Preparation and characterization of thick cubic boron nitride films

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Cubic boron nitride (c-BN) films are prepared by the radio frequency magnetron sputtering technique. The stresses and crystallinities of the films are estimated by the Fourier transform infrared spectroscopy of c-BN samples, including the peak shifts and varieties of full widths at half maximum. The effects of the B–C–N interlayer and the two-stage deposition method on the c-BN films are investigated. Then the thick and stable c-BN films are prepared by a combination of the two methods. The properties of the interlayer and film are also characterized.

Keywords: cubic BN films, B–C–N interlayer, stress, hardness

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1. Introduction

The cubic boron nitride (c-BN) films have many desirable properties and have been used in many industry fields.[1–5] One of the promising application fields, which has long been expected, is to use the c-BN film as a protective coating for cutting tools, because it possesses outstanding mechanical properties such as high hardness, wear resistance, and chemical inertness to ferrous metals at high temperatures.[2–6] The films are always required to be thick enough in order to play a protective role. One of the great hurdles, which restricts its practical usage, is the high compressive stress and the poor adhesion to most of the substrates.[7,8] For a long period, it has been difficult to prepare thick c-BN films with high quality. The conventional physical vapor deposition (PVD) technique can produce only a few hundred-nanometer thick films. Yang *et al.*[8] reviewed the latest progress on the main problems for the preparation of c-BN films and discussed the prospects. How to prepare thick c-BN film with good adhesion on different substrates is one of the most potential directions.

During the past decades, a couple of techniques have been proposed in order to reduce the high stress and improve the adhesion between the c-BN film and the substrates. These techniques include the high temperature deposition,[9] two-stage deposition process,[10] and the addition of a third element such as a small amount of oxygen,[11] hydrogen,[7] and silicon.[10] Besides, various gradient interlayers have been used to improve the film-substrate adhesion. These interlayers include a hexagonal boron nitride (h-BN) buffer layer,[12] a BN_x gradient layer,[13] the ternary B–C–N buffer layers, etc.[7,14]

Fan *et al.*[10] have made a comparison among several stress relief methods for c-BN films deposited by the ion beam assisted deposition technique. It is shown that the combination of the addition of Si with the two-stage deposition process is more favorable for not only reducing the stress but also improving the c-BN crystallinity. They claimed that the production of high quality thick c-BN films should be feasible by a combination of several stress relief methods.

It has been widely reported that the addition of a buffer layer is an effective way to reduce the compressive stress in c-BN films.[7,12–14] Many researchers suggested that the parameter spaces of c-BN nucleation and growth are different; it is feasible to reduce the parameter thresholds within certain limits after the nucleation for the subsequent growth of c-BN.[15,16] Thus a two-stage deposition process, under different nucleation and growth conditions, was adopted to prepare c-BN films with less stress and a higher quality.[10,16] In this work, we prepare thick c-BN films by a combination of two methods: the addition of a B–C–N buffer layer and a two-stage deposition process, during which the substrate bias decreases when the deposition transits from the first to the second stage. First of all, we try to prove the effect on the stress relief of the single method experimentally. The properties of the deposited thick c-BN films are characterized.

2. Experimental details

Cubic BN films were deposited on Si substrates by radio frequency magnetron sputtering. The deposition process included the depositions of the interlayer and the c-BN top layer. The details of the sputtering system have been described in Ref. [17]. The targets were carbon and sintered h-BN (with a purity of 99.99%). The working gases were Ar and N_2 (both with a purity of 99.99%). The substrate was subjected to DC bias voltage. Commercially available (100) oriented Si wafers were used as the substrates. These substrates were

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cleaned ultrasonically in ethanol and then in an acetone bath thoroughly. The background pressure before deposition was less than 5×10^{-3} Pa. The deposition procedure started from Ar^+ cleaning and etching of the substrate for 30 min.

During the etching stage, a higher substrate bias (−500 V) was employed. The deposition of the B–C–N interlayer with an h-BN target and a carbon target was proceeded after etching. There are two key points that should be noted: first, for the deposition of the B–C–N layer, we need to control the power of the carbon target and the gas flow rate of nitrogen so as to form a compositional gradual change between the different layers; second, for the deposition of the c-BN layer, the substrate bias was reduced after the nucleation of the c-BN phase.[14,18] The details of the deposition procedure are demonstrated in Fig. 1.

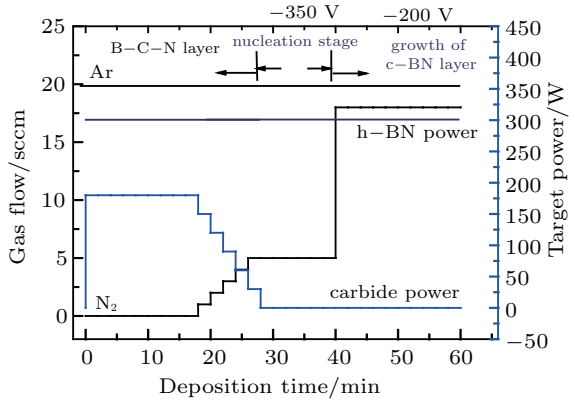


Fig. 1. (color online) The illustration of the deposition details for the thick c-BN films.

For the deposition of the B–C–N layer, the powers for the BN and C target were 300 W and 180 W, respectively. After 18 min, the power of the C target was stepwise reduced down to 0 W in steps of 30 W. The flow of N_2 was stepwise increased up to 5 sccm in steps of 1 sccm. The deposition time for the gradient layer was about 30 min. In the nucleation stage, the C target was switched off while the flow rate of N_2 was fixed at 5 sccm. The substrate bias was fixed at −350 V. This stage was sustained for 10 min.[14] In the growth stage of c-BN film, the flow rate of N_2 was increased to 18 sccm. In order to obtain films with different thickness values, we carried out a couple of experiments with different deposition times. The flow rate of Ar was fixed at 20 sccm during the whole process. In the present paper, three series of films were synthesized. Firstly we prepared a series of films, each with or without interlayer to investigate the effect of the interlayer. Secondly we prepared a series of films at different substrate biases to investigate the effect of the two-stage deposition process. Thirdly we prepared c-BN films by a combination of these two methods.

After deposition, part of the samples were exposed to the atmosphere to check the long-term stability and, for selected samples, structural and mechanical tests were carried out. The thickness values of the films were estimated by profilometry on selected samples. The values of c-BN content,[19] film stress,[20] and the crystal quality[21] were characterized by Fourier transform infrared (FTIR) spectroscopy. The bonding state of the ternary B–C–N interlayer was investigated by X-ray photoelectron (XPS) spectroscopy. The hardness was investigated by Nano-indenter II. Each sample was measured nine times, from which we obtained an averaged value.

3. Results and discussion

3.1. FTIR results: the addition of B–C–N interlayer

The peak position of the c-BN phase depends strongly on the film stress,[20,22] so we can use FTIR to obtain information about the stress in the films. A lower internal stress in the film will lead to a lower IR peak position.[20] First, we prepared c-BN films, each with or without a B–C–N gradient layer to check the effect of the interlayer. The results of the FTIR spectra are shown in Fig. 2.

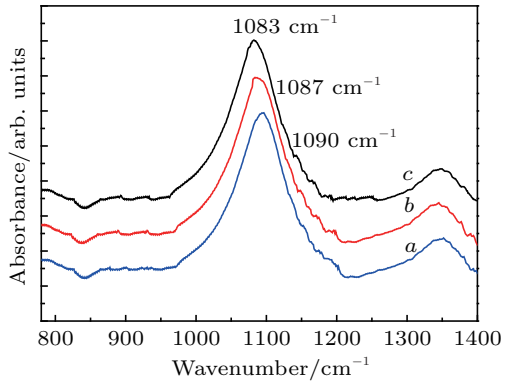


Fig. 2. (color online) The FTIR spectra of c-BN film (curve *a*) without B–C–N interlayer, (curve *b*) with a 150 nm B–C–N interlayer, and (curve *c*) with a 240 nm B–C–N interlayer. The thickness of c-BN film is 600 nm.

In order to eliminate the effect of film thickness on the c-BN peak position,[10] we adjusted the thickness to be 600 nm under monitoring the deposition time. For the sample that directly deposited on the substrate, the peak position is 1090 cm^{-1}; for the sample with a 150-nm B–C–N interlayer, the peak position is 1087 cm^{-1}; for the sample with a 240-nm interlayer, the peak position is 1083 cm^{-1}. One can see that sample curve *c* has the lowest peak position. So the addition of a B–C–N interlayer with a thickness of 240 nm has the best result. In the following experiments, we chose the thickness value of the interlayer to be 240 nm for the films.

3.2. Two-stage deposition process

In the two-stage deposition process, we prepared the second series of c-BN films on BN seed. The growth was initiated by setting the technique parameters (the temperature of the substrate, the flow rates of N_2 and Ar, the substrate bias) at

optimization values. We found that a bias of −350 V produced the largest sp3 binding content. So the initial phase growth of the c-BN nucleation was carried out at this bias. After the growth of the template layer, the bias voltage was reduced to −350 V, −300 V, −250 V, and −200 V. It is known that the growth rates are different for different substrate bias voltages. Generally at a lower substrate bias voltage we can obtain a higher deposition rate.[22] To make sure that the changes in c-BN FTIR peak position and peak width are not dominated by the change of film thickness, we grew these films for different growth times so as to obtain films with the same thickness.

The effects of the substrate bias on the c-BN peak position and the full width at half maximum (FWHM) of c-BN TO mode are shown in Fig. 3. It can be seen that when the substrate bias varies from −350 V to −200 V, the peak position of c-BN film moves from 1086 cm^{-1} to 1082 cm^{-1} correspondingly, which means that the stress decreases. Meanwhile the decreasing of the full width at half maximum (FWHM) from 134 cm^{-1} to 118 cm^{-1} is observed with substrate bias decreasing in the second stage, which indicates an improved crystalline in the c-BN film.[22]

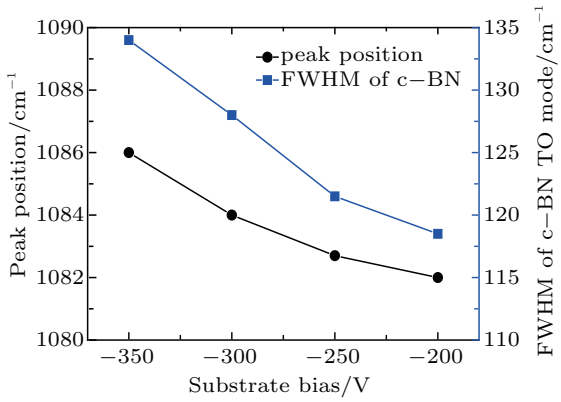


Fig. 3. (color online) Shifts of c-BN peak position and the FWHM of the TO mode of the c-BN films, each as a function of substrate bias in the second stage. The films were prepared in the two-stage deposition process.

The above experimental results show that both of the methods (the addition of the gradient B–C–N interlayer and the two-stage deposition method) can reduce the stress of c-BN film to some extent. The two stage deposition process is effective not only in reducing the stress of c-BN film, but also improving the crystallinity. Therefore, the combination of the two methods should be more favorable for preparing the c-BN film with low stress and high quality.

3.3. Combination of interlayer and two stage process

We prepared the third series of films by combining the two methods. The thickness values of the films are 0.4 μm, 1.2 μm, and 1.8 μm, respectively. Figure 4 shows the FTIR spectra of the films with different thickness values.

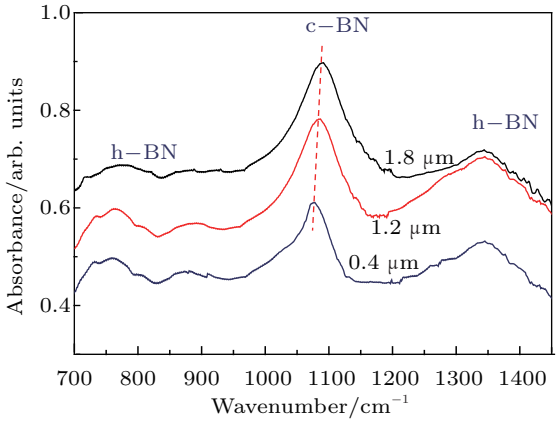


Fig. 4. (color online) The FTIR spectra of the top c-BN layers.

Strong peaks at 1076 cm^{-1} (for 0.4 μm), 1079 cm^{-1} (for 1.2 μm), and 1081 cm^{-1} (for 1.8 μm) can be reasonably assigned to the sp3-coordinated c-BN. The absorption bands at 1380 cm^{-1} and 780 cm^{-1} are known to be indicative, respectively, of the in-plane B–N stretching mode and the out-of – plane B–N–B bending mode for the sp2-bonded boron nitride structure.[18] The c-BN phase content (volume fraction) can be estimated from the relative intensities of c-BN (∼1080 cm^{-1}) and h-BN (∼1380 cm^{-1}).[5] The c-BN content values are 52%, 56%, and 85% for the 0.4 μm, 1.2 μm, and 1.8 μm thick films, respectively. Also, as shown in Fig. 4, the peak position shifts toward a higher wave-number with the thickness of c-BN film increasing.[13] There have been different results of the peak positions in c-BN films, each without internal stress, calculated by different theoretic models.[23–25] According to the models in Refs. [20] and [23], the shift of IR peak position with stress is 4.5 cm^{-1} per GPa. So we can conclude that the stress increased only 1.1 GPa for the thick film compared with the thinner film, while the content value of c-BN increases dramatically (from 52% to 85%). The combination of the two stress relief methods plays a positive role in reducing the compressive stress of the c-BN film. Other properties of the third series films (XPS and hardness) are characterized as below.

3.4. XPS results of B–C–N interlayer

The XPS spectra of the B–C–N interlayer is shown in Fig. 5. The spectrum illustrates the sharp peaks of B, N, O, and C. After 100-s sputtering, the content of O decreases. It can be concluded that the impurity element of O mainly comes from the absorbed O_2 and CO_2 in the storage stage before XPS analysis.

The chemical composition of the ternary B–C–N interlayer is shown in Fig. 6 from an XPS depth profile.

As shown in Fig. 6, the thickness of the interlayer is about 240 nm. At the interface between the c-BN layer and the B–C–N layer, a sharp increase in N concentration is visible, while

the C concentration decreases. The content values of B and O are relatively stable (about 47.5% for B and 5% for O), except for a little more O (8%) on the surface. So a gradual change of chemical composition is formed in the B–C–N layer system. Such an interlayer shows good adhesion to the substrate.[14] The coatings do not peel off after a few months in the atmosphere.

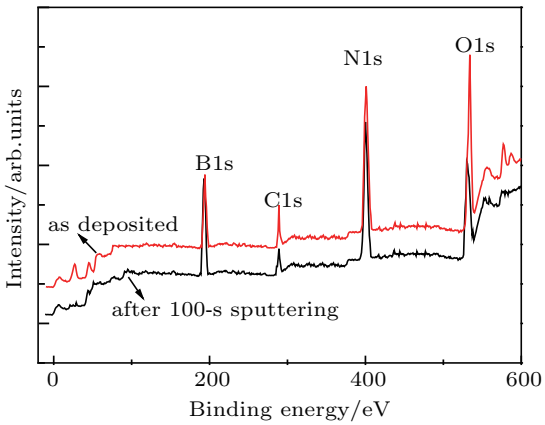


Fig. 5. (color online) The XPS patterns for the ternary B–C–N interlayer after and before sputtering.

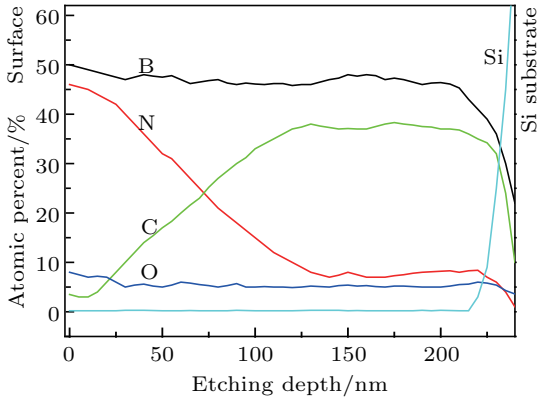


Fig. 6. (color online) The XPS depth profile analyses for the B–C–N interlayer.

The bonding state of the B–C–N layer is obtained by analyzing the XPS spectrum. The XPS spectra of B_{1s} with different sputtering times are shown in Fig. 7. The FWHM of B_{1s} is about 1.9 eV. The much broader peak indicates that there is more than one type of bonding state surrounding each B atom, which are B–C, B–N, B–B and the bonding with oxygen.[26] Some researchers reported that the peaks at around 190 eV and 192 eV are attributed to B–N and B–O bonding.[27–30] The peak position range from 188.4 eV to 189.8 eV is due to the B–C_x.[27,30,31] The signal on the side of lower energy (186.7 eV) is the contribution of B–B bonding.[27,30,31]

Figure 8 shows the decomposition spectra of B_{1s}. As shown in Fig. 8(a), for the as-deposited film (sputtering of 0 s), the B_{1s} consists of about 50.9% B–O bonding and 15.7% B–B bonding. After sputtering of 100 s in Fig. 8(b), the bond of B–B disappears and the bond of B–C_x appears. The intensity of B–N bonding increases from 33.4% to 66.4%, and B–O bonding decreases to less than 10%. The high B–O content on the surface may result from the contamination by oxygen and moisture before XPS analysis.

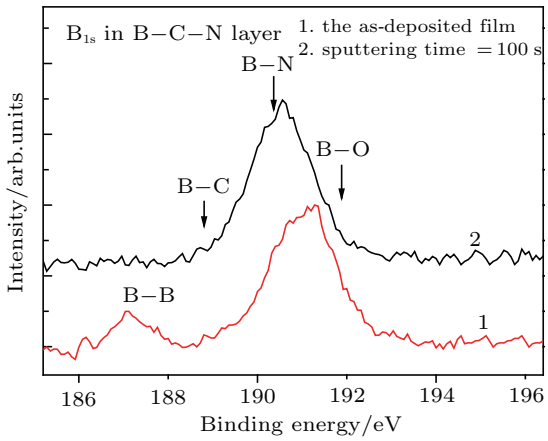


Fig. 7. (color online) The XPS spectra of B_{1s}.

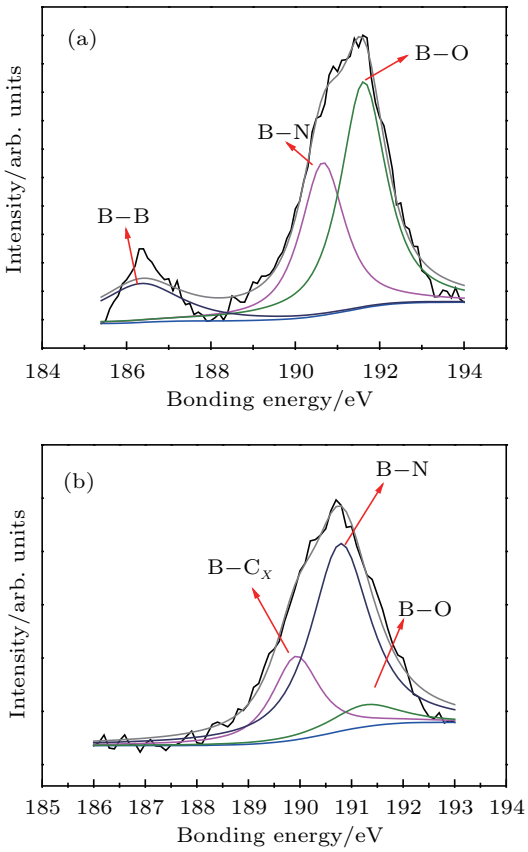


Fig. 8. (color online) The XPS decomposition spectra of B_{1s} (a) before sputtering and (b) after 100-s sputtering.

The hardness value of the B–C–N inter layer, as well as that of the substrate (Si), is measured. The hybridized interlayer has a hardness value of about 22 GPa and the substrate has a hardness value of about 12 GPa, while the c-BN layer has a much higher hardness value (54 GPa for 1.8 μm). It is said

that the moderate hardness of the interlayer plays a key role in improving the adhesion between the film and substrate.[14]

3.5. Nano-hardness

Figures 9(a)–9(c) show the variations of hardness value with the indentation depth of the BN film. For the films with different thickness values, we choose a suitable maximum load so as to obtain a moderate indentation depth. The maximum hardness values of the films are 32 GPa, 42.5 GPa, and 54 GPa, respectively. The hardness value of c-BN film increases with film thickness increasing. One reason is that the films become much thicker and stronger, and the other reason is that the thick films have a much bigger sp3 binding percentage.[32]

We can see that the hardness behaviour changes diversely with the increase of indentation depth. For the 0.4 μm film, a maximum load of about 4 mN was chosen, and the maximum indentation depth was 100 nm. As shown in Fig. 9(a), the hardness value gradually increases as the indentation depth increases, and then reaches a maximum value of about 32 GPa in a depth range of 20 nm, which approximately equals 1/20 of the total film thickness. In the following process, the hardness value gradually decreases as the indentation depth further increases. But when the indentation depth exceeds 60 nm, the curve ascends again. This may be due to the encounter of a hard phase during the test.

For the 1.2-μm thick film (Fig. 9(b)), the maximum load is 14 mN and the maximum indentation depth is 230 nm. The hardness value reaches a maximum value of 42.5 GPa and the high hardness value is in an indentation depth range of 90 nm–120 nm. Then the hardness decreases a little. In the case of the film with a thickness value of 1.8 μm (Fig. 9(c)), the maximum load is 140 mN, the hardness value reaches a maximum value of 54 GPa when the indentation depth is about 300 nm and the high hardness value keeps constant and shows no decrease, even the indentation depth reaches 500 nm. This value is consistent with the reported data in Refs. [8] and [13]. In the case of c-BN film deposited on a silicon substrate, the film is relatively hard and the substrate is soft, thus the smaller the indenter displacement, the less one has to be concerned about substrate effects.[14,33] But if the film is thick enough (in the case of 1.8 μm), the substrate effect from soft substrate cannot be caught.

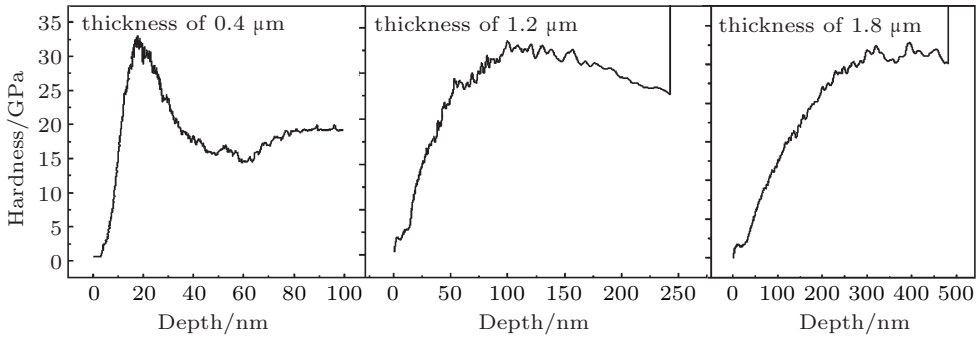


Fig. 9. Curves of hardness value versus indentation depth for the film thickness values of (a) 0.4 μm, (b) 1.2 μm, and (c) 1.8 μm.

4. Conclusions

In this paper, we first show that by adding the B–C–N interlayer, the stress of c-BN film can be reduced. The two-stage deposition process is effective not only to relieve the film stress, but also to improve the film quality. Then we combine the two methods to prepare thick and stable c-BN films. The hardness value is 54 GPa for film 1.8 μm in thickness. The investigation of the chemical component shows that a gradual change of chemical components forms in the B–C–N interlayer. The hardness value of the interlayer is 22 GPa, which is between the hardness value of the substrate and that of the top c-BN layer. The performances (the gradual change of component and hardness) of the interlayer play a positive role in reducing the film stress. Hence, the combination of the addition of the B–C–N interlayer and the two-stage deposition process enables us to prepare thick and stable c-BN films.

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