BN protective coating for high temperature applications


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ABSTRACT

We report on the fabrication, characterization, and processing of boron nitride films for use in high temperature applications such as field passivation, capping layers for thermal annealing of SiC, and protecting metallic filaments from their working environments. The BN films have been fabricated by pulsed laser deposition and spray techniques. The deposited films were characterized by X-ray Diffraction, Fourier Transform Infrared Spectroscopy, Ultraviolet-Visible Spectroscopy, Rutherford Backscattering Spectrometry and Transmission Electron Microscopy. The BN films deposited in the temperature range of 200-500°C have been found to be poorly crystalline, whereas the films fabricated above 600°C have been found to be microcrystalline. The as-deposited films were annealed at various temperatures ranging from 900°C to 1700°C in order to densify the films and study the applicability of the coatings. An AlN buffer layer was also applied in a few cases to improve chemical bonding with the substrate. Adhesion of the films with the heater components was greatly improved for high temperature annealed samples due to good interfacial bonding with the substrate material. Our results on the properties of BN films with an emphasis on characterization, processing, and implications for high temperature applications are discussed.

INTRODUCTION

Protective coatings of ceramic materials are of great interest for high temperature applications. In particular, these coatings are required for the protection of electronic components, high temperature filaments, and parts that are constantly exposed to various atmospheres at high temperatures [1]. For example, Silicon Carbide (SiC) is the most promising wide band gap semiconductor material for high temperature, high power, and high speed electronic devices, which need high temperature annealing treatment at up to 1800°C to remove the ion-implantation induced damage and to electrically activate the dopants [2,3]. The high temperature coatings or passivation layers are required on SiC to prevent surface roughening and changes in the surface composition due to the preferential evaporation of silicon at elevated temperatures during annealing. Another example is the metallic elements that are used in high temperature wafer heaters or furnaces, which are exposed to various atmospheres at high temperatures. The metallic elements can be coated with high temperature stable materials such as BN, Al₂O₃, or MgO. Boron nitride and aluminum nitride thin films and coatings are ideal material candidates in reducing the effects of atmosphere and high temperature due to their structural and chemical stability at temperatures >1400°C [4-6]. Though the properties of BN and AlN are compatible to high temperature applications, a fundamental understanding of the factors that govern the performance of the protective coatings is needed to provide a sound basis for the development of advanced products. In this paper we report on the fabrication, characterization, and processing of BN and BN/AlN dual layer films deposited on SiC, Si, and metallic elements.
EXPERIMENTAL

Our major goal is to fabricate protective coatings of BN and related materials on SiC, metallic filaments and components that are exposed to high temperatures and reactive gases. To investigate the coating materials and optimize the processing parameters we have employed pulsed laser deposition and spray coating techniques. The BN, AlN, and BN/AlN thin films were grown on various substrates such as Si, SiC, sapphire, and components of high temperature wafer heaters. Three-dimensional objects were coated with BN by spray technique. Dual layer BN/AlN films were also fabricated on SiC to improve the high temperature stability and adhesion of the protective layer. The advantage of the dual layer structure is that the AlN can be removed after high temperature annealing by wet etching without harming the SiC surface. In PLD, the film deposition was performed in a chamber evacuated by a turbomolecular pump to a base pressure less than 10^-5 Pa. A KrF excimer laser (\(\lambda=248\) nm, \(\tau=25\) ns) was used for ablation of a pyrolytic h-BN target. The laser beam was focused on the BN target at an incident angle of 45° to the normal of the target surface, with a fluence of about 2 J/cm^2 on the target. The substrate was placed parallel to the target with a suitable distance. The deposition was carried out at different substrate temperatures ranging from room temperature to 1100°C in N₂ or NH₃ ambient. The N₂ or NH₃ background gas pressure was varied from 10^-4 to 10^1 Pa. The deposition rate and the film thickness were controlled by the pulse repetition rate and total deposition time. After deposition, the deposited films were slowly cooled down to room temperature and then taken out for characterization. However, PLD is a tool for prototyping; better methods exist for depositing films on complex 3-dimensional surfaces and large areas (greater than 2^2). We chose to implement spray technique to test the application of our coatings. Large Si wafers, stainless steel sheets, and components of heater elements were deposited by spray technique at room temperature. The as deposited films were annealed at various temperatures ranging from 500°C to 1700°C. The surface morphology and microstructure of the BN thin films were investigated by scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM). The quantitative analysis of the crystalline quality, composition and interface structure of the films was determined by Rutherford backscattering spectroscopy (RBS) and ion channeling techniques. Crystalline quality and lattice constant of the BN films were measured by X-ray diffraction (XRD). The optical properties were studied by UV-Visible and Fourier Transform Infra-Red (FTIR) spectroscopy.

RESULTS AND DISCUSSION

Optimization of the protective coatings on various substrate materials is crucial for developing useful coatings that will have desirable characteristics compatible to high temperature applications. In this regard, pulsed laser deposition technique is suitable for the investigation of thin films on a variety of materials [7]. It is the fastest tool for prototyping thin films of ceramic materials. Using this technique we have investigated BN films and BN/AlN dual layer structures. Hexagonal BN films were deposited on Si substrates (for IR studies) at various deposition temperatures from room temperature to 1000°C and various partial pressures of NH₃ or N₂ gases. The films deposited at lower temperatures (below 600°C) have poor adhesion to the substrates. As the deposition temperature increased, the bonding of the film at the interface improved.

FTIR spectroscopy was used to characterize distinct phases of BN such as hexagonal born nitride (h-BN), rhombohedral (r-BN), cubic zinc-blende (c-BN), and wurtzite-type (w-BN) [8]. As far as structures and bonding are concerned, the h-BN and c-BN are analogous to those of
graphite and diamond, respectively. The c-BN is sp³-bonded, and has hardness and thermal conductivity greater than all known materials except for diamond. The h-BN is a layered graphite-like structure with two-dimensional sp²-bonded six membered rings of alternating boron and nitrogen atoms stacked in an ABAB pattern and is stable up to temperatures of about 3000°C. Fig. 1(a) shows the FTIR spectra of the BN films deposited on Si at various temperatures and various ambient gas pressures. Two characteristic peaks for h-BN (sp² bonded) are clearly observed, one at 800 cm⁻¹, which is associated with the TO out-of-plane B-N-B bending mode, and the other at 1370 cm⁻¹, which is associated with the TO in-plane B-N stretching mode [9]. The room temperature deposited film does not show any peak due to presumably poor BN composition.

Figure 1. (a) FTIR spectroscopy and (b) UV-visible spectroscopy of the BN films (~3000 Å) deposited on Si and Al₂O₃ substrate at various processing conditions.

The optical transmission spectra of the BN films deposited on both sides of polished Al₂O₃ (0001) substrates are shown in Fig. 1(b). The BN nitride films have a high transmittance (near 80%) in the IR, throughout the visible and into the UV, and it drops sharply due to a strong absorption at the band edge of the film. The band gaps were found to vary from 5.4 to 6.3 eV. Variation in band gaps for the BN film may result from nitrogen stoichiometry and/or variation in grain size. We have investigated the microstructure of these films, including interface properties on SiC. The BN films were also characterized by x-ray diffraction, Rutherford backscattering, and high-resolution transmission electron microscopy. Shown in Fig. 2 are the XRD slow scans of h-BN film on Si deposited at 600°C by PLD. The XRD pattern shows only the (002) h-BN peak, which means that the film is oriented along the c-axis, normal to the substrate [10]. Note that the peak intensity is both weak and broad. The weak intensity in the XRD pattern is due to the small atomic masses of both B and N. The peak width is associated with the grain size, indicating the nanometer scale of the BN grains in the film. We did not see any significant difference in the peak intensity and the width for the BN film after being annealed at 1000°C.
Figure 2. XRD pattern of the BN film on Si grown at 600°C by PLD.

Figure 3(a) and (b) show RBS of the BN films on Al₂O₃ and Beryllium (Be) substrates. Due to the heavier mass of aluminum (Al) as compared to boron (B), we were not able to see the boron peak very clearly. To avoid this problem, we fabricated BN films on Be substrates; its RBS spectra is shown in Fig. 4(b). The RBS spectrum clearly indicates the evidence of B as well as N, consistent with the FTIR and XRD results. Quantitative analysis of the composition and stoichiometry is under present investigation and will be reported separately.

Figure 3. RBS spectra of BN films deposited on (a) sapphire and (b) Be.

Detailed studies on the microstructure, thermal stability, and chemical reactivity of the BN films were carried out by transmission electron microscopy. The results presented here belong to dual layer structures that were fabricated on sapphire and SiC. In these structures, the thickness of the BN film, as well as the AlN film, was ~ 2700 Å. After fabrication, the sample was annealed in Ar atmosphere at temperatures up to 1700°C for 30 min. The low magnification image (Fig. 4(a)) indicates that the BN film is very uniform in thickness and reveals excellent adhesion with the underlying AlN. The high-resolution TEM image of the BN/AlN interface for sample annealed at 1700°C is shown in Fig. 4(b). The interface is without voids or any identifiable mechanical failures. There are two distinct regions within the BN film: a layer adjacent to the interface with a thickness of ~ 100 Å revealing darker contrast, and the rest of the BN film with a lighter contrast. The BN film at the BN/AlN interface is identified from its selective area diffraction (SAD) pattern and HRTEM to be the hexagonal BN (h-BN) phase
(a=2.50399Å, c=6.6612Å). The rest of the BN film to the top is identified from HRTEM as the turbostratic BN phase (t-BN). From SAD pattern (not shown), the (0002) t-BN is preferentially parallel to the (10-10) AlN, thus having the [0002] in-plane oriented texture of t-BN [11,12]. The t-BN is occasionally intermixed with nanocrystalline grains of the h-BN phase, as evident from HRTEM (Fig. 4(b)).

Figure 4. (a) Low magnification and (b) high resolution TEM images of BN/AlN dual layer sample annealed at 1700°C in an Ar atmosphere.

Figure 5. (a) Photograph of BN coated Si wafer and metallic component by spray technique and (b) XRD of as-deposited BN film on Si (top) and after annealing at 1000°C in vacuum (bottom).

As established from the above results it is clear that the BN films are stable for our high temperature applications. To apply the BN coatings on metallic components, spray technique was employed, which covers large areas, curved surfaces and coiled filaments. Figure 5(a) shows the photographs of the BN coated wafers, stainless steel plates, and heater coils. The BN
deposition was uniform with good adhesion on the surface of the samples. The as-deposited films were annealed at various temperatures ranging from 500°C to 1200°C. Adhesion of the films with the heater components was also greatly improved after high temperature annealing due to good interfacial bonding with the substrate material. The Fig. 5(b) shows the XRD patterns of as-deposited (top) and after annealing at 1000°C in vacuum (bottom). No significant change is seen in the XRD pattern indicating good stability of the BN coatings. We have observed that the grain size of the BN coating increases (on SiC) only at high temperatures above 1500°C. An investigation on the adhesion and cracking of the coatings with thermal shocks is under present study and will be addressed elsewhere.

CONCLUSIONS

BN films have been deposited on Si, Al₂O₃, and SiC by pulsed laser deposition, and also on a variety of metallic substrates and large Si wafers by spray technique. Our results clearly indicate that the BN films are stable at high temperature. The highly oriented films were grown above 600°C by PLD. The band gaps were found to vary from 5.4 to 6.3 eV. Variation in band gaps for the BN films may be the result of nitrogen stoichiometry and/or variation of grain size. The TEM study shows that BN films are very uniform in thickness and reveals very good adhesion with the underlying AlN film at high temperature (1700°C) annealing conditions; also, the interface was without voids or any identifiable mechanical failures indicating that the BN films and coatings provide excellent capping properties for SiC and metallic components for high temperature applications.

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REFERENCES