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BCN thin films near the B_4C composition deposited by radio frequency magnetron sputtering

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Abstract

Materials with composition within the system B–C–N are very interesting because they are expected to combine some of the excellent properties of BN, B_4C and C_3N_4. In this work our interest is focused on the region around B_4C in the B–C–N composition diagram. Films were deposited by radio frequency magnetron sputtering using a target of sintered B_4C. A mixture of Ar and N_2 was used as the plasma gas at a constant working pressure of 2×10^{-3} mbar, and with variable N_2/Ar composition. The substrate was heated to 500°C. Film composition, structure, and mechanical properties are presented. As the N_2/Ar content in the plasma gas is varied from 0 to 10%, both secondary ion mass spectroscopy and X-ray photoelectron spectroscopy analyses show a continuous increase in the nitrogen incorporated into the film. From the Fourier transform IR spectra, a structure evolution from B_4C towards h-BN can be deduced. Film growth rate increased from 0.5 μm/h to 1 μm/h, whereas film stress decreased from 5 GPa to 2 GPa, and film hardness also decreased from 26 GPa to 12 GPa. From these results, a suitable value of the N_2/Ar plasma gas composition can be selected in order to deposit films with a satisfactory low stress while keeping a sufficiently high hardness, as required in hard coating applications. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Carbides; Hard materials; Magnetron sputtering; Thin films

1. Introduction

Materials with composition within the system B–C–N are very interesting because they are expected to combine some of the excellent properties of BN, B_4C and C_3N_4.

Most of the studies reported on the deposition of BCN thin films deal with chemical vapor deposition techniques, which use different chemical precursors and, usually, high deposition temperatures. These films generally present a miscellaneous composition — mostly high carbon content — and low hardness. A good selection of references can be found in some recent papers [1,2].

The attempts to deposit BCN thin films by physical vapor deposition techniques are almost limited to reactive sputtering. The most simple and natural way to achieve this is using either a B_4C target and a plasma gas that contains N_2, or a BN target and a plasma gas containing some C compound.

BCN films from a hexagonal boron nitride target were deposited [1] by reactive radio frequency (rf) magnetron sputtering in 0.05% acetylene/argon atmosphere at a gas pressure of 2×10^{-2} mbar. The films consisted in a mixture of c-BN, amorphous carbon and amorphous boron in B_5CN_3 stoichiometry.

BCN films from a B_4C target in an argon/nitrogen atmosphere were deposited in reactive processes by rf diode sputtering at a gas pressure of 0.4 to 2.7 Pa [3], and at a gas pressure of 2.7 Pa [4], by DC-magnetron sputtering at a gas pressure of 0.4 Pa [5] and at a gas pressure of 0.5 Pa [6]. Even though materials with different composition were indeed obtained in these studies, the common principal goal of these researches was to find the specific conditions to deposit almost pure c-BN. Little or no attention was devoted to the material deposited in other conditions.

In this work we present the results of the deposition of BCN thin films by reactive rf-magnetron sputtering of a boron carbide target in an argon/nitrogen atmosphere. In previous papers [7,8] we reported the deposition of hard B_4C thin films under different ion

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bombardment conditions in an argon atmosphere. Our interest is now focused on the systematic study of the evolution of the constitutive and mechanical properties of the variable composition BCN material resulting from a progressive incorporation of nitrogen to the sputtered B_4C. A suggestive aspect of this work is the possibility of decreasing the high intrinsic stress common to high hardness films by incorporating nitrogen in low concentration.

2. Experimental details

Films were deposited by rf magnetron sputtering, using a 3 in diameter target of sintered boron carbide B_4C on the cathode, powered to 300 W rf (13.56 MHz). The chamber base pressure was below 10^{-4} Pa. A mixture of N_2 and Ar was used as processing gas. Two independent mass flow controllers regulated both fluxes. The total working pressure was 0.20 Pa, and the deposition time was 1 h. A set of samples was deposited with different N_2/Ar plasma gas compositions ranging from 0 to 10%, which covers the range in which increasing nitrogen concentration in the plasma gas leads to increasing nitrogen incorporation in BCN films deposited by rf diode sputtering [3]. The target was submitted to a pre-sputtering process for 30 min in order to stabilize the negative voltage developed at the target.

The substrate holder was 5 cm away from the target and was heated by a quartz lamp to a substrate temperature of 500°C. Polished c-Si crystalline wafers were used as substrates. The intensity of the ion bombardment during the film growth was controlled by the 'tuned substrate' technique, which is described in detail elsewhere [9]. This technique allows a fine external control of the DC bias voltage V_{S0} developed at the anode, from a positive value of some few tens of volts to a negative value slightly greater than a 100 V even for insulating materials. For the purpose of this work, we selected a fixed value close to the antiresonant condition, which corresponded to a substrate bias of +15 V (referred to ground). In this way the intensity of the ion bombardment on the growing film is minimized and so the intrinsic mechanism of nitrogen incorporation from the plasma to the film can be studied. As the value of the plasma potential V_{P0} for our conditions is 40 V, and $V_{PS}=V_{P0}-V_{S0}$, the corresponding Ar^+ average energy bombarding the sample during growth was 25 eV.

Film thickness and stress-induced curvature were measured by a Dektak 3030 surface profiler. Films were characterized by X-ray photoelectron spectroscopy (XPS), secondary ion mass spectroscopy (SIMS), Fourier transform (FT) IR and Raman spectroscopies. Stress was calculated from the substrate curvature by Stoney's equation [10]. Microhardness and Young's modulus were evaluated by the dynamical microindentation technique as previously reported [8]

3. Results and discussion

Fig. 1 shows the strong effect of increasing the N_2 content in the plasma gas from 0 to 10% on the film growth rate. A linear dependence is observed in which the value for pure B_4C films increases by a factor higher than two for BCN films deposited with an N_2/Ar of 10%. This behavior indicates a highly effective mechanism by which N^+ ions are incorporated to the growing film together with the B and C atoms sputtered from the B_4C target. This result is confirmed by XPS compositional measurements. Fig. 2 shows the dependence of the film composition on N_2/Ar plasma gas composition. It can be seen that the nitrogen content in the film increases as N_2/Ar plasma gas composition increases, from an initial value of zero (pure B_4C film) to saturation at a value of about 40% for N_2/Ar gas concentrations higher than 6–8%. Boron-to-carbon composition remained constant at B/C=4. This composition can be described as B_4CN_x $(0<x<3)$, and follows a straight line in the B–C–N triangle composition.

SIMS depth profiles of all our samples revealed a good uniformity of composition over the whole thickness of the film. The boron and carbon signals remained constant for all the samples, whereas the nitrogen signal increased for films deposited under a more nitrogen-rich N_2/Ar atmosphere. Even though SIMS analysis is not quantitative due to matrix effects, a good linear correlation is found in our samples between the nitrogen content measured by XPS and the SIMS nitrogen signal.

Fig. 3 shows the FTIR spectra of the deposited B_4CN_x films. A clear evolution is observed as nitrogen

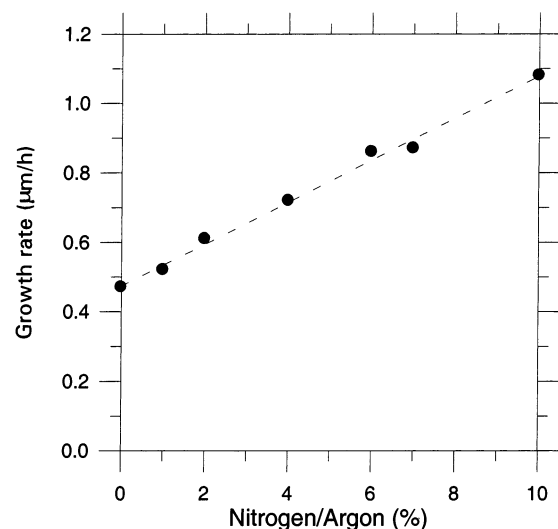

Fig. 1. Dependence of BCN film growth rate on nitrogen/argon plasma gas composition.

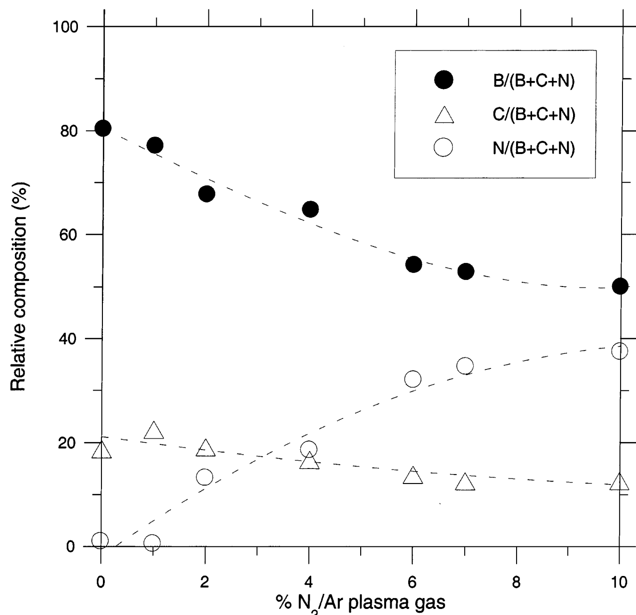

Fig. 2. Dependence of B, C and N relative atomic composition in BCN films on nitrogen/argon plasma gas composition.

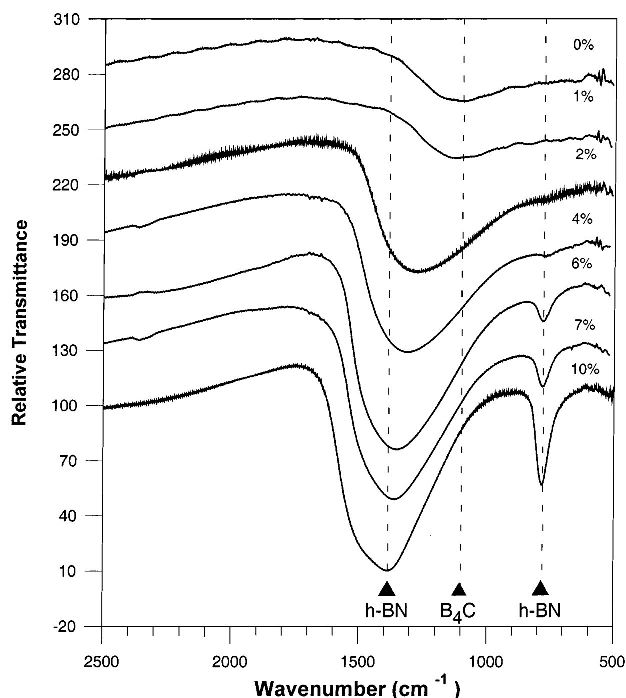

Fig. 3. FTIR spectra evolution of the BCN films deposited with different nitrogen/argon plasma gas composition. The spectra have been shifted but not scaled.

content increases in the films. The single strong absorption band near 1100 cm^{-1} for the film deposited in pure Ar is characteristic of the icosahedral vibrations in the B_4C structure, and corresponds well to the measured composition in this film. Films with nitrogen content higher than 20% present a clear and progressive contribution of peaks at 780 cm^{-1} and 1385 cm^{-1}, which can be attributed to the formation of hexagonal boron nitride (h-BN). Films with nitrogen content lower than 20% present a single band that shifts from 1100 cm^{-1} to 1300 cm^{-1}. The origin of this shift may be explained either by a distortion of the B_4C structure caused by the incorporation of N (B_4C:N films), or by the overlap of the B_4C band at 1100 cm^{-1} and the h-BN peak at 1385 cm^{-1}. As a preferential orientation cannot be expected, the absence of the h-BN peak at 780 cm^{-1} suggests B_4C:N as the most likely structure. As no other peak was detected, the presence of C—N bonds can be ruled out.

In order to determine the state of the chemical bonding we have studied the XPS spectra of the BCN films. The B 1s and C 1s core-level XPS spectra for pure B_4C film can be deconvoluted into single peaks centered at binding energies of 188 eV and 282.5 eV respectively, which are characteristic of the B—C binding energy in the B_4C structure. For films with increasing nitrogen content, a second contribution to the B 1s spectrum appears at 190.4 eV that becomes the dominant contribution for the film with 40% of nitrogen content, and can be assigned to B—N binding energy. At the same time, the N 1s spectrum shows an increasing peak at 397.6 eV corresponding to the N—B binding energy, and the C 1s spectrum shows a second contribution at 284.6 eV, which is assigned to non-polar C—C bonds such as graphite.

The Raman spectra of boron carbide and boron nitride are difficult to measure, because the Raman effect is very weak and probably affected by structure distortions in low crystalline thin films. Only signal corresponding to the highly Raman-sensitive carbon was detected in some of our films (Fig. 4). These spectra are very similar to that of amorphous carbon, with two bands centered at 1583 cm^{-1} (G band) and at 1352 cm^{-1} (D1 band). The pure B_4C film shows a flat spectrum, whereas the films with increasing nitrogen content show spectra with increasing intensity, which evidence the presence of amorphous carbon regions in them.

The results of the characterizations of our B_4CN_x films can be explained as a phase separation mechanism, analogous to that observed in films with B_5CN_3 stoichiometry, deposited by rf-magnetron sputtering of an h-BN target for which carbon is incorporated from the plasma gas [1]. The B and C atoms sputtered from the target arrive at the substrate in a ratio of 4:1, together with a flux of low energetic N^+ and Ar^+ ions and N_2 molecules. As the nitrogen gas concentration is increased, an increasing amount of nitrogen is available to be incorporated in the growing film. Boron binds preferably to nitrogen than to carbon, leading to the formation of a mixture of h-BN and B_4C with increasing h-BN content, which explains the nitrogen content increase and the evolution of the FTIR spectra. On the

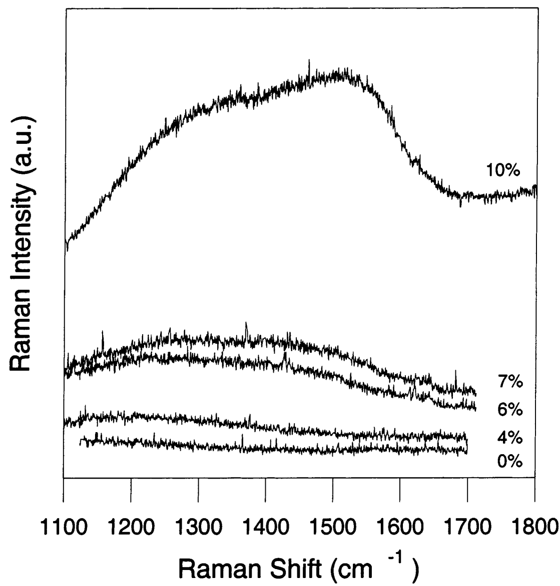

Fig. 4. Raman spectra evolution of the BCN films deposited with different nitrogen/argon plasma gas composition. The spectra have been shifted but not scaled.

other hand, the results of the Raman characterization suggest that the excess of C not bound to B is present as amorphous carbon. There is no evidence of the presence of C—N bonds in our samples.

Fig. 5 shows the stress in the BCN films as a function of its nitrogen content. Films present a compressive stress that decreases quickly from 5 to 2 GPa as nitrogen is incorporated into the film up to a concentration of 30%, and remains practically constant for higher N concentrations corresponding to a high h-BN and amorphous C content. On the other hand, nanoindentation measurements indicate that hardness remains almost constant at 25–26 GPa up to a nitrogen content of 15% and decreases to 12 GPa for films with higher nitrogen content.

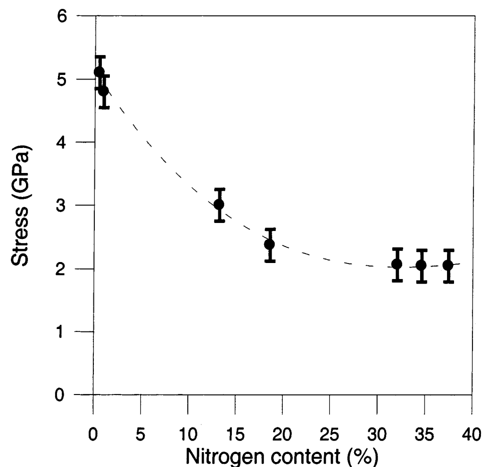

Fig. 5. Dependence of compressive stress on N/(B+C+N) relative atomic composition in B_4CN_x films (B/C=4).

From the results of our study, a value of 2% for N_2/Ar plasma gas composition can be selected as the optimum deposition parameter, from the point of view of practical applications of our B_4CN_x films as hard coatings. Films deposited under this condition present practically the same high hardness (25 GPa) as pure B_4C films, they have a growth rate 20% higher (0.6 μm/h) and a much lower stress (3 GPa).

4. Conclusions

BCN films deposited by reactive rf-magnetron sputtering of B_4C in a nitrogen/argon atmosphere show a highly efficient nitrogen incorporation mechanism. As the N_2/Ar is varied from 0 to 10%: (a) the N content in films increases from 0 to 40%, while keeping constant the relative atomic composition B/C=4; (b) film structure changes from B_4C to a mixture of h-BN and amorphous C; (c) film stress and hardness values change with a different rate, showing an optimum value for hard coating applications at an N_2/Ar plasma gas composition of 2%.

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