A NEW APPROACH TO THE DISSOCIATION OF BN_9 FOR BN THIN FILMS.

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Abstract

A new approach to the dissociation of boron triazide for the generation of boron nitride thin films is reported. The method utilizes active nitrogen to invoke dissociation of precursor molecules. We report phase and composition analyses of the resulting films to support the assumption that boron nitride films have been grown.

Introduction

The two main crystal structures for solid boron nitride are hexagonal boron nitride (h-BN) and cubic boron nitride (c-BN). Hexagonal BN has a structure and properties similar to graphite. Cubic BN is similar to diamond structure, and has numerous industrial and technological applications. Cubic BN has a hardness second only to diamond, and has been employed in the manufacture of high temperature cutting tools because it has proven to be unreactive with ferrous metals at high temperatures.[1] Cubic BN has also shown to be useful as a wide band-gap semiconductor material, and can be doped to form both n-type and p-type semiconductors.[2]

Current methods for producing c-BN films normally involve very high energy processes. Chemical vapor deposition (CVD) and inductively coupled plasma (ICP) deposition are just two of the many high energy methods used to produce c-BN films.[1,3] It would be of great advantage to find a method of reproducibly depositing stable c-BN films without the tremendous expenditure of energy.

Previous research in our lab[4] has led to a candidate for a low temperature method of forming c-BN films from highly energetic gas phase molecules. In 1995 it was found that by mixing a 3:1 ratio of hydrogen azide (HN_3) and boron trichloride (BCl_3) in the gas phase, the molecule boron triazide (BN_9) could be formed. The structure of BN_9 is shown in figure 1. BN_9 was shown to be stable at room temperature and 0.3 Torr for 30 minutes, but due to the high energy contained in the molecule it was prone to decomposition at longer times.[4] It is believed that the final decomposition products of BN_9 are $BN_{(s)}$ and N_2.
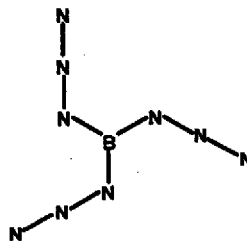

Figure 1. Structure of boron triazide

One method of decomposition currently under study in our lab is based on work by Benard in which carbon nitride films were grown from the dissociation of cyanogen azide.[5] The principal means of decomposition in these experiments was by interaction with active nitrogen (i.e. nitrogen atoms and N_2 metastables) created in an electrical discharge. We believe that active nitrogen will impart enough energy, through collisions, to rapidly dissociate BN_9. When done in close proximity to a substrate material, the result is a potentially nitrogen rich boron nitride film. Therefore, by choosing a substrate with lattice parameters similar to those of c-BN, we believe that we can produce c-BN films in a continuous flow system, at temperatures much lower than previously recognized.

The current research underway in our laboratory is directed toward the development of a low energy method for forming pure BN films, and determination of the effects of variable experimental conditions on the formation of different types of film. We hope to be able to control the type of film grown by making minor changes in the experimental conditions. We are also developing a fundamental understanding of the molecular mechanisms underlying growth of the film.

Experiment

A diagram of the experimental apparatus used for depositing BN films is shown in figure 2. HN_3 was synthesized using the known reaction[6] of sodium azide and stearic acid. Mixtures of HN_3 (5% in nitrogen) and BCl_3 (1% in nitrogen) were flowed through a low vacuum (~20 mTorr) system in a controlled manner. It was found that approximately five minutes were needed for the HN_3 and BCl_3 to mix and react completely to form BN_9, so a reaction volume was added in situ to allow for this mixing/reaction time.
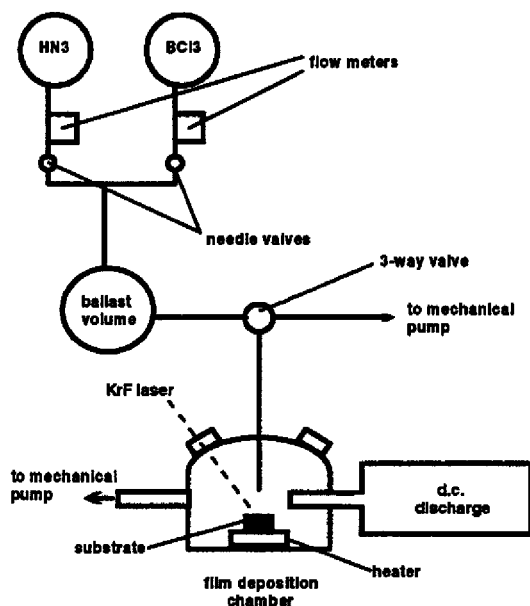

Figure 2. Experimental apparatus

The substrates are cleaned with soap and water, then rinsed with methanol before being placed in the deposition chamber. It has been shown[7] that cleaning a substrate with UV radiation from an eximer laser will greatly increase the sticking coefficient of films on many substrates by removing hydrocarbons that may have been adsorbed from laboratory air. We used this method for in situ cleaning of substrates, using a KrF laser operated at ~400mJ/pulse and 1 Hz for approximately three minutes.

The HN_3 and BCl_3 mixtures are flowed (at 1.5 sccm and 4.0 sccm respectively) for 5 minutes prior to being introduced into the deposition chamber, to allow for effective BN_9 production. During this time the dc discharge is turned on and allowed to stabilize. The gases used in the dc discharge are He (used as a carrier gas and flowed at ~220 sccm) and N_2 (flowed at ~50 sccm), and the discharge is operated at ~100 mA. The presence of active nitrogen in the dc discharge is apparent from the glows of the N_2 first positive ($B^3\Pi_g$

$\rightarrow A^3\Sigma_u^+$) and second positive ($C^3\Pi_u \rightarrow B^3\Pi_g$) transitions seen in the deposition chamber. The first and second positive transitions are seen as light red and blue after-glows, respectively. The presence of these transitions has also been confirmed from emission profiles of the after-glows.

The films are deposited on polycrystalline alumina (Al_2O_3), sapphire (Al_2O_3), or single crystal silicon substrates. The substrate temperature during deposition is held at about 150°C. The films are deposited at an operating pressure of 1 Torr for 1-2 hours.

Following film deposition the films are analyzed to determine composition and crystal phase. When silicon substrates are used, the analyses can be conducted with infrared (IR) spectroscopy, because the IR absorptions of h-BN and c-BN are well known[8] and Si has some transparency in the appropriate frequency range. Films have also been analyzed by x-ray photoelectron spectroscopy (XPS) to determine chemical composition. All films are analyzed by x-ray diffraction (XRD) to determine crystallinity.

Results

Film Growth Results

A great deal of data has been collected that supports the identification of the films we have grown as BN. The IR spectrum of a film grown on a silicon substrate is shown in figure 3. The characteristic peaks for h-BN at 1390 cm^{-1} and 800 cm^{-1} can be seen.
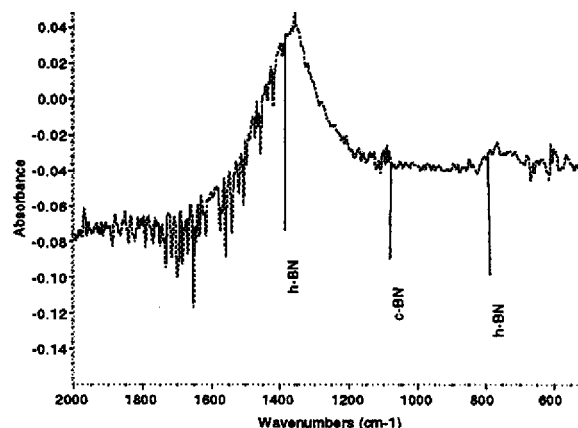

Figure 3. IR spectrum of film grown on silicon substrate. Peak markings are from reference 8.

A small peak representing c-BN at 1080 cm^{-1} can be seen, but is too weak to make any definite assignment. We believe that this spectrum clearly shows the presence of sp^2 bonded boron nitride.

However, it is evident from the single, broad peak seen in the diffraction pattern of this film that there is no long-range crystal structure in the film. The

XRD pattern for the film is shown in figure 4, and the broad peak can be seen centered around 56° (2-θ scale). The two sharp peaks at 52.5° and 54° are too narrow to represent film peaks and are likely electronic noise spikes. These data show that for a silicon substrate we can generate a BN film with local sp^2 bonded boron nitride, but the film itself is amorphous. It is known[9] that the graphitic, turbostratic and amorphous phases of boron nitride contain the same IR absorption peaks. Therefore, a BN film with clear hexagonal-type bonding in the IR spectrum may not present a clear XRD pattern. This is not surprising, however, considering the ~40% lattice mismatch between BN films and single crystal silicon.[10]
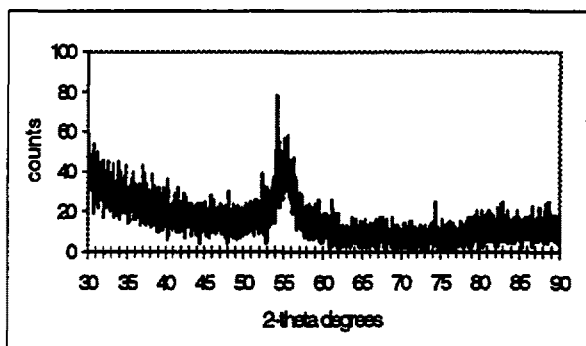

Figure 4. 2θ scale XRD pattern for BN film grown on Si (100).

Although the lattice mismatch is much smaller for films grown on sapphire, we were unable to obtain firm evidence of polycrystalline BN for films grown with the substrate at 150°C. Figure 5 shows a typical XRD pattern. Weak peaks are seen for the film at 33° and 37°. We know that these are not substrate peaks from comparison with patterns of clean sapphire substrates.
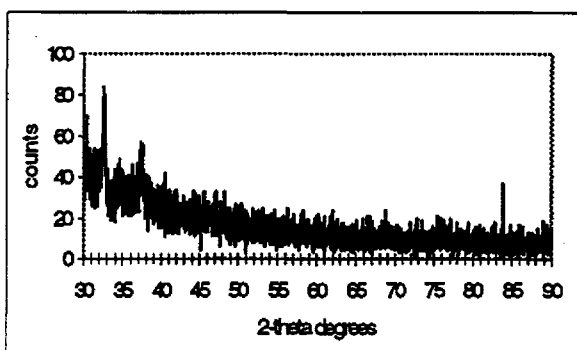

Figure 5. 2θ scale XRD pattern for BN film grown on sapphire.

The peaks seen for the film are too wide to be noise spikes, but are too weak to determine true crystal

structure. The film may be either too thin for determination of crystal structure, or simply amorphous with some minor crystal structure. The presence of some crystalline regimes within an otherwise amorphous film could explain the weak peaks seen in the diffraction pattern. These peaks however, can not be definitely assigned to any known crystal structures of boron nitride.

The XPS data show however, that a boron nitride film can be grown on sapphire substrates. The XPS spectrum of a film grown on sapphire is shown in figure 6. The film was sputtered for 2 minutes with an Ar$^+$ beam prior to obtaining this spectrum to remove adsorbed hydrocarbons. The peaks at binding energies of 194.5 eV and 400.5 eV are boron 1s and nitrogen 1s peaks, respectively. When the peak intensities are scaled for sensitivity, we see that the atomic concentrations of boron and nitrogen in the film are at about a 1:1 ratio. The peak at a binding energy of 534.7 eV is the oxygen 1s peak. The presence of oxygen in the film may be attributed to exposure of the film to the atmosphere prior to XPS analysis. This notion is supported by etching experiments. When the film is further etched with the Ar$^+$ beam, the concentration of oxygen decreases with depth, but the relative atomic concentrations of boron and nitrogen remain the same.
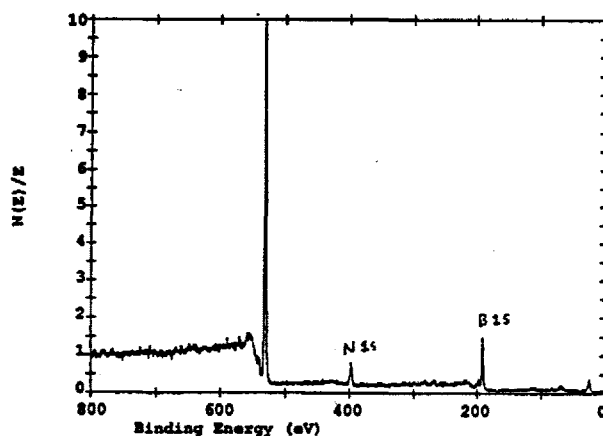

Figure 6. XPS spectrum of BN film on sapphire

The films grown on all substrates, though thin, are clearly visible to the naked eye. When the substrates are removed from the deposition chamber, a film can be seen on the surface by the diffraction of room light.

Active Nitrogen Species
    The species of active nitrogen generated in an electrical discharge have been well characterized. These include: N$_2$ metastables (N$_2$ C$^3\Pi_u$, N$_2$ B$^3\Pi_g$, N$_2$ A$^3\Sigma_u^+$), vibrationally excited N$_2$ (X$^1\Sigma_g^+$), and nitrogen atoms. Due to the short lifetimes of the N$_2$ B and C

states, we believe that these species are not responsible for the dissociation of BN_9.

The N_2 $A^3\Sigma_u^+$ and $X^1\Sigma_g^+$ species and the nitrogen atoms created in the discharge have considerably longer lifetimes. The activity of these species can be tested by placing a nickel gauze in the flow of the discharge just before the deposition chamber. The Ni gauze removes the nitrogen atoms, allowing only vibrationally excited N_2 to enter the deposition chamber. The presence of the gauze resulted in the disappearance of the after-glows in the deposition chamber, indicating the effective removal of nitrogen atoms.

When the Ni gauze is placed in the discharge flow during film deposition, no films can be grown on the substrates. This suggests that the vibrationally excited N_2 is not responsible for the dissociation of BN_9. Because the density of nitrogen atoms made in the discharge is considerably greater than the density of N_2 $A^3\Sigma_u^+$ metastables, we have tentatively assigned the dissociation of BN_9 to the nitrogen atoms created in the dc discharge.

Conclusion

It is evident from the presented IR and XPS data that we have successfully grown boron nitride films from the dissociation of BN_9. The IR data shows that sp^2 bonded boron nitride can be grown on a silicon substrate. The XPS data shows that films grown on sapphire contain boron and nitrogen in a near 1:1 ratio, with few impurities. Based on the XRD data, the films grown are amorphous or turbostratic (randomly rotated arrangement of hexagonal layers[10]) BN films because of the absence of any definite crystal structure.

We believe that because of its simplicity, our system has an advantage over other single source precursor molecules used to generate BN thin films. Our precursor molecule (BN_9) contains only boron and nitrogen, therefore there is little chance of incorporating unwanted atoms into the film. This is sometimes a problem when growing BN films from single source precursor molecules.

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