LOW ENERGY METHODS FOR THE DEPOSITION OF BN THIN FILMS

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Abstract

We report the growth of boron nitride thin films from plasma-assisted dissociation of the precursor molecule boron triazide. Stable films containing mainly $sp^2$-bonded BN have been grown for comparison with films grown by other dissociation methods. We conclude that the plasma-assisted dissociation method is superior to previous methods for growing boron nitride thin films from boron triazide.

Introduction

Boron nitride is isoelectronic to carbon and exhibits $sp^2$-bonded hexagonal (h-BN) and $sp^3$-bonded cubic (c-BN) structures in the solid phase. Current methods for producing thin films of BN normally involve high-energy processes such as chemical vapor deposition or inductively coupled plasma deposition. A number of such methods employing single source precursor molecules have been reported. While BN films have been successfully grown from these single source precursors, unwanted species are sometimes incorporated in the films. Previous research in our laboratory has investigated the deposition of group III nitride films from the decomposition of group III azides. These molecules are highly energetic, offering the promise of low energy deposition, and consist of only group III and nitrogen atoms such that the incorporation of unwanted species may be considerably mitigated.

We have shown that boron triazide, B(N$_3$)$_3$, can be produced by the room temperature gas phase reaction between HN$_3$ and BCl$_3$. Gilbert and co-workers have shown that the molecule NNBN is a product of B(N$_3$)$_3$ photolysis at wavelengths near the strong absorption feature at 230 nm. NNBN is likely formed by rearrangement of a trigonal BN$_3$ photoprodud and it may be that the BN films ultimately produced arise from self-assembly of NNBN molecules with the subsequent loss of N$_2$. We have also shown that B(N$_3$)$_3$ dissociation can be triggered by collisions with N$_2$ ($A^3Σ_u^{+-}$) metastable molecules. These metastable molecules are readily created when N$_2$ is admitted (as the B(N$_3$)$_3$ diluent gas) into a stream of Ar($^3P_{0,2}$) metastable atoms generated in a dc discharge. Films grown using this technique consist of $sp^2$-bonded BN, with a B:N ratio near unity. These films are quite stable and adherent, but do not exhibit any crystalline structure. Current experiments involve the dissociation of B(N$_3$)$_3$ in an argon plasma [Ar($^3P_{0,2}$) and Ar$^+]$. Kester and Messier have shown a direct link between BN crystalline phase and the energy imparted to the surface from Ar$^+$ during film growth. The films grown in our experiments utilizing plasma-assisted deposition on silicon substrates are even more stable and adherent than those grown from B(N$_3$)$_3$ dissociation by N$_2$ ($A^3Σ_u^{+-}$), but still contain primarily $sp^2$-bonded BN.

In this paper, we report the growth of BN films on room temperature silicon substrates from plasma-assisted dissociation of B(N$_3$)$_3$. We also report new insights into the previous B(N$_3$)$_3$ dissociation mechanisms that have been studied in our laboratory, and possible methods for the growth of more stable BN films from the photolysis of B(N$_3$)$_3$ with subsequent excitation of the photoproducts.

Experiment

For synthesis of gaseous B(N$_3$)$_3$, flows of HN$_3$ and BCl$_3$ were metered into the system to produce a stoichiometric (3:1) reaction mixture. The HN$_3$ used in the experiments was synthesized in our lab via the well-known reaction of NaN$_3$ with stearic acid. It was then diluted to a 5% mixture in uhp Ar (99.998% stated purity). The c.p. grade BCl$_3$ (99.9% stated purity) was diluted to a 1% mixture in uhp Ar. The flows of HN$_3$ and BCl$_3$ were mixed and passed through a 2.0-liter ballast volume to insure complete reaction. The total pressure in the ballast cell was typically 0.08 Torr. The generation of B(N$_3$)$_3$ was monitored in situ by FTIR absorption spectroscopy. Comparison of reagent and product features in the spectra allowed the production of B(N$_3$)$_3$ to be maximized. For near stoichiometric flows, the spectra indicated that B(N$_3$)$_3$ was the only IR active species present in the effluent. Once the flow of B(N$_3$)$_3$ was established, it was passed through the synthesis system and FTIR spectrometer for a period of five minutes before being diverted to the deposition chamber in order to ensure stability of the reagent flows.

A schematic representation of the film deposition chamber is shown in figure 1. The chamber
consisted of a Plexiglas cell with a removable face for sample manipulation. The system was pumped with a mechanical pump to a base pressure of 10 mTorr. The intended application for this chamber was the photolysis of B(N\(_3\)\(_3\)) and excitation of the photoproducts with the Ar plasma. As seen in the diagram, the B(N\(_3\)\(_3\)) flowed through a photolysis tube prior to being admitted to the deposition chamber. The photolysis tube consisted of various diameter supra sil quartz tubes. The photolysis was performed by irradiating the tube with a 7W cadmium lamp (228.8nm line). The gas stream was then directed to the substrate through \(\frac{1}{4}''\) glass tubing. The Ar plasma was directed toward the substrate through a similar tube. The plasma was generated by a dc discharge through 99.998% pure Ar. The discharge consisted of Ta foil electrodes, and was run at a current of 30mA and a voltage of 300V. The pressure of the Ar in the chamber during deposition was typically 0.8 Torr. The substrate sat upon an aluminum stage that was grounded to insure Ar\(^+\) impact on the film as it was grown.

Substrates used in these experiments were \(\sim2\)cm\(^2\) silicon squares cut from a single-crystal (100) silicon wafer (Wafernet inc.). Prior to placement in the deposition chamber, the substrates were cleaned with soap and water followed by ultrasonic cleaning in a methanol bath. A 1\(^{\text{st}}\) dia. Sapphire window in the top of the deposition chamber allowed for in-situ cleaning of the substrates with 308nm radiation from a XeCl eximer laser. Substrates were typically irradiated at 5 Hz for 30 seconds with laser pulses at \(\sim10\)mJ/cm\(^2\) prior to deposition of films. The films were typically grown on room temperature substrates for 45 minutes. Because of silicon’s transparency in the 4000-500cm\(^{-1}\) spectral range, the films could be analyzed using IR absorption spectroscopy. Film structure and morphology were further characterized using scanning electron microscopy (SEM) and x-ray diffraction (XRD).

IR spectra of the B(N\(_3\)\(_3\)) flow in the generator were recorded with a Midac Prospect FTIR spectrometer, at a resolution of 2 cm\(^{-1}\). IR spectra of the films were collected with either a Nicolet 5XDC FTIR spectrometer or Nicolet Protégé FTIR spectrometer, at 2 cm\(^{-1}\) resolution. XRD patterns of the films were recorded using Cu k\(_{\alpha}\) x-rays with a Siemens D500 diffractometer. SEM micrographs were recorded with a Jeol 5800LV scanning electron microscope.

**Results/Discussion**

As noted earlier, the intended purpose of this experimental setup was for the photolysis of B(N\(_3\)\(_3\)) with plasma excitation of the photoproducts. However, given the relatively low power of the cadmium lamp, only a fraction of the B(N\(_3\)\(_3\)) could be photolyzed. The largest tube used for the photolysis zone had an i.d. of 1.1cm. Using the cross-sectional area, pressure, and mass flow rates of the gases a residence time for the B(N\(_3\)\(_3\)) in the photolysis zone was calculated to be about 0.3 second. A series of experiments were conducted the photolysis rate of B(N\(_3\)\(_3\)) using the cadmium lamp and a 5 Torr static fill of the gas in a quartz-walled IR cell. Figure 2 shows a plot of % B(N\(_3\)\(_3\)) photolyzed, determined by IR peak intensities, as a function of time. It can be seen that the photolysis rate using a single cadmium lamp is about 6% per second.

![Figure 1. BN thin film deposition chamber.](image_url)

![Figure 2. Photolysis rate of 5 Torr static B(N\(_3\)\(_3\)) using one cadmium lamp.](image_url)
of just 4% of the B(N₃)₃ would be photolyzed. We therefore have attributed the major mode of B(N₃)₃ dissociation to interactions within the Ar plasma.

Attempts were made to couple more of the light from the cadmium lamp, a diffuse source, with the photolysis tube by wrapping the two together with aluminum foil. This led instead to the thermal decomposition of B(N₃)₃ in the tube. In this case, IR features were seen in the films similar to those observed previously when the thermal decomposition of B(N₃)₃ was the primary means of film growth. As shown in figure 3, the known IR absorption frequency for the ring breathing motion in sp²-bonded BN (1390cm⁻¹) is shifted about 100cm⁻¹ to the red for thermal decomposition of the azide. We speculate that this shift is a function of incomplete B(N₃)₃ dissociation, resulting in the presence of excess nitrogen (N₂) groups on a sp²-bonded BN ring. It is also possible that the deviation in frequency of the 1390cm⁻¹ IR absorption peak could give an indication of the overall nitrogen concentration in the film, and effectiveness of the B(N₃)₃ dissociation method used to grow the film.

Figure 3. IR spectrum of BN film grown on silicon by thermolysis of B(N₃)₃.

Figure 4 shows an IR absorption spectrum of a film grown from Ar plasma-assisted deposition. The characteristic peaks for sp²-bonded BN at 1390cm⁻¹ and 800cm⁻¹ are clearly present, but again red-shifted due to possible nitrogen excess. The possible formation of some sp³-bonded BN, with a characteristic peak at 1082cm⁻¹, can be seen in the shoulder on the major sp²-BN peak. These films are very adherent to the silicon surface. Unlike previous films grown from the dissociation of B(N₃)₃, they can not be “washed” from the surface with methanol, or removed by vigorous rubbing with a rubber eraser.

A SEM micrograph of an intentional scratch in the film, Figure 5, reveals a fracture pattern indicative of crystalline structure in the film. The scratch runs horizontally down the center of the image, with BN film on either side. A film thickness of 4µm was determined by running a stylus scanner (Tencor Instruments) over a similar scratch in a film. This result implies a film growth rate of about 900Å/minute, almost 30 times higher than the growth rates reported for films grown from N₂ (A³Σ_u⁺) collisions.

XRD patterns of the films did not display any indication of polycrystalline structure. This could indicate that the films are amorphous or, given the pattern of the fissures evident in SEM data, that the films are single crystal BN grown epitaxially on the silicon. Ballal and coworkers have shown that this is possible when using ion-assisted processes. Because our XRD patterns were collected using low incidence angle (2θ) theta-2theta scans, the presence of a single crystal film would not be recognized.

At this time, it is still unclear as to which species in the Ar plasma are responsible for B(N₃)₃
dissociation. Because we would expect Ar metastable species to live longer than Ar\(^+\) in our system, we have tentatively assigned the dissociation to collisions with Ar (\(^3\)P\(_0,2\)). The flux of Ar\(^+\) impinging on the film and the role of these species on film growth are also still unclear at this time.

**Conclusion**

Stable, hard BN films have been grown from the dissociation of B(N\(_3\))\(_3\) by interactions with an Ar plasma. The films consist primarily of sp\(^2\)-bonded BN, with the possibility of some sp\(^3\)-bonded BN present. Plasma-assisted dissociation of B(N\(_3\))\(_3\) appears to be superior to previously reported methods used for the growth of films from this molecule (e.g. thermolysis or collisions with N\(_2\) (\(\overset{\text{A}}{\overset{\text{3}}{\Sigma}}\text{u}^+\))). Films are grown at a considerably higher rate, and are more adherent to the substrate material than previously recognized. A possible route for the growth of BN films that needs further study is photolysis of B(N\(_3\))\(_3\), or photolysis followed by excitation of the photoproducts. We have begun to examine this path, but have not yet established conditions in which the photolysis of B(N\(_3\))\(_3\) dominates the dissociation.

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**Literature Cited**