Hard boron–suboxide-based films deposited in a sputter-sourced, high-density plasma deposition system

C. Doughty[a] and S. M. Gorbatkin
Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

T. Y. Tsui and G. M. Pharr
Rice University, Houston, Texas 77005

D. L. Medlin
Sandia National Laboratory, Livermore, California 94551

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Boron–suboxide-based thin films have been deposited on Si in an electron cyclotron resonance microwave plasma using a radio frequency (rf) magnetron as a source of boron. Variations of the oxygen fraction in the deposition ambient and of the rf bias applied to the substrate were related to film tribology. The best films have hardnesses of ~28 GPa and moduli of ~240 GPa and were deposited in oxygen fractions <1% at substrate temperatures <350 °C. The films contain 4%–15% O and ~15% C, with carbon originating from the sputter target. They are amorphous and have surface roughnesses of ~0.2 nm. Boron–oxide films may form a self-generating lubricating layer of $B(OH)_3$ in ambient atmosphere. Compositional depth profiling of these films reveals an oxygen-enriched surface of ~10 nm thickness. Initial nanoscratch test results indicate that these films fail at high critical loads and have low friction coefficients relative to other hard coatings.
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I. INTRODUCTION

Abrasion resistant hard coatings find numerous technical applications and attract considerable research interest. The material properties required for a hard coating depend on the application envisioned, although hardness, modulus, and resistance to scratching are clearly important parameters. Boron, boron nitride, and boron carbide are generally hard, and also well investigated. Boron suboxides, B_xO, $x>1$,[1] are less widely known but merit attention on several grounds. Badzian has reported high-temperature/high-pressure synthesis of bulk $B_{22}O$ capable of scratching diamond {111} faces.[2] In addition, the boron surface can oxidize to B_2O_3 and react with ambient water vapor to form $B(OH)_3$, a layered compound which can function as a lubricant.[3] Thus, boron suboxide potentially forms an attractive tribological system consisting of a hard coating together with an integral lubrication layer.

Thin films of boron suboxide are poorly investigated at present. Boron–suboxide films have been previously deposited in an effusion-cell-sourced electron cyclotron resonance (ECR) microwave plasma deposition system.[4] These initial efforts resulted in films of hardness, $H\sim30$ GPa and modulus, $E\sim300$ GPa. An evaporative source is not ideal for scale-up, and, in addition, a number of fundamental process parameter/structure relationships were not addressed in this early work.

This article describes new results obtained on a sputter-sourced system. Adopting a sputter source changes the energetic particle bombardment of the growing film in several ways. First, an evaporative source is characterized by thermal neutrals with energies ~0.2 eV, while sputtered neutrals have much higher energies ~1–10 eV. This decreases the probability of B ionization between the source and the substrate and, thus, the contribution of B ions to the depositing flux. Second, some small fraction of the high-energy (~500 eV) ions impacting the sputter target may be neutralized and reflected from the sputter target surface, resulting in a flux of high-energy neutrals away from the target. Depending on the mean-free path in the deposition ambient and the chamber geometry, some of these high-energy neutrals may reach the substrate with substantial energies. Third, with electronegative gases such as oxygen, negative ions formed at the target surface can be accelerated back into the plasma volume, resulting in high-energy negative ions. These also may reach the substrate, depending on the deposition conditions. Although these fluxes may be small, their high energies may make them important. Ions are also accelerated across the sheath separating the substrate from the plasma, but their energy is given approximately by the plasma potential, ~15 V for a low-pressure ECR discharge, and is substantially less than that of the reflected neutral and negative ions.

II. EXPERIMENT

Adopting a sputter source may also complicate the film composition. High-density boron targets (>50% theoretical density) are difficult to fabricate because of the high melting temperature of elemental B. Such targets have recently been fabricated[5] but remain expensive. The boron sputter target used in this work (Kurt Lesker, Inc.), was ~45% dense, and thus, contains significant porosity. X-ray photoelectron spec-

[a]Current address: PlasmaQuest, Inc., Richardson, Texas 75081; Electronic mail: cdoughty@plasmaquest.com

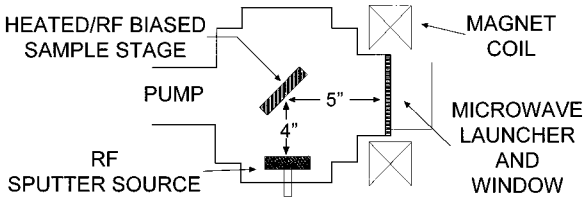

FIG. 1. Schematic of deposition system.

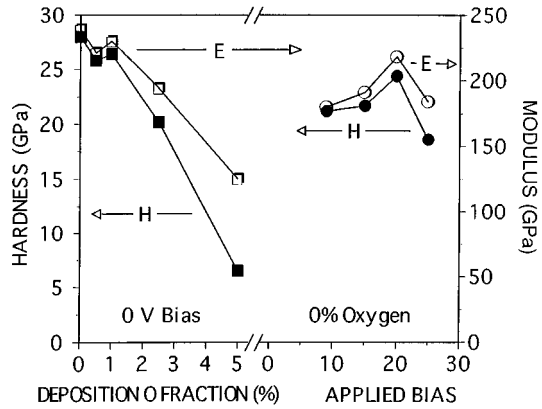

FIG. 2. Hardness and modulus as a function of oxygen fraction in the deposition ambient with no applied bias (left), and as a function of applied bias in 0% O (right).

troscopy (XPS) analysis indicated that the target used here contained ~12% O and ~30% C, even following a 10 min sputter clean with 1.5 kV Ar^+ ions, and after use in the deposition system for a total time of >10 h. Although the target is nominally 99.9% pure, this refers to starting materials, and includes only metallic impurities. The target was hot pressed in a graphite crucible providing one source of carbon contamination, and given the low density of the target, substantial C and O might also be present on the surface of the grains making up the target. The films deposited from these targets are composed primarily of B, O, and C. Boron carbide is also a hard material[6] and might increase film hardness. Films incorporating C are thus, imporant for both fundamental reasons, and because deposition of high quality films from low-cost/low-density targets has economic advantages.

The deposition system is illustrated schematically in Fig. 1, and is similar to the system used previously.[4] The chamber is a 25.4 cm cube. A coil electromagnet (168 turn, 30 cm diam) generates a dipole magnetic field centered on the microwave entrance window, 2.45 GHz microwaves are injected parallel to the magnetic-field lines and are absorbed in a region several cm from the inner window surface. The microwave power and magnet coil current were held constant at 1 kW and 200 A, respectively. Under typical deposition conditions, Langmuir probe measurements indicate that the plasma has an ion density $\sim 10^{11}-10^{12}/cm^3$ and electron temperature ~5 eV in the microwave absorption region.

Boron neutrals were supplied to the plasma by a 3 in. diam radio frequency (rf) biased magnetron source (Mighty MAK, U.S. Thin Film Products), which replaced the differentially pumped chamber and effusion cell used previously.[4] The source was operated at ~150 W rf, resulting in a deposition rate of 5 nm/min. Films were deposited to a thickness of 300 nm on Si (100) substrates introduced via a differentially pumped load lock to a sample stage mounted at 45° to both the microwave window and sputter source. The sample stage could be independently rf biased and heated. The substrates were cleaned by exposure to an Ar plasma for 10 min, and the source was presputtered for 5 min prior to beginning the deposition.

Previous experience with an evaporative source indicated that the oxygen fraction in the deposition ambient was an important process variable. In this study, microwave power, magnet current, and total pressure were held constant, and both the oxygen fraction in the ambient and the applied bias during deposition were systematically varied. Films were deposited in a 0.75 mTorr ambient consisting of 0%–5% O_2 in Ar. Total gas flow into the system was 6 sccm. The system was characterized by quandrupole mass spectrometry before and after individual deposition runs and had a base pressure of 2×10^{-8} Torr. The partial pressure of oxygen containing species ($<5\times10^{-9}$ Torr) was maintained at least three orders of magnitude below the oxygen partial pressure due to the process gas ($>5\times10^{-6}$ Torr). Following deposition, the films were cooled in vacuum to room temperature.

The temperature of the Si substrates was varied between 300 and 600 °C, but no systematic trend was observed. The films detailed below were obtained with no applied heating, in which case the substrate temperature was ~300 °C due to heating from the plasma. Lower temperature deposition on a cooled sample stage may allow deposition of hard films on polymer substrates and will be investigated in the future.

The hardness, H, and modulus, E, were measured as a function of indent depth between 20 and 100 nm by nanoindentation (Nanoindenter II) using the method of Oliver and Pharr.[7] The effect of varying the oxygen fraction during deposition (substrate floating) and of varying the substrate bias (0% O_2) on H and E measured at a depth of 20 nm are shown in the left half of Fig. 2. The films divide broadly into two types determined by the oxygen fraction during deposition. Films deposited at oxygen fractions >2.5% are relatively soft (~5 GPa), while those deposited at lower oxygen fractions are much harder, approaching 30 GPa. H and E are constant for oxygen fractions <1%.

The effect of substrate bias is also shown in Fig. 2. The substrates were rf biased at 0–20 W, generating a dc bias on the sample stage of 0–35 V with respect to the grounded chamber. At higher biases, sputtering of the film is substantial and for $V_B>30$ V, no net deposition occurs. A peak in H and E occurs at $V_B\sim20$ V.

The composition of the films was determined by XPS and was investigated as a function of depth by sputtering with a 1.5 kV Ar^+ ion beam. All samples were presputtered for 10 s to remove any surface contamination. The films consist primarily of B, O, and C. The oxygen content is determined

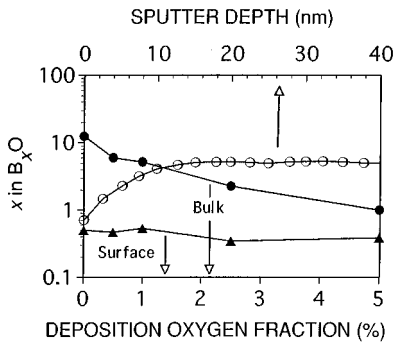

FIG. 3. Boron/oxygen stoichiometry at the surface and in the film bulk as a function of deposition ambient, and for film deposited in 1% O, as a function of depth.

by the deposition conditions and depth in the film. The carbon content is relatively constant at ~15 at. %.

The ratio of boron to oxygen (x in B_xO) is plotted in Fig. 3, both as a function of deposition conditions (bottom axis) and as a function of depth (top axis) for a film deposited in 1% O. At the surface, the composition is independent of deposition conditions and consistent with either B_2O_3 or $B(OH)_3$ stoichiometry. The bulk composition was determined by sputtering the film for 2 min with 1.5 keV Ar. In the bulk, x depends on the deposition conditions. For oxygen fractions <2.5%, x changes rapidly, although in this range H and E are relatively constant. Hard films can be obtained over a range of O stoichiometries and a wide process window exists over which hard films can be deposited.

A depth profile of a film deposited in 1% O is plotted in Fig. 3. The composition changes from ~B_2O_3 to ~B_5O over a depth of <10 nm. Prior to depth profiling, the film was stored in ambient atmosphere for six weeks, hence, the surface oxide is either self-passivating or oxidation proceeds slowly. $B(OH)_3$ generates spontaneously in the presence of atmospheric moisture on a B_2O_3 surface and has been proposed as a lubricating layer by Erdemir *et al.*[3] Such a self-generating layer may be desirable in tribological applications, provided the surface is also self-passivating and stable.

Adventitious carbon and CO species are evident at the surface of all the films. These may be removed with a short (10 s) sputter treatment at which point the films all contain ~15 at. % C due to C present in the sputter target. In the bulk, the carbon content and bonding are independent of depth, but do depend on the deposition conditions and oxygen content. In the softer, high oxygen content films, the carbon is bound as CC, CO, and CO_2 throughout the film bulk. This might be due to surface adsorption on a highly porous microstructure following exposure to the ambient. In the harder films, the carbon is carbide bound. The large values of H and the results of scratch tests presented below suggest that C incorporation results in films of higher hardness, and that controlled manipulation of the C content should be investigated in the future.

Fe was also incorporated in the films from sputtering of chamber fixtures during deposition, but can be eliminated by shielding areas prone to sputtering with a quartz liner, as was done for the series of samples in Fig. 2 deposited at varying substrate bias. For these samples, the Fe content is <0.1 at. %, while the hardness remained high, confirming that Fe incorporation is not necessary for high hardness.

Application of these films as hard coatings requires that the films have good long-term stability. Boron films tend to have high residual stress and may delaminate over a period of days. Films previously deposited in the ECR system with an evaporative source, however, show no change in H and E after ~18 months. The films are also insoluble in common acids (HNO_3, H_2SO_4, H_3PO_4, HF), alcohol, and water.

The structure and morphology of the films were investigated by transmission electron microscopy (TEM) and atomic force microscopy (AFM). The hardest films are extremely flat, with rms roughness ~0.19 nm over a $5 \times 5\ \mu m^2$ area as measured by AFM. Films deposited with both the sputter source and the evaporative source used previously[4] were also investigated by TEM. No significant differences were observed. Both have an amorphous structure evident in the bright-field image and are characterized by diffuse diffraction rings at positions of 2.1, 3.5, and $6.4\ nm^{-1}$, suggesting that both evaporated and sputtered films poses a similar local structural configuration. Softer films (H<10 GPa) deposited using the evaporative source contain crystalline inclusions of ~1 nm diam in an amorphous matrix.

The films deposited in this work appear to be quite promising for a variety of tribological applications. A summary of the mechanical properties of these films and of other materials utilized for similar applications is presented in Table I. Hard carbon $CH_x(x\sim0.2)$ and $CN_x(x\sim0.25)$ films of interest for hard disk applications[8] are included, as well as bulk boron, diamond,[9] and sapphire.[7] The B_xO films are characterized by relatively high hardness, however, this is only one parameter which tends to indicate scratch and abrasion resistance. In general, a low modulus is also desirable as it allows the given load to be distributed over a wider area. The combination H^3/E^2 has been proposed as a figure of merit by Tsui *et al.*[10] The boron–suboxide films have a much lower modulus than pure B, and a value of $H^3/E^2 = 0.38$ GPa exceeded only by diamond.

Nanoindentation is an essentially static procedure. A more realistic test of tribological performance involves translating the sample while ramping the load on the diamond tip: a scratch test.[11] By performing a low-load scan before and after the ramped load scratch, the resulting scratch may be profiled. From the lateral and normal forces, a friction coefficient (diamond tip on film) may be defined, while the load at which permanent damage to the film occurs defines a critical load. The results of scratch tests are also summarized in Table I. More complete results of nanoscratch tests as a function of various process parameters will be published elsewhere.[12]

The scratch test results show that boron suboxide may offer an important new tribological system. The friction coefficient is significantly lower than the other material shown

TABLE I. Comparison of boron–suboxide-based hard films and other hard coatings and hard materials.

Material	Hardness (GPa)	Modulus (GPa)	H^3/E^2 (GPa)	Friction coefficient	Critical load (mN)
Sputtered boron–suboxide film ($B_{x=6}O$)	28	239	0.38	0.081	>65
Hard carbon film ($CH_{0.2}$)[a]	17	175	0.16	0.15	39
Carbon nitride film ($CN_{0.25}$)[a]	25	225	0.31	0.12	59
Diamond[b]	100	1050	0.91	⋯	⋯
Boron[c]	35	470	0.19	⋯	⋯
Sapphire[d]	30	441	0.14	⋯	⋯

[a]Reference 8.
[b]Reference 9.
[c]Reference 4.
[d]Reference 7.

in Table I, perhaps reflecting a surface lubricating layer of $B(OH)_3$ or the extremely low surface roughness of sputtered B_xO films. In addition, the sputtered films tend to fail at high loads relative to the other films, and, when failure occurs, it does so in a relatively benign mode, which results in little debris. The high critical load and mode of failure are desirable traits for a variety of hard coating applications.

III. CONCLUSION

In summary, boron–suboxide-based thin films have been deposited in an ECR microwave plasma using a rf magnetron as a source of boron. The films have $H=28$ GPa and $E=240$ GPa, and were deposited in a <1% O, balance Ar, ambient at relatively low substrate temperatures (<350 °C). The stoichiometric coefficient x in B_xO can be controlled by varying the oxygen fraction in the deposition ambient. For $x>4$, however, the hardness remains uniformly high and, hence, the process should have a wide process window. The use of commercially available, low-density sputter targets may lead to significant C incorporation (~15%) due to C incorporation in the sputter target. The films remain hard, however, and these results may imply that C incorporation is beneficial and should be investigated systematically in the future. The films are amorphous and are extremely flat, with surface roughness ~0.2 nm. Initial nanoscratch test results indicate that these films fail at a high critical load and have a low friction coefficient relative to other hard coatings. These results are consistent with both the large value $H^3/E^2=0.38$ GPa measured and with the possible formation of a self-generating lubricating layer of $B(OH)_3$ at the film surface. XPS depth profiling confirms the existence of an oxygen-enriched surface of ~10 nm thickness.

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