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Structural and mechanical properties of $(B_{0.5-x}Si_x)N_{0.5}$ films synthesized by dual-ion-beam deposition

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The structural and mechanical properties of ion-beam deposited $(B_{0.5-x}Si_x)N_{0.5}$ films $(0 \leqslant x \leqslant 0.5)$ were characterized by x-ray photoelectron spectroscopy, infrared absorption experiments, and nanoindentation tests. A single-layer BN film $(x=0)$ has 70 vol. % in cubic phase (c-BN), and a hardness of 38 GPa. However, it peeled off very soon after deposition due to the high internal stress. If a buffer layer was deposited first, followed by a $(B_{0.5-x}Si_x)N_{0.5}$ film with $x \approx 0.013$, the whole configuration adhered very firmly to both quartz and silicon substrates. This improvement in adhesion was probably due to the formation of Si–N bonds, which served to release partly the stress inside the $(B_{0.5-x}Si_x)N_{0.5}$ films. Since the Si content was low, the film structure remained highly cubic, and there was no observable drop in hardness. For higher x, the cubic structure in $(B_{0.5-x}Si_x)N_{0.5}$ films disappeared rapidly and was replaced by a hexagonal structure. This structural change led to a rapid drop in hardness from 38 to 12 GPa. As x was further increased, more Si–N bonds were formed in the $(B_{0.5-x}Si_x)N_{0.5}$ layers. As a result, the hardness increased from the minimum value to a value ≈24 GPa.
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Cubic boron nitride (c-BN) has a strong potential for technical applications because it has the second highest hardness after diamond. c-BN films have been successfully synthesized by ion assisted techniques.[1,2] However, c-BN films are affected by high intrinsic internal stress, such that they are too brittle and difficult to grow to a thickness suitable for practical use.[3,4] Moreover, poor adhesion of c-BN films to silicon substrate was reported.[5] One approach to modify the film structure is to incorporate a third element into BN films. For example, the addition of titanium into BN produces a stable superhard Ti–B–N ternary system.[3,6] In this work, we initiated the study on the structural and mechanical properties of a new ternary system $(B_{0.5-x}Si_x)N_{0.5}$ $(0 \leqslant x \leqslant 0.5)$. This study is proposed based on the intuitive conjecture that the Si atoms incorporated may combine with some of the N atoms to form Si–N bonds so as to release partially the internal stress coming from the cubic structure. It is expected that the adhesion of the deposits to the substrate may thus be improved. Another reason to add Si is that it is one of the few elements which can generate sp^3 (σ) bonds, such that it is compatible with the zinc-blende structure of c-BN. The next purpose of this study is to see how the Si content affects the structure and the hardness of $(B_{0.5-x}Si_x)N_{0.5}$ films.

A series of $(B_{0.5-x}Si_x)N_{0.5}$ films have been prepared using a dual-ion-beam deposition system. The system consists of two 3 cm-filament-type Kaufman sources (Ion Tech., Inc. Model 3-1500-100), denoted as gun I and II, respectively. Gun I was used to preclean the substrate, and for surface assist during deposition. Gun II was used to sputter B and Si from a target, which was a 100 mm diam boron disk (ϕ 100 nm, purity≈99.9%) partially covered by a Si strip with a width L (inset to Fig. 1). By varying L, the Si content in the film can be adjusted. Quartz and p-type (100) silicon substrates were mounted on a resistively heated substrate holder at 500 °C, and were rotated at a rate of 2.7 rpm during deposition to ensure uniform film thickness.

Before deposition, the system was evacuated to 6×10^{-7} Torr, and the substrate was cleaned for ten minutes by an Ar^+/N_2^+ beam generated by gun I at a beam energy and current of 600 eV and 53 mA, respectively. The flow ratio $Ar:N_2$ was controlled by two mass flow controllers (MKS Model 1259) to be 1.4:1. The incident angle of the assist beam was 16° to the substrate's normal. To improve the adhesion of the $(B_{0.5-x}Si_x)N_{0.5}$ layer, a buffer layer was

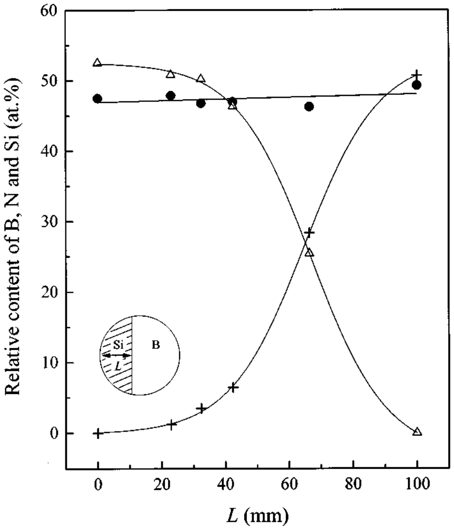

FIG. 1. Relative contents of B, Si, and N in $(B_{0.5-x}Si_x)N_{0.5}$ films as a function of the width, L, of the silicon strip partially covering the boron target. Δ B, + Si, ● N.

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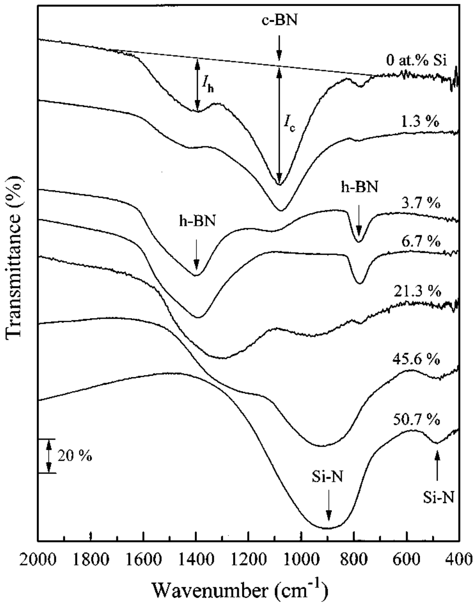

FIG. 2. FTIR spectra of $(B_{0.5-x}Si_x)N_{0.5}$ films with various silicon contents.

deposited on the substrate by sputtering the target with an Ar^+ beam (1200 eV, 70 mA) generated by gun *II*, meanwhile, the energy of the assist beam from gun *I* was increased from 200 to 360 eV (20 mA) in three equal steps (10 min each). In fact, the improvement of the adherence of *c*-BN films to Si by introduction of B and BN_x (x from 0 to 0.6) buffer layers was reported.[7] The thickness of the buffer layers was found to vary from 60 to 400 nm with increasing Si coverage on the target, due to the larger sputtering rate of Si. Finally, a $(B_{0.5-x}Si_x)N_{0.5}$ layer was deposited using the same operating conditions for the sputtering beam, but increasing the assist beam energy and current to 450 eV and 25 mA, respectively. The deposition time for this layer was 120 min. The thickness of the $(B_{0.5-x}Si_x)N_{0.5}$ films varied from 200 to 720 nm. Attached to each sample, a single buffer layer on silicon was deposited separately using the same procedures for preparing the buffer layer in the sample, which was used as a reference in the IR absorption experiment.

An x-ray photoelectron spectroscopy (XPS) (Kratos Analytical) was used to determine the composition of the $(B_{0.5-x}Si_x)N_{0.5}$ films. The spectra of B 1*s*, N 1*s*, Si 2*p*, and O 1*s* electrons before and after surface cleaning were recorded. The background of the spectra was first removed by Shirley's method.[8] The elemental contents were calculated from the areas under the spectrum lines and the sensitivity factors of B (0.13), N (0.42), Si (0.27), and O (0.66), respectively. The oxygen content detected before surface cleaning was high (10–40 at.%), but it was reduced to below 2 at.% after cleaning the surface by an Ar^+ beam (4 keV, 20 mA) for three minutes. It is seen from Fig. 1 that, as L increases from 0 to 100 mm, the Si content in the films increases from 0 to 50 at.%, whereas the boron content drops from 50 to 0 at.%, while the nitrogen content remains at about 50 at.% over the whole experimental range of L.

Figure 2 shows the infrared (IR) absorption spectra of the films with various Si contents (Nicolet's Magna-TR™ System 750). Each curve represents the net IR absorption of a $(B_{0.5-x}Si_x)N_{0.5}$ layer, obtained by subtracting the spectrum of a reference buffer layer (with silicon substrate) from the overall IR spectrum of the sample. As mentioned above, the reference buffer layer was produced separately by following the same procedures for preparing the buffer layer in the sample. First, the spectrum of the film with $x=0$ comprises a strong absorption band at 1090 cm^{-1} associated with the *c*-BN structure,[9] along with two small absorption bands at 800 and 1400 cm^{-1} related to the *h*-BN structure. This result indicates that the film consists mainly of a *c*-BN phase and a small fraction of *h*-BN phase. The volume fraction of *c*-BN phase ($\Phi_{c\mathrm{BN}}$) is estimated to be 70 vol. %, according to the expression proposed by Lu *et al.*:[10]

$$\Phi_{c\mathrm{BN}}=\frac{I_c}{I_c+I_h}\times 100,$$

where I_c and I_h are the peak heights at 1090 and 1400 cm^{-1}, respectively. Second, when x increased up to 0.013, the intensity of the band at 1090 cm^{-1} remained strong, indicating that at this low Si level, the structure of the $(B_{0.5-x}Si_x)N_{0.5}$ films was still mainly cubic. However, as x increased just slightly above 0.013, the intensity of the band at 1090 cm^{-1} reduced rapidly, and the bands at 800 and 1400 cm^{-1} associated to a hexagonal structure grew instead. This implies that the cubic structure in $(B_{0.5-x}Si_x)N_{0.5}$ layers was disrupted to become hexagonal, once the Si content in the films exceeded a threshold of about 0.013. When x was further increased to above 0.067, two absorption bands at 480 and 900 cm^{-1} associated with the vibrational modes of Si–N bonds emerged and became stronger, showing that $(B_{0.5-x}Si_x)N_{0.5}$ layers contained more Si–N bonds if more Si atoms were added.[11] On the other hand, the two bands associated to the hexagonal structure became smaller and finally completely disappeared when $x=0.5$. For $x=0$, an x-ray (Cu K_α) diffraction peak appeared at $2\theta=42.7°$, associated with the (111) planes of *c*-BN. It shifted to 42.2° and then disappeared as $x>0.067$, consistent with a structural change from *c*- to *h*-BN and the dissociation of the *h*-BN structure. Another peak at $2\theta\approx 30°$ has become observable as x increased to 0.013, showing that some Si–N domains have been formed at such a low Si content. Detailed analyses of the x-ray data will be reported elsewhere.

The hardness of the films was measured using a nanoindenter (Nano Instruments, Inc., Model IIs). For each sample, indents with different depths ranging from 30 to 100 nm were made, with each depth to be repeated for ten times at different positions on the film surface to give an average. The results of shallow indents are not sensitive to the indentation depths, indicating that if there is substrate deformation, it's influence must be negligibly small in the hardness measurements. Consequently, the results obtained at depths around 40 nm ($\leqslant$1/5 of the film thicknesses) are used to represent the film hardness, which are shown as a function of Si content in Fig. 3. First, pure BN films with $x=0$ have a hardness of 38 GPa, which is comparable with that of *c*-BN as reported by some authors.[12] Indeed, the films are highly cubic as revealed by the results of IR experiments. Probably due to the high internal stress, *c*-BN films peeled off completely about one or two days after deposition if no

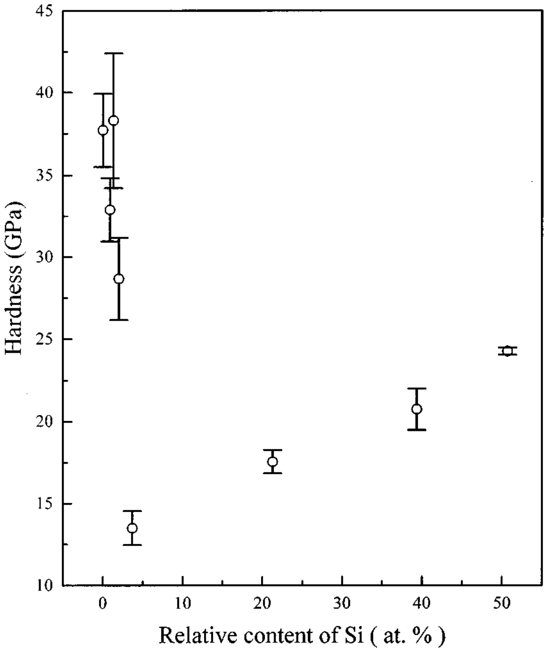

FIG. 3. The plot of the hardness of $(B_{0.5-x}Si_x)N_{0.5}$ films versus silicon content.

buffer layers were added. Even after adding buffer layers, *c*-BN films still completely peeled off from silicon substrate, or partially peeled off from quartz substrates two weeks after deposition. However, if small amount of Si ($x \approx 0.013$) was incorporated, $(B_{0.5-x}Si_x)N_{0.5}$ films would adhere very firmly to both quartz and silicon substrates. The most important point is that such a low level of Si incorporation does not affect the cubic structure in $(B_{0.5-x}Si_x)N_{0.5}$ films. As a result, the hardness does not have an observable drop, and remains the same as that of *c*-BN films ($\approx$38 GPa). This can be explained by assuming that the Si atoms incorporated may form Si–N bonds, which serve to release partially the internal stress associated with the cubic structure. For $(B_{0.5-x}Si_x)N_{0.5}$ films with x between 0.013 and 0.067, the hardness dropped steeply to a minimum of 12 GPa, consistent with the rapid change from cubic structure to hexagonal structure as confirmed by the IR data. This feature can be understood if we accepted the suggestion that compressive stress is required in order to form *c*-BN structure,[13] and hence the addition of more Si content into the $(B_{0.5-x}Si_x)N_{0.5}$ films would eventually reduce the internal stress to a level that the cubic structure cannot be sustained. Finally, as $x > 0.067$, the hardness increased progressively from the minimum value towards 24 GPa, and can be attributed to the increase in the fraction of Si–N bonds in the films.

In conclusion, $(B_{0.5-x}Si_x)N_{0.5}$ films were synthesized by ion beam deposition. When $x = 0$, the films have a predominantly *c*-BN structure and a hardness of 38 GPa. However, they peeled off very soon after deposition due to the high internal stress. Good adhesion was achieved if a small number of Si atoms ($x \approx 0.013$) were incorporated into the films, thereby partially releasing the stress by the formation of Si–N bonds. For Si content $\leqslant$1.3 at. %, both cubic structure and hardness were not affected. For higher Si content, the cubic structure in the $(B_{0.5-x}Si_x)N_{0.5}$ films disappeared and a hexagonal structure dominated, since the internal stress was further reduced to a level that the cubic structure cannot be sustained. Accompanied by this structural change, the hardness dropped to a minimum value of 12 GPa. For further increase in Si content, the hardness approaches that of silicon nitride (24 GPa), as a result of the formation of a large number of Si–N bonds.

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