Boron Nitride: Composition, Optical Properties, and Mechanical Behavior

John J. Pouch, Samuel A. Alterovitz, Kazuhisa Miyoshi, and Joseph D. Warner
Lewis Research Center
Cleveland, Ohio

Prepared for the
1987 Spring Meeting of the Materials Research Society
Anaheim, California, April 21-25, 1987
BORON NITRIDE: COMPOSITION, OPTICAL PROPERTIES, AND MECHANICAL BEHAVIOR

John J. Pouch, Samuel A. Alterovitz, Kazuhisa Miyoshi, and Joseph D. Warner
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

SUMMARY

A low energy ion beam deposition technique was used to grow boron nitride films on quartz, germanium, silicon, gallium arsenide, and indium phosphide. The film structure was amorphous with evidence of a hexagonal phase. The peak boron concentration was 82 at.%. The carbon and oxygen impurities were in the 5 to 8 at.% range. Boron-nitrogen and boron-boron bonds were revealed by x-ray photoelectron spectroscopy. The index of refraction varied from 1.65 to 1.67 for films deposited on the III-V compound semiconductors. The coefficient of friction for boron nitride in sliding contact with diamond was less than 0.1.

INTRODUCTION

Thin boron nitride (BN) films can be useful for passivation, as gate dielectrics, and masks in x-ray lithography. BN, a high temperature, wear-resistant, corrosion-resistant material, is chemically inert. Several techniques are used to synthesize BN: chemical vapor deposition (refs. 1 and 2), sputter deposition (ref. 3), ion implantation (ref. 4), reactive evaporation (ref. 5), and ion beam deposition (ref. 6).

In the present study, the compositional and optical properties, as well as the mechanical characteristics of the films are reported.

EXPERIMENTAL

The BN samples were deposited on quartz, germanium, silicon, n-type gallium arsenide, and n-type indium phosphide substrates. The ion beam deposition technique utilized a borazine plasma. The ion bombardment energies were 150 and 500 eV, and the substrate temperatures were 200 and 350 °C. The films adhered to all the substrates.

The microstructural data for BN were obtained by means of transmission electron microscopy (TEM) and electron diffraction. The film was mechanically removed from the substrate for the microstructural studies by ion etching. (The film could not be pried off in the same manner as pyrolytic BN.)

The chemical bonding states of boron, nitrogen, carbon, and oxygen were studied by means of x-ray photoelectron spectroscopy (XPS). The x-ray source was an aluminum anode. The measurements were taken at a power of 400 W. The binding energy of the gold 4f7/2 peak was set at 83.8 eV.

The BN film surface was analyzed by Auger electron spectroscopy (AES). Depth profiling was performed by rastering of a focused, 3 keV argon ion beam.
The stoichiometry of the film was calculated using standard elemental sensitivity factors (ref. 7).

The transmission spectrum for BN deposited on a germanium multiple internal reflection (MIR) plate was measured from 2.5 to 50 \( \mu \text{m} \) by spectrophotometry. In addition, absorption studies of BN-on-quartz were made in the 0.19 to 3.2 \( \mu \text{m} \) range.

Refractive indices, extinction coefficients, and film thicknesses were determined using a rotating analyzer ellipsometer. A Xe arc lamp produced the incident light. The multiple angles and wavelengths technique was applied to the experimental data (ref. 8). At least five angles of incidence were utilized at each wavelength.

Single-pass scratch tests of the BN surface were conducted in a friction and wear apparatus operating in air. One end of a rod contained the diamond pin. Dead weights were placed in a pan located at the other end of the rod, thus permitting the film to be loaded. The diamond and BN surfaces were brought into contact and loaded. The contact time, prior to a sliding experiment, was 30 sec. The total sliding distance was approximately 10 mm; the sliding velocity was of the order of 12 mm/min.

RESULTS AND DISCUSSIONS

Results from TEM and electron diffraction studies indicate that the films are predominantly amorphous. In addition, a crystalline phase, exhibiting features in the 8 to 30 nm range, is identified. The diffuse rings, noted in the electron diffraction pattern, are due to hexagonal BN.

XPS scans (pass energy, 50 eV) of the B(1s), N(1s), C(1s), and O(1s) photoelectron lines for the as-deposited BN film surface (InP substrate) confirm the AES data. After argon ion sputtering for 65 min, the C(1s) line is at an energy representative of a carbide (ref. 9); the O(1s) peak, related to B\(_2\)O\(_3\), is diminished (ref. 9). The B(1s) spectrum results from B-N and B-B bonds (ref. 10). The N(1s) structure is principally due to B-N (ref. 10).

AES analysis of the as-deposited BN film indicates the presence of the B(KLL) and N(KLL) peaks, as well as the adsorbed C(KLL) and O(KLL) contaminants. A depth profile of the elements is presented in figure 1 for BN deposited on GaAs (substrate temperature, 200 °C; ion beam energy, 500 eV, film thickness, 1290 Å). The B and N signals increase after the contamination layer is removed. The C and O impurities are in the 5 to 8 at % range. Discharges occurring on the walls within the deposition chamber can produce impurity incorporation (ref. 6). The B concentration is approximately 75 at % near the film surface, and drops to about 52 at % near the BN-GaAs interface. In contrast, the N concentration ranges from 6 to 8 at %. The C, O, and N levels peak in the interfacial region. Similar results are obtained for a 1160 Å thick BN film deposited on InP; the maximum B concentration is 82 at %. The AES results for films deposited on GaAs and InP substrates are summarized in table I. We used the elemental sensitivity factors to calculate the atomic concentrations. Another possibility is to use the sensitivity factors derived from stoichiometric BN; however, those factors are different from ours, with the elemental factor giving more weight to B (ref. 4). In the present case, we have a material which is neither elemental B, N, nor BN. Results obtained
by XPS indicate B-N and B-B bonds. Thus, neither choice of sensitivity factors will be accurate. The elemental factors were selected in order to be consistent with the other published work (ref. 4).

Several absorption bands are found in the transmission spectrum for BN-on-Ge. The peak at 6.9 µm is due to the B-N bending mode (ref. 5). The maximum near 6.5 µm is associated with N = 0. The B-H vibration is observed at 4 µm (ref. 5). A broad structure in the vicinity of 2.9 µm results from O-H.

The Tauc plot, i.e., $\sqrt{\alpha E}$ versus $E$ is presented in figure 2. The absorbance is $A$, and the photon energy is $E$. The sample is BN-on-quartz (substrate temperature, 200 °C; ion beam energy, 500 eV). According to an existing theory of amorphous solids, a linear relationship between $\sqrt{\alpha E}$ and $E$ can be used to determine $E_0$, the optical band gap (ref. 11). Referring to the data shown in figure 2, we find $E_0$ to be of the order of 4.8 eV. Our previous results indicate that for B/N of the order of 2, $E_0$ is 5.1 eV (ref. 12). Therefore, there is a trend which suggests that $E_0$ decreases as the B concentration increases, but at a lower rate than the published data (ref. 3).

The ellipsometric results for ion beam deposited BN-on-GaAs (substrate temperature, 200 °C; ion beam energy, 500 eV) are summarized in table II. According to the AES measurements, the film is nonstoichiometric. Alternatively, the film can be referred to as heavily-doped B. The refractive index varies from 1.66 to 1.67 for the wavelength region investigated. The maximum absorption coefficient is approximately $1.29 \times 10^4$ cm$^{-1}$ (4300 Å). The refractive index for BN-on-InP (substrate temperature, 200 °C; ion beam energy, 500 eV) is in the 1.65 to 1.67 range (see table I). Discernible absorption is observed at 5000 Å. The maximum absorption coefficient is of the order of $0.35 \times 10^4$ cm$^{-1}$ (4000 Å). At fixed wavelength, the absorption coefficient for the BN film on InP is smaller than that found for BN-on-GaAs. It is interesting to note that the refractive index for BN-on-Si (substrate temperature, 200 °C; ion beam energy, 150 eV) changes from about 1.71 to 1.81 over a similar wavelength region (ref. 12). The maximum absorption coefficient is estimated to be $0.16 \times 10^4$ cm$^{-1}$.

The coefficient of friction as a function of load is shown in figure 3 for the Si substrate, and BN-on-Si at two temperatures: 200 and 350 °C (ion beam energy, 150 eV). The coefficient of friction is greater for the diamond pin in contact with the bare Si. When the diamond contacts the BN surface, the coefficient of friction is reduced. The coefficient is relatively insensitive to the substrate temperature. The contact area between the diamond and BN causes a permanent groove to be formed in the film. Complex elastic and plastic processes are responsible for the wear track. The critical load required to fracture Si in sliding contact with diamond is 5N. Moreover, when a BN film is deposited on Si, the critical load needed to fracture the Si surface is increased to 7N.

CONCLUSIONS

Ion beam deposited thin BN films can contain up to 82 at% boron. Carbon and oxygen impurities are also present. The BN structure is amorphous, with evidence of a hexagonal phase. Boron-nitrogen and boron-boron bonds are
detected. Although the films are boron-rich, the optical band gaps are of the order of 4.8 eV. We find that the optical band gap decreases as the boron content increases, but at a slower rate than the published results (ref. 3). The measured index of refraction varies from 1.65 to 1.67. The coefficient of friction for BN in sliding contact with diamond is less than 0.1. The critical load needed to fracture the silicon surface is increased by 40 percent when a BN film is used.

ACKNOWLEDGMENTS

The authors would like to thank Dr. W. Halverson of Spire Corporation for providing the samples, and N. Shoemaker for assistance with some of the measurements.

REFERENCES


### TABLE I. - AES RESULTS FOR BN FILMS DEPOSITED
ON GaAs AND InP

[Substrate temperature, 200 °C; ion beam energy, 500 eV.]

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Film thickness, Å</th>
<th>Maximum %B</th>
<th>Maximum %N</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs</td>
<td>1290</td>
<td>75</td>
<td>8</td>
</tr>
<tr>
<td>InP</td>
<td>1160</td>
<td>82</td>
<td>8</td>
</tr>
</tbody>
</table>

### TABLE II. - REFRACTIVE INDICES, n, AND EXTINCTION COEFFICIENTS, k, FOR BN FILMS DEPOSITED ON GaAs AND InP

[The wavelength is λ. Substrate temperature, 200 °C; ion beam energy, 500 eV.]

<table>
<thead>
<tr>
<th>λ, (Å)</th>
<th>BN-on-GaAs</th>
<th>BN-on-InP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n</td>
<td>k</td>
</tr>
<tr>
<td>4000</td>
<td>1.667</td>
<td>0.035</td>
</tr>
<tr>
<td>4300</td>
<td>1.661</td>
<td>0.044</td>
</tr>
<tr>
<td>4600</td>
<td>1.672</td>
<td>0.045</td>
</tr>
<tr>
<td>5000</td>
<td>1.663</td>
<td>0.050</td>
</tr>
<tr>
<td>5500</td>
<td>1.666</td>
<td>0.042</td>
</tr>
<tr>
<td>6000</td>
<td>1.662</td>
<td>0.033</td>
</tr>
</tbody>
</table>
FIGURE 1. - AUGER DEPTH PROFILE OF ION BEAM DEPOSITED BN-ON-GAAS. SUBSTRATE TEMPERATURE, 200 °C; ION BEAM ENERGY, 500 EV.
FIGURE 2. - Tauc plot, $(AE)^{1/2}$ versus $E$, for ion beam deposited BN-on-quartz. Substrate temperature, 200 $^\circ$C; ion beam energy, 500 eV.

FIGURE 3. - Coefficient of friction versus applied load. Ion beam energy, 150 eV; sliding velocity, 12 mm/min.
A low energy ion beam deposition technique was used to grow boron nitride films on quartz, germanium, silicon, gallium arsenide, and indium phosphide. The film structure was amorphous with evidence of a hexagonal phase. The peak boron concentration was 82 at %. The carbon and oxygen impurities were in the 5 to 8 at % range. Boron-nitrogen and boron-boron bonds were revealed by x-ray photoelectron spectroscopy. The index of refraction varied from 1.65 to 1.67 for films deposited on the III-V compound semiconductors. The coefficient of friction for boron nitride in sliding contact with diamond was less than 0.1. The substrate was silicon.