Surface composition of BN, CN, and BCN thin films

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(Received 6 November 1997; accepted 19 June 1998)

Boron nitride (BN), carbon nitride (CN), and boron carbon nitride (BCN) thin films were deposited on sapphire and silicon using ion beam and electron cyclotron resonance plasma assisted physical vapor deposition. *In situ* Auger electron spectroscopy was used to investigate the effect of different growth parameters and postgrowth processing on the thin film surface composition. The bulk composition was determined by electron energy loss spectroscopy and electron microprobe analysis. Both BN and CN films show thermal stability up to 900 and 700 °C, respectively. Low growth temperatures favor nitrogen incorporation in CN films and the optimum temperature for quasistoichiometric BN is between 450 and 600 °C, depending on the nitrogen sources. © *1998 American Vacuum Society.* [S0734-2101(98)05805-9]

I. INTRODUCTION

The need to realize devices which reliably operate in extreme environments requires the development of novel materials with appropriate properties. Owing to its excellent thermal conductivity and wide band gap, cubic boron nitride (c-BN) is a promising candidate for the fabrication of UV detectors and high temperature electronic devices. The extreme hardness of c-BN and the predicted hardness of the hypothetical compound β -C₃N₄ (Refs. 1 and 2) make them ideal for hard/inert coatings. Recent research has therefore focused on understanding the growth of these materials in thin film form. Interest in their tribological (high hardness, low friction), chemical (inertness), and electrical properties requires the understanding and the control of these properties. So far it is impossible to prepare pure single-phase *c*-BN and β -C₃N₄ thin films. Usually it is reported that the difficulty in their synthesis stems from nitrogen incorporation and phase control. However, several researchers have succeeded in the synthesis of thin films containing small crystals of c-BN under low pressure, by physical vapor deposition (PVD) or chemical vapor deposition (CVD) methods. The use of deposition techniques that supply energetic particles during growth is recognized to be essential to the synthesis of c-BN thin films. Such methods include dual ion-beam deposition,3,4 plasma-enhanced chemical vapor deposition,^{5,6} e-beam evaporation of boron combined with N_2/Ar ion bombardment, ⁷⁻¹⁰ rf sputter deposition of hexagonal BN (h-BN) with rf substrate bias¹¹ and ion beam assisted pulsed laser deposition.¹² As for CN, even though several groups¹³⁻¹⁵ claimed the synthesis of small grains of β -C₃N₄ embedded in an amorphous matrix, CN films are usually amorphous and nitrogen deficient. The boron carbon nitride (BCN) alloy is also regarded as a potentially interesting material because of the structural similarity of graphite and h-BN as well as diamond and c-BN. Despite the numerous reports on obtaining boron carbon nitrides in a variety of chemical processes using different precursors, there is still a lack of evidence that all or, at least, some of the reported B-C-N materials are substitutional solid solutions of all three elements rather than mechanical mixtures of graphite and hexagonal boron nitride both turbostratically distorted. There are few speculations on this particular matter along with a selection of approaches suitable for deciding or, more precisely, guessing the nature of the compounds obtained. Thus it is likely that, with this object in view, an accumulation of additional data from various experimental techniques are needed.

In this article, we report on the synthesis of BN, CN, and BCN thin films using ion beam and electron cyclotron resonance (ECR) plasma assisted physical vapor deposition. We describe the effect of growth parameters (i.e., ion beam current and energy, growth temperature) on the surface stoichiometry of the deposited thin films. The stability of the thin film surface under high vacuum annealing is also reported.

II. EXPERIMENTS

BN, CN, and BCN thin films were grown in a high vacuum reactor equipped with an Auger spectrometer. High purity graphite and boron were evaporated by electron beams and controlled by a quartz crystal monitor rate. The nitrogen species were delivered by two sources fed with high purity (99.9999%) N₂: a gridless End Hall ion source (Commonwealth Scientific Mark II) and an electron cyclotron resonance (ECR)-ASTEX plasma source. The End Hall ion source provides nitrogen species with energy from 20 to 100 eV and ion beam current from 30 to 300 mA. The ECR source operates at 2.45 GHz and a power from 0 to 250 W. This power range defines the kinetic energy range (from 4 to 20 eV) of the nitrogen species. The N_2 flow through the ECR source (varied from 2 to 5 sccm) is proportional to the flux density of the nitrogen beam. In ion-assisted deposition, the nitrogen beam used in the experiment consists of a mixture of N_2^+ and N^+ with typical $N_2^+/N^+=6$. In the ECR plasma

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source, and beside the radical species, approximately 10% of the molecular nitrogen gas is converted into atomic nitrogen.

BN, CN, and BCN thin films were deposited on 1-in.diam sapphire (0001) and silicon (001) oriented substrates. Prior to deposition, substrates were degreased using standard solvents, etched in an acid solution (HF and H_2SO_4/H_3PO_4 for silicon and sapphire, respectively), rinsed in de-ionized water, and dried with N2. The substrates were degassed in *situ* at 850 °C for 15 min at 10^{-8} Torr. The pressure during deposition was in the mid 10^{-4} Torr image. In situ Auger electron spectroscopy (AES) measurements were performed to check the cleanliness of the substrate prior to deposition and to determine the postgrowth surface composition. The relative atomic composition of the films was calculated from peak heights of the Auger KLL boron, carbon, and nitrogen transitions. Thickness was measured by an α -step profilometer. Electron microprobe analysis (EMPA) as well as electron energy loss spectroscopy (EELS) were used ex situ to determine the bulk stoichiometry of the thin films.

First, experiments were carried out to find out the evaporation rates for carbon and boron to maximize the nitrogen content. In this case, the End Hall ion source was used for nitrogen delivery. For both BN and CN, the ion beam current and energy were varied between 50–110 mA and 30–60 eV, respectively. An evaporation rate of approximately 0.1 Å/s for both carbon and boron yielded the maximum surface nitrogen content. Thus, for BN and CN, B and C evaporation rates were maintained at 0.1 Å/s, giving thin film deposition rates of approximately 100 nm/h for BN and 25 nm/h for CN. The thickness of both BN and CN thin films ranges from 100 to 400 nm. No effect of the incidence angle of the End Hall nitrogen beam relative to the substrate on the surface composition was found.

III. RESULTS

A. Boron nitride

To study the effect of the energy of the nitrogen beam on the surface composition, two films were deposited at 500 °C with the End Hall ion source using 40 and 60 eV at 190 mA total current, and two films were deposited at 450 °C with the ECR source using a power of 70 and 200 W at a 3 sccm N₂ flow. For both sources, the effect of the nitrogen beam energy on the surface stoichiometry was not significant. The influence of the End Hall ion beam current on the BN surface composition was studied in the 30-200 mA range. Figure 1 shows the results of the experiments performed for a nitrogen ion beam energy of 40 eV and a deposition temperature of 500 °C. The surface nitrogen content increases with the nitrogen ion beam current up to 110 mA to reach 42% of nitrogen and then remains essentially constant. With nitrogen delivered by the ECR source, two sets of experiments were performed at a fixed power of 75 W, and at temperatures of 450 and 500 °C. Figure 2 shows that, for both temperatures, the nitrogen content slightly increases in the 2-4 sccm range and then drops for 5 sccm. The optimum nitrogen incorporation (41%) is reached for a N₂ flow of 4 sccm. The influence of the growth temperature using both sources was also



FIG. 1. N/B atomic ratio as a function of the nitrogen ion beam current. The BN films are deposited at 500 °C and with a 40 eV nitrogen ion beam.

investigated. The nitrogen ion beam conditions were fixed at 190 mA and 60 eV. For the ECR source, a N₂ flow of 3 sccm and a power of 75 W were used. These data points are presented in Fig. 3. The best surface stoichiometry (43% N) is reached at 450 °C with the End Hall ion source and 600 °C with the ECR source (Fig. 3). The nitrogen surface composition is a complicated function of temperature. In order to determine the phase of our deposited BN films, Fourier transform infrared (FTIR) measurements were carried out on a BN film grown with the End Hall ion source (2500 Å thick). The spectrum is shown in Fig. 4. Two main absorption bands around 1380 cm^{-1} (in-plane B–N stretching) and 780-840 cm⁻¹ (out-of-plane B-N-B bending) are characteristics of h-BN. The first band was broadened and shifted toward lower wave numbers. An additional band at 1080 cm^{-1} could be attributed to the *c*-BN phase. The *c*-BN phase concentration in this film is estimated to about 30%.



FIG. 2. N/B atomic ratio as a function of the N₂ flow through the ECR. Comparison for BN thin films grown at 450 °C (\triangle) and 500 °C (\square). The films are deposited using an ECR power of 75 W.



FIG. 3. N/B atomic ratio as a function of growth temperature. Comparison for BN thin films grown using the ECR (\triangle) and End Hall ion (\Box) sources. The nitrogen ion beam current and energy were 190 mA and 60 eV, respectively. The ECR is set at 75 W and the N₂ flow at 3 sccm.

The surface thermal stability was investigated for a film grown using the End Hall ion source (at a beam energy of 60 eV and a beam current of 270 mA) at a growth temperature of 450 °C. As shown in Fig. 5, the BN film surface composition was stable over the temperature range 450-950 °C.

B. Carbon nitride

As in BN, the influence of the nitrogen energy, for either source, on the CN surface nitrogen content is insignificant. The dependence of the nitrogen content on the ion beam current in the 30–200 mA range is shown in Fig. 6. The surface nitrogen content in CN thin films increases sharply with the ion current up to 60 mA (reaching 15%) and then is relatively constant. The effect of the nitrogen flux from the ECR plasma on the surface stoichiometry was studied for CN films grown at a fixed power (80 W) and at room temperature (RT). As shown in Fig. 7, a maximum of 27% nitrogen was reached at a N₂ flow of 4 sccm. The influence of



FIG. 4. FTIR spectrum of a BN thin film deposited with the End Hall ion source (190 mA and 60 eV) at 500 $^\circ$ C.



FIG. 5. Surface thermal stability of BN and CN thin films: surface nitrogen content vs the annealing temperature. The data for BN (\Box) are from a film grown at 450 °C, using the End Hall ion source at 60 eV and 190 mA as nitrogen beam energy and ion beam current, respectively. Comparison for CN films grown using the ECR source at RT (\blacklozenge), 450 (\bigcirc), 650 (\blacklozenge), and 800 °C (\triangle). The ECR is set at 80 W and the N₂ flow at 4 sccm. The first point of each plot represents the composition of the as grown film.

the growth temperature on CN surface composition was also studied for both sources. As shown in Fig. 8, for both nitrogen sources, low deposition temperatures give a higher incorporation of nitrogen. We find also that the ECR source yields films richer in nitrogen as compared to the End Hall ion source. The highest nitrogen content (27%) was achieved at room temperature with the ECR source.

In order to study the thermal surface stability of CN thin films, experiments were carried out on CN films deposited at the optimized ECR conditions (80 W and 4 sccm) and at temperatures from RT to 800 °C. Figure 5 summarizes these results. The CN films are thermally stable up to 700 °C. A



FIG. 6. N/C atomic ratio as a function of the nitrogen ion beam current. These CN films were grown at 500 $^\circ$ C and using a 60 eV nitrogen ion beam.



FIG. 7. N/C atomic ratio in CN films as a function of the N_2 flow through the ECR source. These CN films are deposited using an ECR power of 80 W and at room temperature.

nitrogen loss is observed around 800 °C. The relative nitrogen loss, from annealing at growth temperatures up to 800 °C, of the CN thin films deposited at different temperatures decreases with increasing growth temperatures—from 48% at room temperature to 33% at 650 °C. Figure 5 shows also that an annealed specimen grown at low temperature always contains more nitrogen than the film grown at the same annealing temperature.

C. Boron carbon nitride

In the case of BCN film deposition, the carbon sublimation rate was 0.1 Å/s while the boron evaporation rate was varied. For these experiments, the nitrogen End Hall ion beam current and energy were 190 mA and 60 eV, respec-



FIG. 8. N/C atomic ratio as a function of growth temperature. Comparison for thin films grown using the ECR (\Box) and End Hall ion (\triangle) sources. The nitrogen ion beam current and energy were 30 mA and 60 eV, respectively. The ECR was set at 80 W and the N₂ flow at 4 sccm.



FIG. 9. Nitrogen (\bigcirc) and carbon (\Box) contents in BCN films as a function of the boron content. The boron evaporation rate was varied up to 0.1 Å/s and the growth temperature maintained at 500 °C. The nitrogen End Hall ion beam energy and current were 60 eV and 190 mA, respectively.

tively, and the growth temperature was 500 °C. A boron nitride layer was deposited first under the same conditions and its composition as measured by AES was found to have a N/B=0.63. As shown in Fig. 9, the surface nitrogen content increases with the boron concentration. Using the above ion beam conditions, BCN thin films were deposited at constant boron, carbon, and nitrogen rates but at different temperatures (RT to 700 °C). The surface nitrogen content was found to slightly decrease with the growth temperature, from 38.5% at room temperature to 35% at 700 °C.

IV. DISCUSSION

In the case of BN, both nitrogen sources gave a similar surface composition, with a maximum nitrogen concentration of 43%. In the case of CN, the surface is more nitrogen deficient, and is far from the desired stoichiometry (a maximum of 22% and 27% nitrogen with the End Hall ion and ECR nitrogen sources, respectively). For CN thin film deposition, the ECR source was more efficient than the End Hall ion source. The End Hall ion source was however superior for the production of BN thin films with good adhesion characteristics. Delamination of ECR-deposited BN films was usually observed after air exposure. Although no information on residual stress in our thin films is available, high flux bombardment from an energetic ion beam is most likely responsible for the enhanced adhesion properties of the films. This is even more relevant in the case of Si substrates where exposure to a nitrogen beam results always in the formation of a thin silicon nitride layer which can significantly reduce the adhesion characteristics of the surface. Our data suggest that the End Hall ion source appears to be a good compromise between the Kaufman-type ion source which delivers a more energetic beam that causes damage and significant resputtering, and an ECR source which delivers a very low energy plasma flux.⁹

As far as BCN thin film is concerned, the surface nitrogen content increases with the boron concentration. We found that the N/B ratio in this ternary is always higher than the one determined from BN thin films grown under the same conditions. Assuming that the nitrogen excess is allocated within C-N bonds, BCN thin films might achieve CN_r-like materials with higher nitrogen content than those attainable in binary CN compounds. CN compounds with a maximum of 27% nitrogen were achieved using the ECR source while nitrogen concentrations as high as 47% could be allocated to CN bonds in BCN ternaries grown with the ion beam source. The lower carbon (10% for films with high N%) incorporation rate compared to that of boron (46% in similar thin films), for identical evaporation rates is consistent with the higher difficulty to form CN than BN bonds. This is further supported by the observed growth rates for the binaries (100 nm/h for BN vs 25 nm/h for CN).

For both BN and CN thin films, regardless of the nitrogen source used, temperature is the growth parameter giving the greatest variation in the surface composition. However, CN and BN thin films have different optimum growth temperatures: room temperature for CN and 450–600 °C for BN.

The actual bulk versus surface composition in these B– C–N compounds was not systematically investigated in our studies. However, EELS and EMPA measurements performed on a few of these BN and CN films indicate a significant difference between the bulk and the surface composition. Chemical analysis from EELS and EMPA data yields a stoichiometric bulk N/B ratio and an oxygen content around 5% in a BN film grown with an End Hall ion source. *In situ* AES measurements on the same sample give a surface nitrogen content of only 40% and no oxygen. Similar to BN films, EELS measurements of a CN film yield a bulk nitrogen content of 30% (no oxygen) while AES gives a surface composition of 17% N and no oxygen (this film was deposited with the End Hall ion source using an energy of 40 eV and a beam current of 190 mA).

While materials with even higher nitrogen content are important for a variety of applications, the surface composition is a critical parameter that needs to be precisely controlled if one wants to develop tribological coatings based on BN–CN thin films materials. In fact, preliminary friction and hardness measurements on BN and BCN thin films on silicon and sapphire clearly show a correlation with the surface nitrogen

content.¹⁶ When compared to other deposition techniques, high vacuum methods should prove superior for these applications since the control and monitoring of the surface composition can be easily implemented.

V. CONCLUSIONS

The effect of growth parameters on the surface composition of BN, CN, and BCN has been determined by *in situ* AES measurements. In both BN and CN thin films, the growth temperature is the strongest factor controlling the surface composition. Adherent near-stoichiometry BN films were deposited at 450 °C with the End Hall ion beam while the ECR source achieved CN films containing 30% nitrogen. For both nitrogen sources, the surface nitrogen incorporation did not significantly vary with the energy or the flux of the species. BN and CN films show good thermal stability up to 800 °C under vacuum annealing.

ACKNOWLEDGMENTS

This work is supported by funds from a NASA cooperative agreement, No. NCC8-127, to SVEC and from an advanced research program from the state of Texas (ARP No. 1-1-27764). The authors would like to thank Dr. D. Starikov, Dr. A. Schultz and Dr. K. Waters for their help and support.

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