

Investigation of wurtzite (B,Al)N films prepared on polycrystalline diamond

J.H. Song^a, J.L. Huang^{a,*}, H.H. Lu^b, J.C. Sung^c

^a Department of Materials Science and Engineering, National Cheng-Kung University, Tainan 701, Taiwan

^b Department of Mechanical Engineering, National Chin-Yi Institute of Technology, Taichung 411, Taiwan

^c Kinik Company, and National Taipei University of Technology, Taipei, Taiwan

Available online 1 August 2007

Abstract

The growth of epitaxial GaN on polycrystalline diamond using highly *c*-axis orientated AlN as a buffer layer is an attractive application for heat dissipation of LED devices. In this study, the (B,Al)N layer was used to bridge the gap of lattice mismatch between diamond and AlN. For the preparation of (B,Al)N films on a diamond substrate, an aluminum target was sputtered in DC mode and hBN in RF mode simultaneously in a pure nitrogen plasma. The results showed boron content in (B,Al)N film which were determined by X-ray photoelectron spectroscopy (XPS) increased with increase of RF sputtering power. The lattice constant of (B,Al)N films were smaller than pure AlN, suggesting the substitution of smaller boron atoms at Al positions. As the boron content increased, the crystallinity of (B,Al)N films decreased. The crystal qualities of AlN films was analyzed by rocking curve, and AlN was deposited on low boron content (B,Al)N layer with higher *c*-axis preferential orientation than if it had been grown on diamond directly.

© 2007 Elsevier B.V. All rights reserved.

Keywords: BN; AlN; (B,Al)N; Polycrystalline diamond; Wurtzite type structure

1. Introduction

Nitride semiconductors, such as GaN, are the mainstream of today's LED devices. A typical nitride semiconductor is deposited on a sapphire substrate that has a poor thermal conductivity (about 25 W/mK). With the trend of increasing power (e.g. >5 W) for LEDs, high temperatures tend to dim the light output and reduce its life expectancy. If the semiconductor can be deposited on a CVD diamond film with its extremely high thermal conductivity (>1000 W/mK), the performance of the LED may be improved substantially [1,2]. However, the GaN lattice is too open for epitaxial alignment of atoms on the tight structure of diamond. In order to make the polycrystalline diamond suitable for growth of an epitaxial layer, a buffer layer should be used to convert the random orientation of the diamond grains into a preferred orientation for epitaxial growth of GaN.

An ideal buffer layer will have similar crystal structure and similar atomic size with the joining layer. Generally, GaN growth on a sapphire substrate includes an AlN buffer layer,

which is well aligned to the *c*-axis by adjusting process parameters [3–5]. In case of GaN growth on polycrystalline diamond, a *c*-axis AlN layer was also used as a buffer layer because of the lower mismatch with GaN layers. Recent research of AlN films mainly focuses on precise control of the (002) *c*-axis textures which are perpendicular to the substrate by process parameters such as distance between substrate and target, N₂ gas ratio and deposited power [6,7]. However, there is large atomic size difference between the aluminum atoms of the AlN buffer layer and the carbon atoms of a diamond substrate. The difference of atomic size will cause defects (dislocations) and the decrement of *c*-axis preferential orientation for AlN layers. A buffer layer of wurtzite AlN may be deposited on polished diamond films by doping with small boron atoms. Boron nitride (BN) can take two phases of a low pressure phase (h-BN) and a high pressure phase (w-BN, c-BN) according to the conditions of synthesis [8]. Wurtzitic AlN and w-BN are identical in crystal structure so the bonding between them is almost seamless. The atomic size of boron is between carbon and aluminum so that it can serve to adjust the variation of interface atomic size effectively. Noreika and Fancombe [9] produced single-phase B–Al–N thin films by reactive sputtering and suggested boron substitution on aluminum sites or by

* Corresponding author.

E-mail address: jlh888@mail.ncku.edu.tw (J.L. Huang).

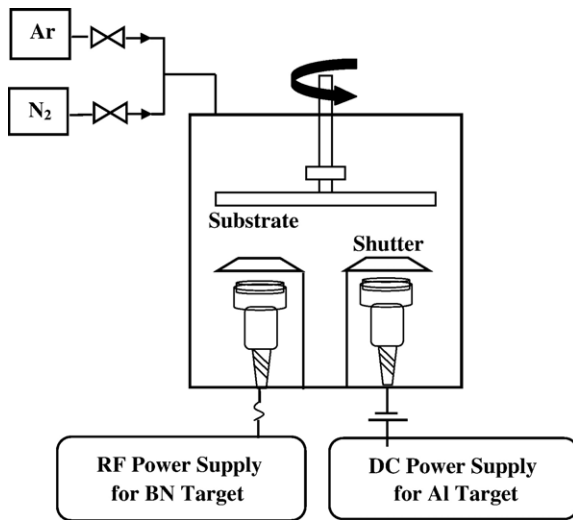


Fig. 1. Magnetron co-sputtering system.

the formation of Al–B compounds. The same results are also reported by Edgar [10]. Therefore the (Al,B)N mixed crystals can substantially reduce the lattice constant with a high degree of preferred orientation along $\langle 002 \rangle$. Such a lattice can pave the way for the growth of GaN single crystal for making LED devices. In this case, the LED will contain a built-in heat spreader for high power applications, such as for high brightness back lighting as required for illuminating LCD TV screens.

In this study, an aluminum target was sputtered by DC and a boron target, by RF in vacuum with nitrogen intake. We used boron to displace aluminum sites of the AlN buffer layer to form a (B,Al)N film as a new interface between diamond and AlN. The properties of (B,Al)N film on diamond were discussed and the crystal qualities of AlN films was also analyzed.

2. Experimental

The (B,Al)N films were deposited on diamond wafer substrates with 36 rpm spin rate by magnetron co-sputtering system as shown in Fig. 1. The right target in Fig. 1 is pure aluminum in DC mode and the left one is pure hBN in RF mode. The (B,Al)N films were deposited at 200 °C using Ar and N₂ mixture gases under fixed DC power and various RF power. Diamond wafer substrates were diamond films (thickness was about 20 μm) grown on a silicon wafer by hot filament CVD method and then polished surface to less than 1 nm in roughness. The details of the deposition process were summarized and listed in Table 1.

Table 1
(B,Al)N film deposition sputtering conditions

Target in DC mode	Al 99.999% pure
Target in RF mode	hBN 99.9% pure
DC power	300 W
RF power	0 to 200 W
Substrate temperature	200 °C
Gas pressure	0.4 Pa
Gas composition	N ₂ /Ar: 2/1
Substrate spin rate	36 rpm

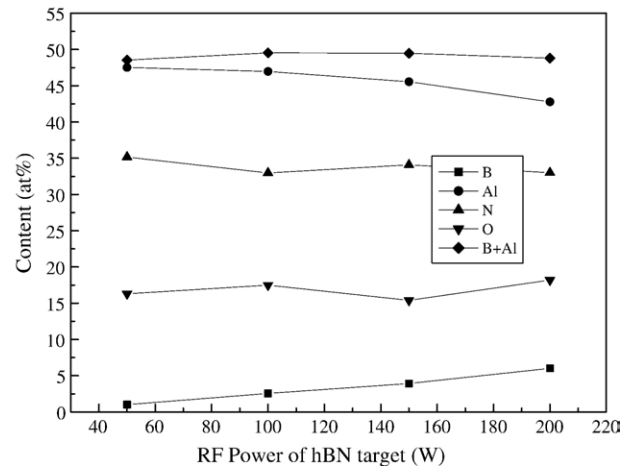


Fig. 2. XPS analysis for Al, B, O, and N concentrations in (B, Al)N films.

The composition of films was analyzed by secondary ion mass spectrometer (SIMS) and X-ray photoelectron spectroscopy (XPS). The thickness and growth rate of the deposited films was determined by α -step. Scanning electron microscopy (SEM) and X-ray diffractometry were used to characterize microstructure of (B,Al)N films.

3. Results and discussion

3.1. Composition of (B,Al)N films

Trends of B and Al content with RF power levels applied to the hBN target in (B,Al)N films (thickness were 0.5 μm) were determined by SIMS analysis. In this co-sputtering system the substrates were rotated at 36 rpm. Consequently, the depth profile of B and Al in (B,Al)N films revealed a uniform film composition. With increasing RF power, the B content increased and the Al content decreased. Under the same gas atmosphere, an increase of RF power will decrease the sputtering efficiency of DC power. Changing RF power resulted in the variation of both B and Al content in the (B, Al)N films.

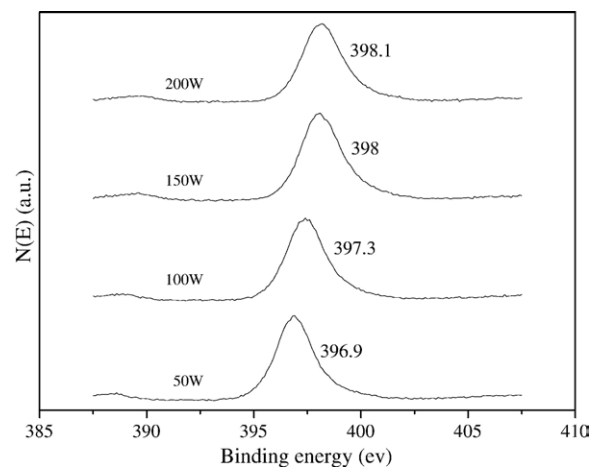


Fig. 3. The N 1s peaks of (B, Al)N films were with various RF power (B content).

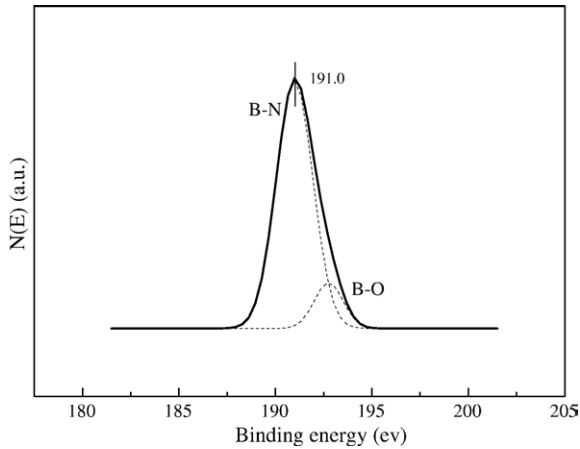


Fig. 4. The B 1s peak of (B, Al)N film Was with 6 at.% B content.

The Al, B, N and O concentrations in (B, Al)N films were also determined by XPS and the results are presented in Fig. 2. In order to obtain the practical values of the (B, Al)N films composition, AlN and BN as standard stoichiometric samples were used. However, the value had about 1% error. The nitrogen content and the oxidation status at the surface of the film are shown in Fig. 2. Surface oxidation could not be avoided and this situation caused the surface nitrogen content to vary far away from 50 at.% (stoichiometric (B, Al)N). Fig. 2 also showed that the relative concentration of B and Al content was in accordance with the result of SIMS analysis. The range of B content was from 1 at.% to 6 at.% when RF power controlled from 50 W to 200 W in Fig. 2. It also showed that the sum of B and Al amount was almost the same and the value maintained 50 at.%. Edgar et al. suggested that the single-phase AlN–w-BN alloy was formed at low BN content (lower than 10 at.%), but that phase separation occurs for higher BN content [10]. Therefore this phenomenon might explain B atom substitution for Al positions in AlN films to form a single phase.

3.2. The composition of the films

The results of XPS could describe the composition of (B, Al)N films. Fig. 3 shows the N 1s peaks of (B, Al)N films with various RF power (B content). In previous studies, the peak position of the N 1s peak in AlN and BN were in the range of 396.4–396.8 eV and 398.0–399.0 eV [11–13]. In Fig. 3 the N 1s peak position of the low B content film was in a good agreement with the N 1s peak in AlN, and a continuous shift of these N 1s peaks with increasing B content could be observed. In the case of the ternary films, no two-peak structure of the N 1s was detectable, as could be expected with a two-phase mixture of AlN and BN, but rather a continuous shift with increasing B content, which is an indication of single-phase ternary film [14]. Fig. 4 showed the B 1s peak of (B, Al)N film with 6 at.% B content. The peak position was higher than the 190.0–191.0 eV values of Refs. [15,16]. By the way of peak assay, there were only B–N and B–O bonds, the bonds of B–B and B–Al were not observed.

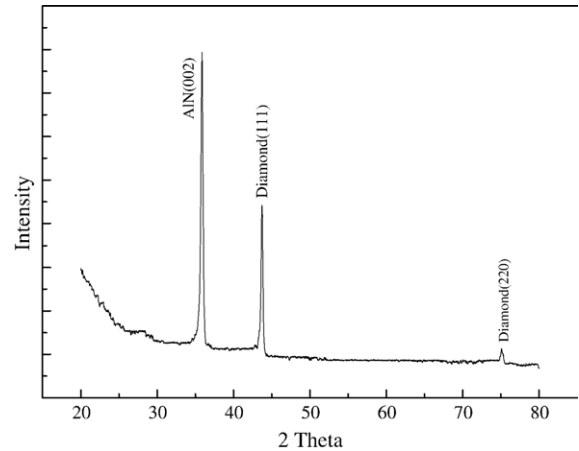


Fig. 5. A θ – 2θ X-ray diffraction pattern of pure AlN deposited on diamond substrate.

3.3. Deposition rate of the films

The net deposition rate depends on the different sputtering rates of Al (DC) and BN (RF). However, in this case, B content in (B, Al)N films which were evaluated from the analysis of composition was low. Changing the RF power did not affect the deposition rate. The thickness of (B,Al)N films were determined by the deposition rate and the time.

3.4. Microstructure of the films

Fig. 5 showed a θ – 2θ X-ray diffraction pattern of pure AlN deposited on diamond substrate. Only (002) diffraction peak was presented in the pattern which means the films were highly aligned with the *c*-axis perpendicular to the substrate. All of various B content in (B,Al)N films had the same result. With the addition of B to AlN to form (B,Al)N films, no X-ray diffraction peaks of BN were observed and the structure of AlN kept the preferred *c*-axis orientated state. This result was due to either amorphous or very small size grains of BN. The BN plan-view

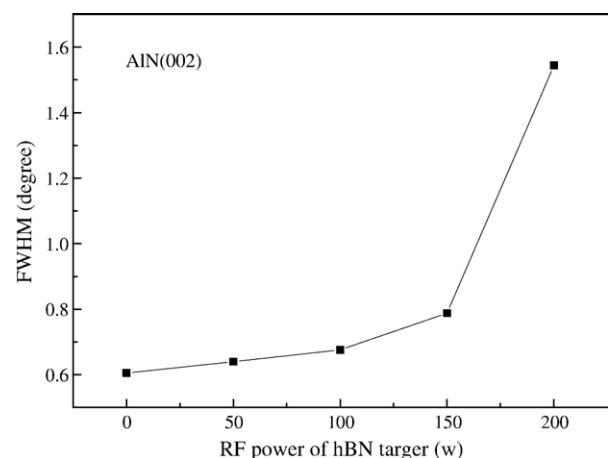


Fig. 6. FWHM of rocking curve analysis of the films with various RF power of hBN target at (002) reflection.

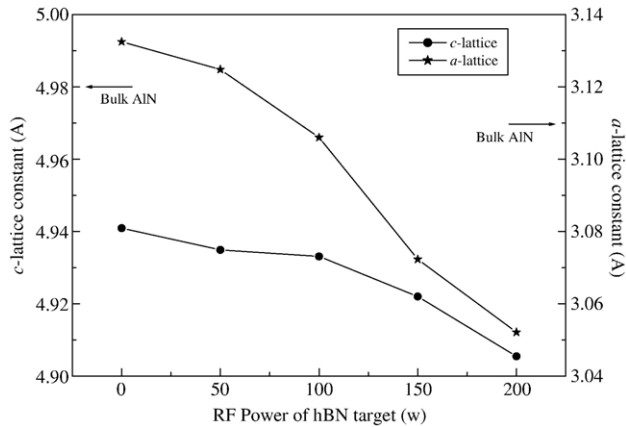


Fig. 7. Variation of c - and a -lattice constant of deposited film with different RF power of hBN target.

transmission electron microscopy (TEM) in Edgar's study revealed that the film was polycrystalline, but composed of very fine grains. Therefore the BN with very small size grains in AlN be the reason for XRD results.

However, there are two noticeable effects in the X-ray diffraction pattern of the films. The broadening of peak width and a shift in the peak positions to greater angles follow the addition of B to AlN. The peak broadening was probably due to greater structure disorder (less texturing degrees) in the film compared with pure AlN. The peak shift may be due to the substitution of smaller B atoms at Al positions.

The texturing degrees were deduced by the value of FWHM or intensity of rocking curve. The full width at half maximum (FWHM) of rocking curve analysis of the films with various RF power at (002) reflection were shown in Fig. 6. In Fig. 6, the FWHM of rocking curve of (B,Al)N films increased with RF power (B content) increasing and relative to pure AlN. The change of FWHM revealed that the different lattice constants between BN (w -BN, $c=4.213$ Å) and AlN ($c=4.98$ Å) exists in (B,Al)N films and the influence of structure disorder is greater as B content is increased. Fig. 7 showed the c -lattice and a -lattice constant change of deposited films decreasing with increasing RF power (B content). And there was a large difference of lattice constant of pure bulk AlN and the measured value in Fig. 7 (0 W). The c -lattice constant of pure AlN film was lower than bulk one. On the contrary, the a -lattice constant of pure AlN film was higher than bulk one. That showed the film existed a compressive residual stress in c -axis and a tensile residual stress in a -axis induced by the sputtering process. Film stress can cause the shift of lattice constant, and B substitution at Al lattice site in a single phase wurtzite (B,Al)N films was also suggested.

3.5. A (B,Al)N film as a inter layer between diamond and AlN

The crystal structure of (B,Al)N film with 1% B content is the closest to pure AlN and in our opinion, B atoms can adjust the variation of AlN/diamond interface atomic size to enhance the crystal qualities of c -axis AlN films. Fig. 8 showed the SEM

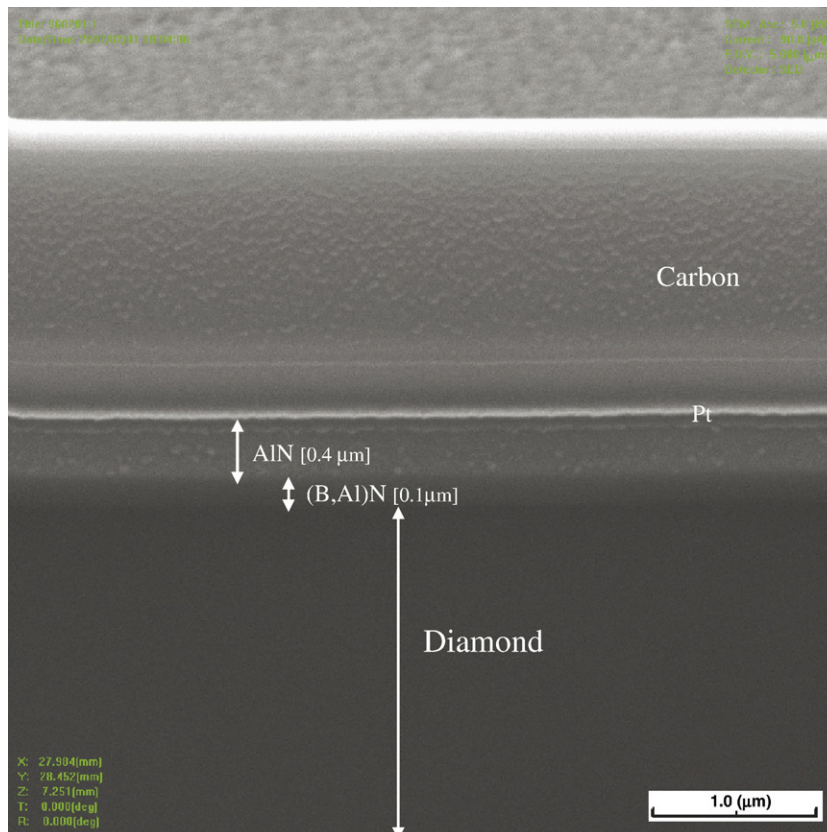


Fig. 8. SEM cross-section of deposited AlN/(B,Al)N film on diamond.

cross-section of deposited AlN/(B,Al)N film on diamond. (B, Al)N film was deposited until the thickness reach 0.1 μm , then turned off RF power (BN target) immediately, and still continued depositing AlN to form AlN (0.4 μm)/(B,Al)N (0.1 μm) structure on diamond. The diamond surface roughness was quite low in our case. The interface atomic size difference became very important. The rocking curve analysis of AlN (002) with or without the (B,Al)N interlayer indicated a FWHM of $\sim 0.6^\circ$ which was the same as pure AlN (0.5). The AlN (0.4 μm)/(B,Al)N (0.1 μm) structure had higher intensity B atoms do appear to improve the variation of AlN/diamond interface atomic size successfully, and AlN was deposited on low boron content (B,Al)N layer with higher *c*-axis preferential orientation than if it had been grown on diamond directly.

4. Conclusions

The (B,Al)N films were deposited on diamond by co-sputtering system. Changing the RF power (from 50 W to 200 W) resulted in the variation of B content (from 1 at.% to 6 at.%) in the (B, Al)N films, and the B content increased as the Al content decreased. The sum of B and Al content was almost the same and the value remained constant at 50 at.%. When the (B,Al)N films formed, either films stress or formation of single phase wurtzite (B,Al)N films makes the changed the *c*-lattice constant. The decrement of (B,Al)N films rocking curve FWHM revealed that influence of structure disorder was lower at low B content (B,Al)N films. If the (B,Al)N films act as interlayer between AlN and diamond, then it can lower the interface atomic size difference to enhance the crystal qualities of *c*-AlN films further.

Acknowledgement

This paper was supported by the National Science Council of Taiwan (project number: NSC-95-2623-7-006-008-D).

References

- [1] M. Oba, T. Sugino, *Diamond Relat. Mater.* 10 (2001) 1343.
- [2] P.R. Hageman, J.J. Schermer, P.K. Larsen, *Thin Solid Films* 443 (2003) 9.
- [3] H. Lahreche, P. Vennegues, O. Tottereau, M. Laugt, P. Lorenzini, M. Leroux, B. Beaumont, P. Gibart, *J. Cryst. Growth* 217 (2000) 13.
- [4] K. Hiramatsu, T. Detchprohm, H. Amano, I. Akasaki, *Adv. Crystal Growth Mechanisms* (1997) 399.
- [5] J.C. Zhang, D.G. Zhao, J.F. Wang, Y.T. Wang, J. Chen, J.P. Liu, H. Yang, *J. Cryst. Growth* 268 (2004) 24.
- [6] W.J. Liu, S.J. Wu, C.M. Chen, Y.C. Lai, C.H. Chuang, *J. Cryst. Growth* 276 (2005) 525.
- [7] J.X. Zhang, H. Cheng, Y.Z. Chen, A. Uddin, Shu Yuan, S.J. Geng, S. Zhang, *Surf. Coat. Technol.* 198 (2005) 68.
- [8] P.B. Mirkarimi, K.F. McMarty, D.L. Medlin, *Mater. Sci. Eng. R21* (1997) 47.
- [9] A.J. Noreike, M.H. Fancome, *J. Vac. Sci. Technol.* 6 (1967) 722.
- [10] J.H. Edgar, D.T. Smith, C.R. Eddy Jr., C.A. Carosella, B.D. Sartwell, *Thin Solid Films* 298 (1997) 33.
- [11] J.A. Kovacich, J. Kasperkiewicz, D. Lichtman, C.R. Aita, *J. Appl. Phys.* 55 (1984) 2935.
- [12] J. Chastain, *Handbook of X-ray Photoelectron Spectroscopy*.
- [13] G.M. Ingo, G. Padeletti, *Thin Solid Films* 228 (1993) 276.
- [14] M. Witthaut, R. Cremer, D. Neuschütz, *Surf. Interface Anal.* 30 (2000) 580.
- [15] D.N. Hendrickson, J.M. Hollsnder, W.L. Jolly, *Inorg. Chem.* 9 (1970) 612.
- [16] S. Kohiki, T. Ohmura, K. Kusao, *J. Electron Spectrosc. Relat. Phenom.* 31 (1983) 85.