

BORON NITRIDE THIN FILMS FROM HIGH ENERGY GAS PHASE REACTANTS

Keith Hobbs and Robert D. Coombe
University of Denver
Department of Chemistry and Biochemistry
Denver, CO 80208

Abstract

A novel method for generating boron nitride thin films is currently being developed. This method utilizes the energy stored in the precursor molecules to grow films at low temperatures. The mechanism for film growth has been studied, both experimentally and computationally, with promising results.

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 temperatures¹. 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 semiconductors².

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 lab⁴ 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 (HN₃) and boron trichloride (BCl₃) in the gas phase, the molecule boron triazide (BN₃) could be formed. The structure of BN₃ is shown in figure 1.

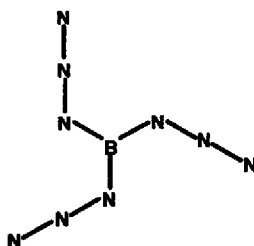


Figure 1. structure of boron triazide

BN₃ 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 times⁴. It is believed that the final decomposition products of BN₃ are BN_(s) and N₂.

The two means of decomposition of BN₃ that are under study in our lab are thermal decomposition and photodissociation. An ultraviolet/ visible spectrum of BN₃ shows⁴ that it has a strong absorption band at 230 nm. Matrix isolation studies⁵ on the photolysis of BN₃ have shown that one of the primary photolysis intermediates is the NNBN molecule. We believe that this NNBN molecule may form dimers or trimers, either in the gas phase or on surfaces reaction, and that these dimers or trimers are precursors to film formation. For example, a trimer of NNBN would form a six membered ring structure that could lead to the formation of h-BN film. Other structures formed from the NNBN intermediates may lead to the formation of c-BN films. The films formed by these methods would be very nitrogen rich. We believe that it would be possible to drive the excess nitrogen off during film formation with gentle heating, or after film formation by annealing the film.

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 find a way 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. We are currently using computational methods to help determine these mechanisms.

Experiment

A diagram of the experimental apparatus used for depositing BN films is shown in figure 2. HN_3 was synthesized using the known reaction⁶ of sodium azide and stearic acid. Mixtures of HN_3 (5% in argon) and BCl_3 (1% in argon) were flowed through a low vacuum (~ 20 mTorr) system in a controlled manner. The system contains a cell where the production of BN_9 may be monitored using infrared (IR) spectroscopy. 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.

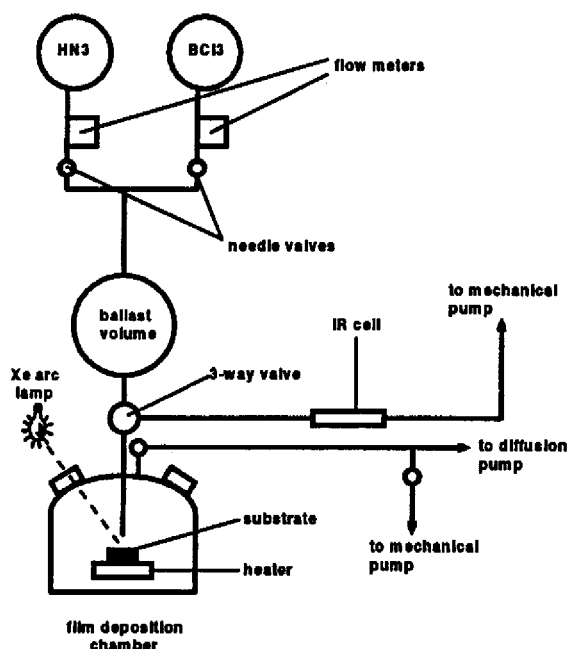


Figure 2. Experimental apparatus

Once suitable BN_9 (no reactants present in the gas flow) is observed in the IR spectrum, the gas flow is diverted via the 3-way valve to a system under higher vacuum ($\sim 10^{-4}$ - 10^{-6} Torr). This system contains the substrate on which the BN film is to be deposited. The substrate was first placed on a block heater that would be held around 100°C during deposition, in the hope of driving off excess N_2 as the film was formed. This heater has been recently replaced with a cold "finger" like stage that can hold liquid nitrogen and cool the substrate considerably. We believe that using a cold substrate greatly increases the sticking coefficients of film precursor molecules, and may promote epitaxial growth. The deposition chamber is also equipped with windows that allow for photolysis of the BN_9 with a Xenon arc lamp during the experiment.

The preliminary substrate chosen for the deposition of films was a polished KCl disk. KCl was chosen so that the deposited film could be easily analyzed using IR spectroscopy. The IR absorption spectra of BN films have been well characterized⁷. Spectra for h-BN and c-BN are shown in figure 3. Identifying peaks for h-BN and c-BN, 1390 cm^{-1} and 1080 cm^{-1} respectively, were sought in the films deposited on the KCl substrates. The KCl substrates were replaced with n-doped silicon (100) wafers after the conditions for film growth were determined. The lattice parameters of silicon match those of c-BN much better than do those of KCl⁸.

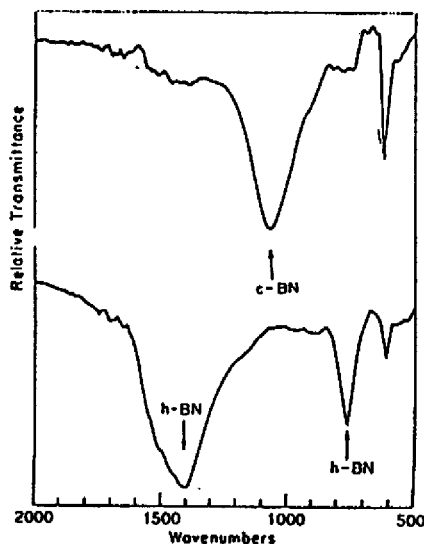


Figure 3. Spectra of h-BN and c-BN

Attempts have been made to grow films under various conditions. When the substrates were held at room temperature and elevated temperatures, films were deposited from a static fill of about 10 Torr of the BN_9 gas mixture (0.5% BN_9 in Ar) held inside the deposition chamber. The gas would be held in the chamber for about an hour, then would be replaced with a fresh sample. The Xenon lamp output was focused on the substrate in order to photolyze the BN_9 directly above the surface. This procedure was repeated numerous times without breaking the vacuum in the chamber.

Recent attempts to grow a film on cooled substrates have been much more successful. In this case, BN_9 gas mixture is constantly flowed over the surface. Because the low temperature of the stage greatly increases the sticking coefficient, continuous flow conditions were used. Experiments were conducted with the Xenon light both on and off, in order to determine the effects of photolysis on the resulting film.

Films were analyzed, following the various experiments, using IR spectroscopy. Subsequent analyses by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and x-ray diffraction (XRD) were conducted if the IR spectra showed promise. The energy dispersive spectroscopy was conducted on the substrate while it was in the electron microscope, but may not be reliable due to the low molecular weight of boron and nitrogen.

Results

Film Growth Results

At this point in our research we have found two main obstacles to growing films from reactive gas phase molecules. One obstacle that we have begun to overcome is the sticking coefficients of the molecules on the substrates. This problem can be observed by comparison of films grown on substrates at room or elevated temperature, to those grown on cold substrates. By comparing peak intensities of selected IR absorption bands from the films grown under varying conditions, one can estimate the relative thickness of the films. It was very obvious that the films grown on cold substrates formed much more rapidly than ones grown under higher temperature conditions. This is an indication that sticking coefficients play a roll in the films that form. The other obstacle to our research is the rapid oxidation of the films when exposed to air. This can also be seen in the IR spectra by comparison with spectra of known oxides. The rapid oxidation of the films suggests that the films are amorphous, with the lack of crystal structure in the films leading to a great deal of surface area for oxidation to occur.

Figure 4 shows IR spectra of two different substrates after the completion of subsequent experiments. In both cases KCl substrates were used, and backgrounds were taken of the cleaned substrates before the experiment. We were not able to grow a detectable film on silicon substrates at room temperature and above, therefore we present no data for silicon at these temperatures. Figure 4(a) is the spectrum of a film grown on a room temperature substrate. The film was deposited from successive static fills of BN_3 for a total time of 3 hours. Each fill consisted of 10 Torr total pressure (including argon diluent), and was held in the chamber for 30 minutes. Figure 4(b) is the spectrum of a film grown on a cooled substrate. The film was grown with a continuous flow of the BN_3 and diluent at an operating pressure of 2×10^{-4} Torr for 30 minutes. It can be seen from the spectra that the resultant film composition did not depend on the temperature at which the film was grown. It is also clear from comparing relative peak

heights that the film grown on the cold substrate was much thicker that the other. For example, the peak around 1450cm^{-1} has intensities of .02 and .75 absorbance units for the room temperature film and the cold film respectively. This result is typical of all of the experiments that we have conducted thus far.

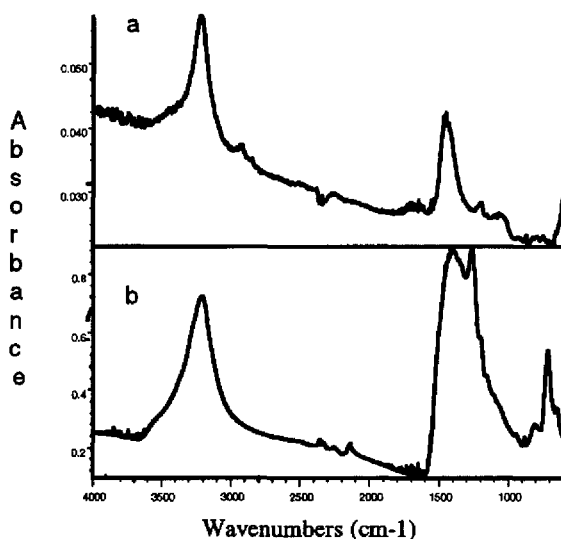


Figure 4. (a) spectrum of film grown on room temperature substrate, deposit time 3 hours. (b) spectrum of film grown on cooled substrate, deposit time 30 minutes.

After we had established a method for growing films on KCl substrates, we replaced the KCl disks with silicon wafers. The films grown on the silicon substrates greatly resembled those grown on the KCl substrates.

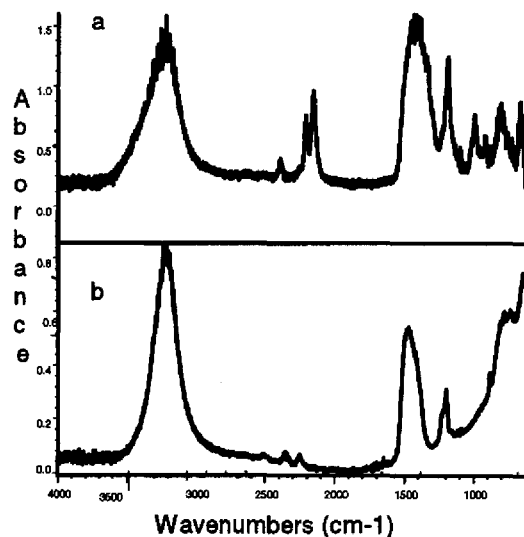


Figure 5. (a) film grown without Xenon lamp used, deposit time 1 hour. (b) film grown with Xenon lamp used, deposit time 1 hour.

Figure 5 shows two spectra of films grown on silicon substrates. Figure 5(a) is the spectrum of a film grown without the Xenon lamp on, 5(b) is of a film grown with the lamp on. Both films were grown using constant flow of the BN_9 at 2×10^{-4} Torr for 1 hour.

These data show that either there is no structural difference in the films grown by photolysis of BN_9 and those grown by thermolysis, or that we are not photolyzing a significant fraction of the BN_9 before it is reaching the surface. We believe the latter is more likely, due to the short interval of time that the gas is exposed to the light before reaching the surface. Other experiments⁵ have shown that several minutes may be needed for significant photolysis of BN_9 to occur. The peak that is seen at about 2100cm^{-1} in spectrum (a) is gaseous HN_3 that was trapped in the film as it grew. This will occasionally happen in films that are grown without the Xenon lamp used. We know that it is gaseous HN_3 because it matches an absorbance band seen in pure HN_3 spectra⁴, and it can be driven off with slight heating.

There is a noticeable difference in the visual appearance, during growth, between films grown with and without the Xenon lamp used during the experiment. When the films are grown on the cold substrates they can be seen as they grow. They are seen by concentric interference rings forming on the surface, independent of use of the Xenon lamp. These rings begin centered below the gas inlet tube and spread outward as they appear to grow, compacting tighter as more form. We believe these rings are interference fringes seen due to room light reflecting off layers of film as they grow. When the Xenon lamp is used, it can only be focused on about one half of the substrate due to the configuration of the growth chamber. When the light is focused on the surface during an experiment a white film will grow, beginning where the light is most intense on the surface and spreading outward. We know that the presence and intensity of the light affects where and how fast the white film will form on the substrate. We have seen this by moving the focused light spot on the substrate, or defocusing the lamp to change the intensity of the light. The white film will grow where we have the light focused; and the more tightly the lamp output is focused on the substrate, the more rapidly the white film will begin to grow. For example, in one experiment the lamp was focused to a 0.5 cm diameter spot on the surface and the white film appeared within 5 minutes of beginning the flow of BN_9 over the surface. In another experiment the lamp was focused to a 2 cm diameter spot on the surface and the film appeared after 20 minutes.

Comparisons of the IR spectra we have collected on our samples to those published for h-BN and c-BN films⁷ have led us to believe that our films have mainly amorphous crystal structure, with some potential h-BN structure. We believe that our films are rapidly oxidizing, due to small air leaks in the system, shortly after the BN_9 gas flow is stopped over the substrate. We have compared the spectra of our films to those of powdered BN (amorphous), old powdered BN (amorphous) that has likely been oxidized, and boron oxide. Our films share characteristics with each. We have tentatively assigned two of the peaks in our spectra based on comparisons with spectra of known samples. The peak around 3200cm^{-1} has been assigned to the formation of boron oxide (B_2O_3), and the peak around 1450cm^{-1} has been assigned to the formation of boron nitride (amorphous). Other supporting evidence comes from EDS in which we have seen high amounts of oxygen in the films, and XRD which showed no sharp peaks eluding to a polycrystalline film.

When the film is being grown, the part of the substrate that is not in the Xenon lamp light shows no signs of film other than the interference fringes. As soon as the BN_9 flow is stopped, the entire surface turns white within a matter of minutes. We have increased the amount of time it takes for the white film to form by several minutes by flowing nitrogen gas over the substrate as the flow of BN_9 is stopped and for a time after the flow has stopped. This increased the time for the film to turn white to 10 minutes, opposed to the 1-2 minute time without the N_2 flow. The formation of the white film may show the oxidation of the film that was deposited on the surface during the experiment. The white film that forms after the experiment has a flaky, rough look that is different than the film that begins to grow in the Xenon lamp spot. It is possible that the white film is indeed BN film, and that it does not oxidize until it is removed from the chamber. In order to test this we must construct a chamber in which we can analyze the substrate without exposing it to the atmosphere.

One explanation for the observations we see in the formation of the white films could lie in the potential excess nitrogen trapped in the film during deposition. If excess nitrogen is being trapped in the film as it grows, the escape of the nitrogen as the substrate heats up to room temperature could cause the cracking we see in all of the films. Figure 6 shows an example of this cracking as seen in the SEM image taken of one of the films. If this is the case, then the white film that forms in the Xenon light can be explained by the light giving the excess nitrogen enough energy to escape as the film grows. The light may also clean the substrate photolytically, increasing

the sticking coefficient of the gas for the clean surface. There is still much work needed to determine the true nature of the white films that are forming, and a mechanism for the film growth.

Reaction Mechanism Calculations

It was mentioned above that an intermediate in the decomposition of BN_9 during photolysis, and possibly thermolysis, is the NNBN molecule⁵. We have begun to study mechanisms for film growth based on the formation of NNBN intermediates. Dimers, trimers, and higher order NNBN moieties might well assemble in a step-wise manner from individual

NNBN molecules. One mechanism that would lead to the formation of an h-BN film involves three NNBN molecules coming together, by excess electron density on terminal nitrogens being donated to electron deficient boron atoms, to form a six membered ring. The ring would be composed of alternating boron and nitrogen atoms, with the excess nitrogens extending outward from the ring at the boron atoms (see figure 7). These rings could assemble on the substrate, and by epitaxial growth form h-BN film. There are many other possible mechanisms that may lead to the formation of c-BN or other films with varying compositions of boron and nitrogen.

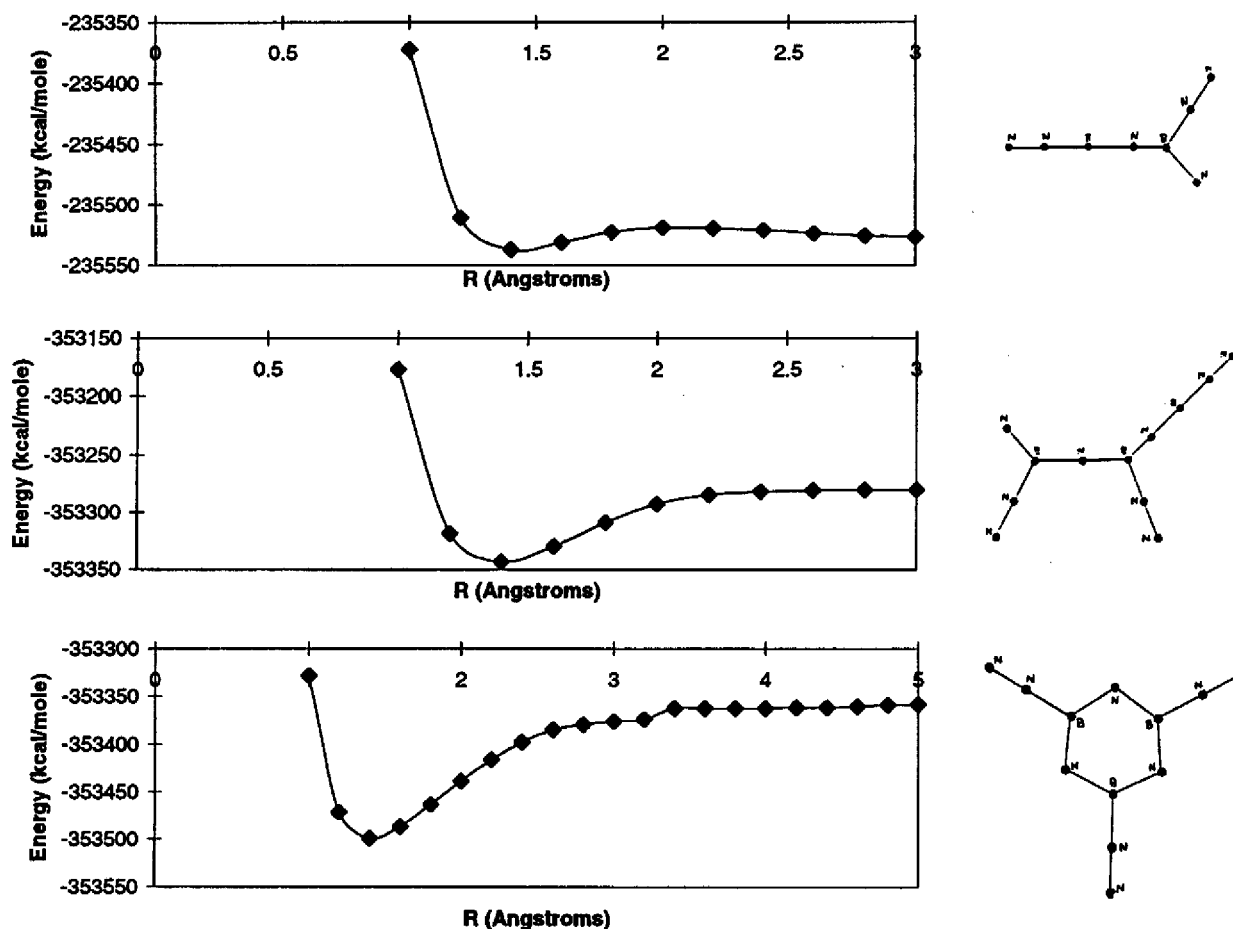


Figure 7. Potential energy curves for the formation of a six membered ring formed by the trimerization of NNBN intermediates. (a) Formation of a dimer from two NNBN molecules. (b) Formation of a trimer from the addition of an NNBN molecule to the structure in (a). (c) Formation of a ring from the structure in (b). In each curve R is the distance between the atoms forming the bond. The minimum energy structure for each step is shown to the right of the corresponding potential well.

Because our films thus far have exhibited more h-BN character than c-BN, we have chosen to start with the mechanism for forming the ring structure mentioned above. We have calculated one-dimensional potential energy surfaces for the formation of a dimer, then a trimer, then the closing of the trimer to form the ring. Figure 7 shows this mechanism with the potential energy surface for each step. On the potential energy curves, R represents the distance between the atoms coming together to form the new bond. The potential energy scans were run at the unrestricted Hartree-Fock level of theory, with a 6-31g(d) basis set. This method was chosen for computational speed, and to get rough estimates of the potential energies. Therefore the energies are an upper limit for the real values, but the geometries should be accurate. The potential energy surfaces show in each case that the proposed structure would be bound. This is just one possible mechanism that could ultimately lead to the formation of h-BN films. More information is needed to determine if there are any more favorable pathways.

Conclusions

We have shown that it may be possible to grow boron nitride thin films using low energy consuming methods. The films we have been able to generate thus far are likely amorphous and very susceptible to rapid oxidation. Pure crystalline boron nitride (e.g. cubic boron nitride or hexagonal boron nitride) would be much less likely to oxidize than amorphous boron nitride films.

Our method of growing films on cooled substrates has shown promising results. The films form much more rapidly than do those grown on room or elevated temperature substrates. However, the films have not proven to be very stable. The cracking of the films as they warm to room temperature must be controlled in order to achieve good crystal structure in the films. If the cracking of the films is indeed due to escaping nitrogen, our method of photolyzing the BN₂ before it reaches the substrate may eliminate this problem. This may be accomplished by increasing the lamp intensity on the gas flow to increase the possibility of photolyzing the BN₂ before it reaches the surface.

Computational studies of the proposed mechanisms of film growth from NNBN intermediates have given promising results. More supporting calculations are needed, and a way to correlate the growing conditions to the proposed mechanism of film growth must still be investigated. We hope that in

time we will be able to control the film that is grown by controlling the experimental conditions.

This is an unusually simple chemical system, with only boron and nitrogen present. It also has the benefit of generating a single, potentially critical reactive intermediate in NNBN. The simplicity of this system combined with the controlled production of a reactive intermediate may allow us to develop control over film growth and morphology.

Acknowledgments

This work was funded by a Rocky Mountain NASA Space Grant, and by the United States Air Force Office of Scientific Research under grant number F49620-97-1-0036. The authors would also like to thank Tom Ely in the Denver University Materials Science department for help with surface analyses.

References

1. L. Vel, G. Demazeau, and J. Etourneau, *Mat. Sci. and Eng.*, B10, 149, (1991).
2. *Synthesis and Properties of Boron Nitride*, Materials Science Forum, Vol. 54/55; Pouch, J., Alterovitz, A., Eds.; Trans Tech: Aedermannsdorf, Switzerland, (1990).
3. H. Saitoh, T. Hirose, H. Matsui, Y. Hirotsu, and Y. Ichinose, *Surf. Coat. Technol.*, 39/40, 256, (1989).
4. R.L. Mulanax, G.S. Okin, and R.D. Coombe, *J. Phys. Chem.*, 99, 6294, (1995).
5. I. Aljihad and J. Gilbert, *J. Phys. Chem.*, accepted for publication, (1998).
6. L.A. Schlie and M.W. Wright, *J. Chem. Phys.*, 92, 934, (1990).
7. D.J. Kester and R. Messier, *J. Appl. Phys.*, Vol. 72, No. 2, 504, (1992).
8. P.B. Mirkarimi, K.F. McCarty, G.F. Cardinale, D.L. Medlin, D.K. Ottesen, and H.A. Johnsen, *J. Vac. Sci. Technol.*, A 14(1), 251, (1996).