The crystal structure of the nitride phase formed on the substrates was characterized by X-ray diffraction with a D8 Advance diffractometer (Bruker AXS) using CuK α radiation. Another trial was carried out with an Xpert MRD diffractometer (Panalytical) to detect diffractions form crystal planes not parallel to the substrate surface.

2.4. Other characterizations

Infrared spectra were measured with an FT/IR-4200 spectrometer (JASCO, Tokyo). This spectrometer can record transmittance and attenuated total reflection (ATR, once-reflection, with a diamond prism) spectra. The UV–Vis transmittance spectra were recorded with Lambda-900 (PerkinElmer). The compositions of the thin films were determined by X-ray photoelectron spectroscopy (ESCA-3400, Kratos Analytical): B $1s_{1/2}$ and N $1s_{1/2}$ spectra were measured for the crystalline *h*-BN bulk sample, and the data was used to calibrate the relative sensitivity factors of the spectrometer for the B and N signals. The compositions of the thin films were calculated using the calibrated sensitivity factors.

3. Results

Table 1 lists the films prepared in this study. The table contains compositions (atomic ratio of N/B) of the samples analyzed by XPS. All films had N/B atomic ratio close to 0.8 or more, showing that the elemental boron reacts with the nitrogen introduced as N₂ gas during the reactive sputtering process to give highly nitrided compositions. As shown in Table 1, working pressure and gas feeding ratios were changed for α -Al₂O₃ (0 0 1) substrate. Working pressure was not influential to the compositions (compare films A and B). Film C had slightly higher N/B ratio compared to Film B. The nitrogen gas feeding rate seems to affect the composition. BN films were grown also on MgO (0 0 1) and Si (0 0 1) substrates (films D and E). These films had N/B ratios similar to those grown on α -Al₂O₃ (0 0 1).

Infrared spectra were taken by ATR method for the boron nitride thin films. The spectra were shown in Fig. 2. The ATR spectrum of bulk polycrystalline *h*-BN as a reference gave a broad peak centered at 1320 cm^{-1} . This signal was assigned to in-plane TO mode vibration in many reports [30–32]. Films A–D had intense

Film	Substrate	W.P. ^a (10 ⁻³ Torr)	Gas flow rate ^b		$t_{\rm d}^{\rm c}({\rm h})$	N/B ^d	B.G. ^e (eV)
			Ar	N ₂			
Α	α -Al ₂ O ₃ (001)	~1	2	15	9.3	0.83	5.9
В	$\alpha - Al_2O_3(001)$	5.2	2	15	8.5	0.79	5.9
С	$\alpha - Al_2O_3(001)$	7.4	5	20	3	0.88	5.9
D	MgO (001)	~1	2	15	9	0.83	6.0
E	Si (001)	~ 1	2	15	9	0.85	-

^a Working pressure.

^b In cm³ (STP) min⁻¹.

^c Deposition time.

^d Atomic ratio determined by XPS.

e Optical band gap.



Fig. 2. Infrared ATR spectra of thin films and bulk h-BN sample.

signal at 1374 cm⁻¹, which had a frequency slightly higher than the TO mode of bulk *h*-BN but coincided with the peak positions of BN thin films reported in the literature [18,21], and the signal was also assigned to the in-plane TO mode. The TO mode signal demonstrates that BN in the films have short-range order of *h*-BN structure, i.e., hexagonal BN sheets shown in Fig. 1. Besides the TO mode absorption, all films prepared in this study gave a signal at a higher frequency around 1540 cm⁻¹. Fig. 3 compares transmission and ATR spectra of the BN film grown on a Si substrate (Film E). In the ATR spectrum (the bottom panel) an intense structure appeared at 1537 cm⁻¹ besides signals due to silicon substrates. On the other hand, in the transmission spectra the structure was not observed. This indicates that the structure in the ATR spectrum is assignable to LO mode, which is detectable at 1510 cm^{-1} in reflection spectra of bulk h-BN [18,30] but is inactive in transmission absorption spectra. It was reported that ATR spectrum is sensible to LO mode signals [33]. Thus, we assigned the signal around 1540 cm^{-1} appeared in ATR spectra to LO mode of *h*-BN.

Fig. 4 shows XPS spectra of thin films prepared in this study and bulk *h*-BN. Table 2 summarizes peak positions and peak widths of the XPS spectra. The peak positions of B $1s_{1/2}$ and N $1s_{1/2}$ for the thin films were identical to that of bulk *h*-BN, and obvious oxidation of boron cannot be measured by XPS. Peak widths of the signals are comparable or slightly wider, probably due to lower crystallinity of *h*-BN in the film compared to that of bulk *h*-BN.



Fig. 3. Infrared spectra of BN/Si (Film E) and Si substrate.

In order to investigate crystallinity of the films, X-ray diffraction measurements were carried out. Fig. 5 focuses on *h*-BN 002 region of X-ray diffraction patterns of the films and bulk *h*-BN. The bulk *h*-BN gave an intense 0 0 2 peak. In the films prepared in this study, Film A showed a diffraction peak and its position was $2\theta = 26.64^{\circ}$ (d = 0.337 nm), of which d value is close to but slightly larger than that of bulk *h*-BN ($2\theta = 26.78^{\circ}$, d = 0.333 nm). This indicates that crystalline BN is formed in Film A. The size of the crystal was estimated to be 48 nm from the FWHM of the diffraction peak. That is close to the film thickness (53 nm). This point will be discussed later. We could not detect other diffraction peaks from crystal planes not parallel to the substrate surface. No diffraction peak of crystalline BN was observed for the other films. It should be noted here that Film A was prepared at the lowest working pressure among the films prepared in this study.

Fig. 6 shows Tauc plots of Film A. The ordinate of the left panel is $(\alpha h v)^{0.5}$, and that of the right panel expresses $(\alpha h v)^2$. The linearity of the plots was higher for the right panel than for the left panel, and this suggest that the BN film had a direct band gap rather than an indirect one. The band gap was estimated to be 5.9 eV from the plots in the right panel. The energy gaps determined from Tauc plots were also listed in Table 1. Single crystal of *h*-BN has been reported to have direct band gap of 5.8 eV [34]. The optical band gap of the films prepared in this study was close to the value reported for single crystal *h*-BN.



Fig. 4. X-ray photoelectron spectra for thin films and bulk *h*-BN sample.



Fig. 5. X-ray diffraction patterns of thin films and bulk *h*-BN sample.

4. Discussion

X-ray diffraction revealed that BN in Film A is crystalline and a peak corresponding to 0 0 2 diffraction of *h*-BN was observed. The crystal thickness from X-ray diffraction peak width was close to the film thickness. This indicates the stacking of the BN sheets continues through almost the whole thickness of the film. In the crystal structure of *h*-BN, the layers stacks so that the atoms align linearly perpendicular to the BN sheets (i.e., parallel to the c axis) like $B \cdots N \cdots B \cdots N$ and the layers interact with adjacent ones through the $B \cdots N$ bonds (Fig. 1). The inter-plane distance for Film A was slightly larger than that of the (002) planes of bulk *h*-BN. Disorders in the stacking of the BN sheets like turbostratic structure may weaken the interaction between them and bring about the slight increase in the inter-layer distance. Formation of turbostratic BN has been reported at the interfaces between substrate surface and cubic BN. In this case, the layer of turbostratic BN grew perpendicular to the substrate surface [35]. In the present study, it is notable that the BN sheets were parallel to the substrate surface and stacked in a long distance along the direction perpendicular to the substrate surface. A possibility is that the hexagonal symmetry of α -Al₂O₃ (001) substrate surface may enhanced the growth of the first BN sheet along the substrate surface. The result that only Film A crystallized may be associated with the working pressure: Film A was

 Table 2

 Data derived from XPS spectra.

Film or sample	Binding energy (eV)		FWHM (eV)	
	B 1s _{1/2}	N 1s _{1/2}	B 1s _{1/2}	N 1s _{1/2}
А	190.4	398.2	2.4	2.0
В	190.5	398.3	2.6	2.1
С	190.3	398.0	2.4	2.0
D	190.7	398.4	2.4	2.0
E	190.2	397.9	2.4	2.0
Bulk <i>h</i> -BN	190.5	398.1	2.1	2.0
$B_2O_3^a$	193.0			

^a Ref. [36].

deposited at the lowest working pressure among the films. A possibility is that deposition at a high working pressure decreases the film crystallinity by the impacts of argon ions onto the surface of the films during the deposition. On the other hand, TO mode absorption observed in IR spectra revealed that all films in this study had short range ordered structure of h-BN. Being consistent with this, the films had an optical band gaps close to that of bulk h-BN. It was easily demonstrated by theoretical calculations that the energy gaps are governed by the structure in the *h*-BN sheets and are little influenced by the stacking way of the sheets. By using a first principle band calculation program (DMol³ solid, Accelrys) we calculated and compared energy gaps of *h*-BN and of a hypothetical structure in which inter-layer distance of *h*-BN was expanded by a factor of 10. The energy gaps of the two structures were very close (not shown). These are consistent with the fact that similar optical band gap was observed for all films, which include crystallized and non-crystallized ones, since all of them had short range ordered structure of *h*-BN indicated by the in-plane TO signals.

5. Conclusions

It was demonstrated that reactive RF magnetron sputtering using an elemental boron target could grow BN films on α -Al₂O₃ (001). X-ray diffraction, IR, and XPS of the film showed the stacking structure of the *h*-BN sheets in a long distance, the short range ordered structure of the *h*-BN sheets, and the nitrogen-well incorporated composition, respectively. The control of the working pressure was crucial to obtain crystallized films. The results of the present study highlight that reactive sputtering is versatile also for



Fig. 6. Tauc plot of BN/α -Al₂O₃ (0 0 1) (Film A).

forming crystalline films of covalent nitride such as hexagonal boron nitrides.

Acknowledgments

This work was partially supported by a Grant-in-Aid on Priority Areas (Nos. 436 and 472) from the Japan Ministry of Education, Culture, Sports, Science and Technology (MEXT), and by a Grant-in-Aid for Scientific Research (S) (No. 19105006) and (B) (No. 20350095), and a Funding Program for World-Leading Innovative R&D on Science and Technology (FIRST) Program from the Japan Society for the Promotion of Science (JSPS).

References

- [1] A. Simon, Angew. Chem. Int. Ed. Eng. 36 (1997) 1789.
- [2] R. Niewa, F.J. DiSalvo, Chem. Mater. 10 (1998) 733-2752.
- [3] D.H. Gregory, Coord. Chem. Rev. 215 (2001) 301-345.
- [4] E. Horvath-Bordon, R. Riedel, R. Zerr, P.F. McMillan, G. Auffermann, Y. Prots, W. Bronger, R. Kniep, P. Kroll, Chem. Soc. Rev. 35 (2006) 987–1014.
- [5] R. Juza, Adv. Inorg. Chem. Radiochem. 9 (1996) 81-131.
- [6] J.L. Hunting, M.M. Szymanski, P.E. Johnson, C.B. Kellar, F.J. DiSalvo, J. Solid State Chem. 180 (2007) 31–40.
- [7] K. Suzuki, T. Suzuki, Y. Fujiwara, T. Kaneko, H. Yoshida, Y. Obi, S. Tomiyoshi, J. Alloys Compd. 360 (2003) 34.
- [8] H.Q. Yang, H. Al-Brithen, A.R. Smith, J.A. Borchers, R.L. Cappelletti, M.D. Vaudin, Appl. Phys. Lett. 78 (2001) 3860.
- [9] L.M. Corliss, N. Elliot, J.M. Hastings, Phys. Rev. 117 (1960) 929.
- [10] X.Y. Zhang, J.S. Chawla, B.M. Hawe, D. Gall, Phys. Rev. B 83 (2011), 165205-1– 165205-10.
- [11] K. Inumaru, K. Koyama, N. Imo-oka, S. Yamanaka, Phys. Rev. B 75 (2007), 054416-1–054416-5.
- [12] T. Hinomura, S. Nasu, Physica B 237-238 (1997) 557.
- [13] K. Suzuki, T. Kaneko, H. Yoshida, H. Morita, F. Fujimori, J. Alloys Compd. 224 (1995) 232.

- [14] K. Inumaru, K. Koyama, Y. Miyaki, K. Tanaka, S. Yamanaka, Appl. Phys. Lett. 91 (2007) 152501-1-152501-3.
- [15] H.F. George, H.K. John, Phys. Rev. 93 (1954) 1004.
- [16] O.N. Pierson, Handbook of Refractory Carbides and Nitrides. Properties, Characteristics, Processing and Applications, Noyes Publications, New Jersey, 1996.
- [17] T. Taguchi, K. Watanabe, J. Cryst. Growth 303 (2007) 525-529.
- [18] M.C. Polo, M. Ben el Mekki, J.L. Andújar, N. Mestres, J. Pscual, Diamond Relat. Mater. 6 (1997) 1550–1554.
- [19] M. Ben el Mekki, N. Mestres, J. Pascual, M.C. Polo, J.L. Andújar, Diamond Relat. Mater. 8 (1999) 398-401.
- [20] K. Kojima, K. Nose, M. Kambara, T. Yoshida, J. Phys. D: Appl. Phys. 42 (2009) 055304-1-055304-5.
- [21] M. Ben el Mekki, M.A. Djouadi, E. Guiot, V. Mortet, J. Pascallon, V. Stambouli, D. Bouchier, N. Mestres, G. Nouet, Surface Coat. Technol. 116–119 (1999) 93–99.
- [22] B. Mitu, P. Bilkova, V. Marotta, S. Orlando, A. Santagata, Appl. Surf. Sci. 247 (2005) 123–127.
- [23] D. Schild, S. Ulrich, J. Ye, M. Stüber, Solid State Sci. 12 (2010) 1903-1906.
- [24] S. Ulrich, J. Ye, M. Stüber, Surf. Coat. Technol. 205 (2010) S96-S98.
- [25] T. Ohori, H. Asami, J. Shirahata, T. Suzuki, T. Nakayama, H. Suematsu, K. Niihara, J. Ceram. Soc. Jpn. 118 (2009) 164–166.
- [26] T. Ohori, H. Asami, J. Shirahata, T. Suzuki, T. Nakayama, H. Suematsu, K. Niihara, J. Ceram. Process. 10 (2009) S14–S18.
- [27] A.J. Noreika, M.H. Francombe, J. Vac. Sci. Technol. 6 (1969) 722-726.
- [28] K. Tanaka, Y. Uemura, M. Iwata, Oyobutsuri 46 (1977) 120-127.
- [29] J.R. Bird, J.S. Williams (Eds.), Ion Beam for Materials Analysis, Academic Press, New South Wales, Australia, 1989, pp. 149–207.
- [30] R. Geick, H. Perry, G. Pupprecht, Phys. Rev. 146 (1966) 543-547.
- [31] E. Borowiak-Palen, T. Pichler, G.G. Fuentes, B. Bendjemil, X. Liu, A. Graff, G. Behr, R.J. Kalenczuk, M. Knupfer, J. Fink, Chem. Commun. (2003) 82–83.
- [32] D.M. Hoffman, G.L. Doll, P.C. Eklund, Phys. Rev. B 30 (1984) 6051-6056.
- [33] N. Kuroda, Y. lida, T. Shigeta, Hasanudin, J. Watanabe, Jpn. J. Appl. Phys. 42 (2003) L1241-L1243.
- [34] K. Watanabe, T. Taguchi, H. Kanda, Nat. Mater. 3 (2004) 404–409.
 [35] M.P. Johansson, L. Hultman, S. Daaud, K. Bewilogua, H. Luthje, A. Schutze, S.
- Kouptsidis, G.S.A.M. Theunissen, Thin Solid Films 287 (1996) 193–201. [36] D. Briggs, M.P. Seah (Eds.), 2nd ed., Practical Surface Analysis, vol. 1, Wiley, 1990,
- p. 599.