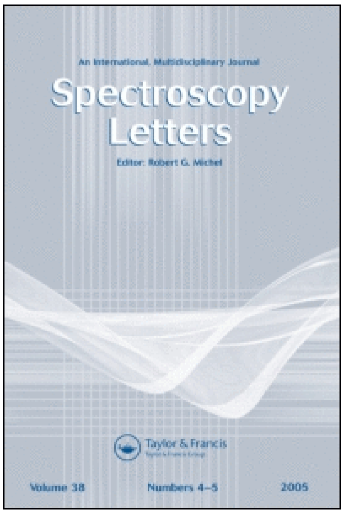

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INFRARED SPECTROSCOPY INVESTIGATION OF CUBIC BORON NITRIDE FILMS

Keywords: cubic boron nitride, film, IR

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ABSTRACT:

FT-IR spectroscopy have been used for identifying both the structure of BN and the intensity of the compressive stress in cubic boron nitride (c-BN) film prepared by a unbalanced rf (13.56 MHz) magnetron sputtering of a hexagonal boron nitride target in a mixture argon and nitride discharge. A T(temperature) - V(negative bias) phase diagram was obtained using the phase structure identify by IR spectra. Comparing the reflection infrared spectra (RIR) with the transmission infrared spectra (TIR) measured from same c-BN film, it is firstly found that RIR peak position of c-BN is lower than

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TIR peak position of c-BN, this means that the compressive stress on the surface layer of c-BN film is smaller than that inside c-BN film, may be this is the reason why thicker c-BN film can not be synthesized. A higher IR peak position of 1064 cm^{-1} and a lower peak position 1004.7 cm^{-1} were detected from a broken and partly peeled off c-BN film. The peak position of 1064 cm^{-1} agrees with that of bulk c-BN at 1065 cm^{-1} which was synthesized at high temperature and high pressure, while the peak position of 1004.7 cm^{-1} accords well with the result calculated (1004 cm^{-1}) by Wentzcovith and it may be closes to that of the stress free value of c-BN. Using the result measured by Ulrich, the shift rate of IR peak position of c-BN in the films is about 3.8 cm^{-1}/Gpa to be obtained.

INTRODUCTION

During the recent years, much effort has been devoted to preparation of c-BN films, because c-BN has many outstanding properties, such as extreme hardness, excellent chemical inertness, higher thermal conductivity, electrical resistively, very high chemical stability at high temperature, good optical transparency over wide range of wavelengths, wide bond gap (>6.4 ev) semiconductor material can be easily doped as a n or p-type, etc., and up to now only hardness property has been applied in using bulk c-BN which was synthesized at high temperature and high pressure. The full utilizing of these outstanding properties is looking forward in the form of the film. Various physical vapor deposition (PVD) and chemical vapor deposition (CVD) techniques were used to synthesize c-BN film, such as rf sputtering[1], ion plating[2], ion beam deposition[3], ion beam-assisted PVD[4], ECR plasma-assisted CVD[5], r.f.

glow discharge deposition[6] and laser deposition[7] etc. The FT-IR spectroscopy was used as a major tool for phase identification because the IR peak for c-BN are clearly distinguished from those for h-BN. A strong unique IR absorption peak in the range from 1075- 1105 cm^{-1} corresponds to the transverse optical (TO) vibration mode of c-BN sp^3 bond, while the two characteristic absorption peaks at 1380 cm^{-1} (in plane B-N stretching) and 780 cm^{-1} (out-of-plane B-N-B bending) are exactly consistent with sp^2 bond of h-BN crystal structure. All above mentioned techniques have in common the use of ion bombardment, thought to be an essential condition of growing c-BN. However, this implies a high compressive stress that generally results in an up shift of IR peak in c-BN films. This can be used for identifying relative intensity of the compressive stress in c-BN films, the large compressive stress the large up shift IR peak position move.

The ratio of the c-BN peak height to the h-BN peak height at 1380 cm^{-1} can be used for deducing the percentage of c-BN in the film, that is $0.6*I_{c\text{-}BN}/I_{1380}$[8].

EXPERIMENT

A rf magnetron sputtering system was employed for preparing c-BN films. A 105 mm diameter disk of pure hexagonal boron nitride (h-BN, 99.8%) was used as the sputtering target. After being evacuated to below $2*10^{-3}$ Pa, the sputtering chamber was filled with highly pure argon (99.99%) and nitrogen (99.99%) gases. A d.c. bias was used in the range 0 - 250 V as the substrate (the wafers of Si (100)) bias. The sputtering parameters are shown below:

Sputtering pressure: 1.3 Pa

N_2/N_2+ Ar: 2 %

RF power: 600 - 800 W

substrate temperature: 430 - 480 °C

substrate d.c basic: 0 - 250 V

Target-substrate space: 5 cm

A Bruker IFS-66V spectrometer equipped with A510 microscopy was used foı measuring FT-IR to confirm the structure of BN films and to identify the intensity oi the compressive stress in c-BN films. The spectra were taken at a 4 cm^{-1} resolution with a liquid nitrogen cooled MCT detector, and typically 512 interferograms were coadded to yield a spectra of high signal-to-noise ratio.

RESULTS AND DISCUSSION

Figure 1 shows IR absorption spectra detected for the BN films deposited aı various substrate bias from -100 V to - 220 V with the substrate temperature of 470 °C. There are two absorption peaks at 1380 cm^{-1} and 780 cm^{-1}, respectively, it presents thaı only pure h-BN film was obtained with the substrate bias below -100 V, at the bias of -160 V, besides 1380 cm^{-1} and 780 cm^{-1}, the characteristic absorption of c-BN at 1080 cm^{-1} also appears in the spectra which shows a mixture phase film h-BN and c-BN was deposited, as the bias increases to -220 V, a strong unique absorption peak of 1105 cm^{-1} finally show up without presence of any secondary peak. A nearly pure c-BN film could be synthesized. At the bias of -250 V, nothing was obtained on the substrate due to resputtering of ions.

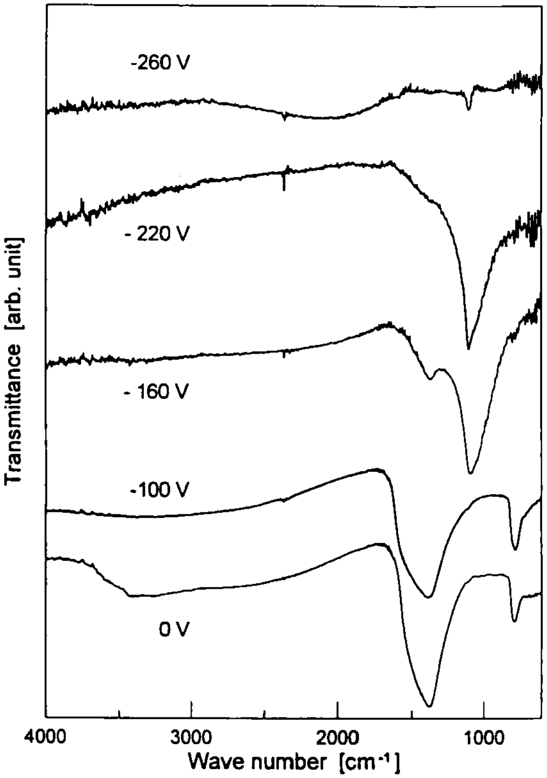

Figure 1. FT-IR spectra of BN films obtained at various bias

The various phase of BN films prepared in term of different the substrate bias and temperature have been identified by IR spectra and put those into the figure 2, it can be clearly seen that there are three phase area, h-BN, h-BN + c-BN and c-BN phase in figure 2. From figure 1 and figure 2 it can be found that at the temperature of 470 °C, the phase change from pure h-BN to h-BN + c-BN finally to pure c-BN, that is, with increasing the substrate bias, the content of c-BN in the films increase. The content of

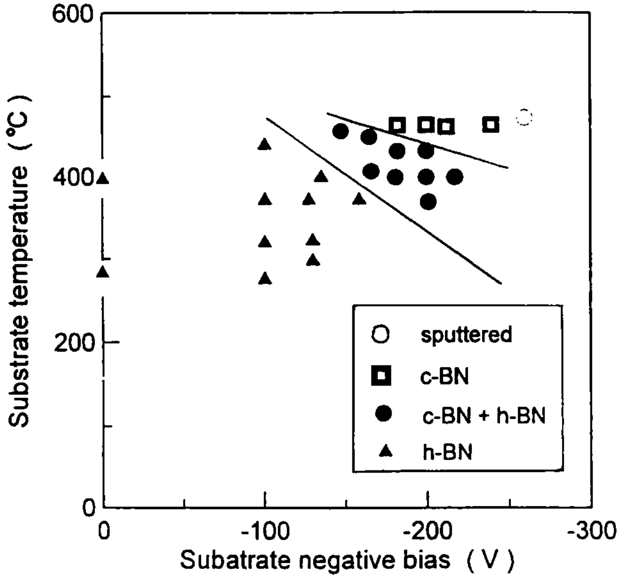

Figure 2. A T – V phase diagram

c-BN inside of films have been obtained by the calculation in term of $0.6{*}I_{c\text{-}BN}/I_{1380}$. And it can also be found that from figure 1 as the bias up from -160 V to -220 V, the IR peak position of c-BN increases from 1080 cm^{-1} to 1105 cm^{-1}, this means that with increasing the bias, the compressive stress off c-BN films increases, those indicate that the bombardment of energetic ions arise from the substrate bias play an important role in both the growth of c-BN and the formation of the compressive stress in the c-BN films.

Figure 3 shows that a RIR and TIR detected from same BN film, it can be seen that the film of the mixture phase h-BN and c-BN has layer-built structure, and a pure c-BN layer appears only on the surface of the BN film, the IR peak position of 1033

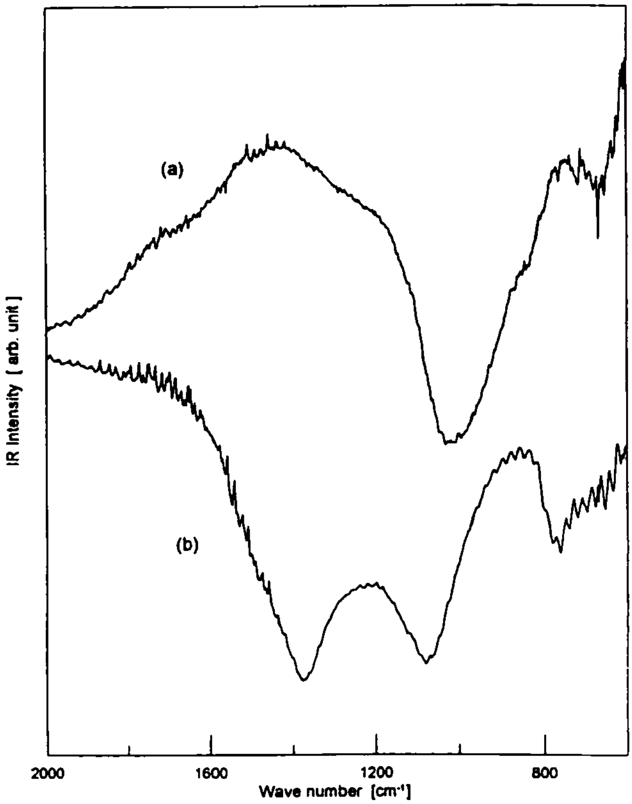

Figure 3. The RIR and TIR of the film with layer-built structure

cm^{-1} of c-BN in the RIR is obviously lower 45 cm^{-1} than that of 1078 cm^{-1} of c-BN in the TIR, this reveals an important fact to be first found that the compressive stress on the c-BN film is smaller than one inside c-BN film. This phenomenon may be used for explaining the reason why thicker c-BN film can not be obtained. With the increase of the thickness of a c-BN film, the compressive stress on the surface of a film will continually decrease, as one goes down to the extent that the growth of c-BN may be

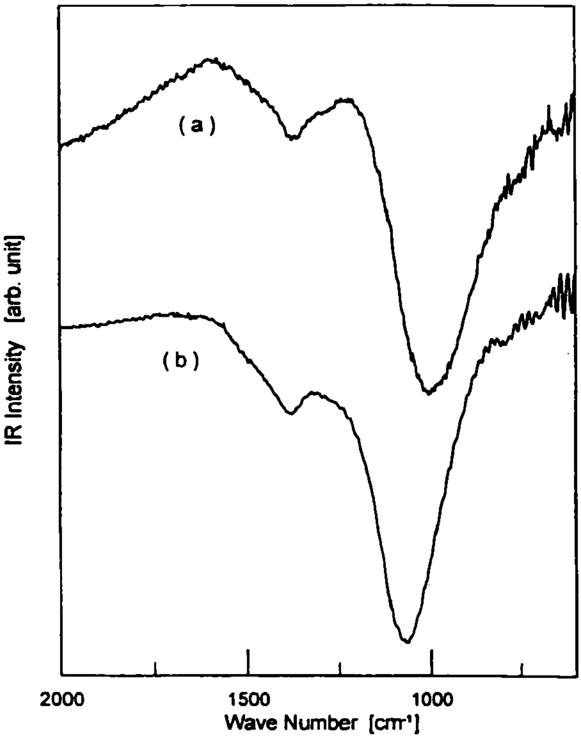

Figure 4. The RIR and TIR of the broken c-BN

stopped, because according to the compressive stress model of the growth of c-BN in a BN film, the growth of c-BN needs certain stress.

The case, the peak position of c-BN in RIR is smaller than that in TIR, have been detected in all c-BN films deposited by us, even including a broken and partly peeled off c-BN film, as shown in figure 4 the peak position of c-BN at 1004.7 cm^{-1} in RIR is smaller 63.3 cm^{-1} than that at 1064 cm^{-1} in TIR. It is noted that the peak position of 1064 cm^{-1} measured in TIR accords well with that of 1065 cm^{-1} measured in the bulk c-

BN (which have been synthesized at high temperature and high pressure), comparing with 1004.7 cm^{-1} to indicate that there is larger stress in the bulk c-BN. The peak position of 1004.7 cm^{-1} detected in RIR agree well with that of 1004 cm^{-1} calculated by Wentzcovitch[10] and it may close to that of stressless. The stress of 25GPa at IR peak position of 1099 cm^{-1} have measured by Ulrich[1], we can obtain an IR spectra shift rate with changing stress, that is (1099-1044) cm^{-1}/25 GPa $\approx$ 3.8 cm^{-1}/GPa.

CONCLUSION

1. Cubic boron nitride (c-BN) film were prepared by a unbalanced rf (13.56 MHz) magnetron sputtering of a hexagonal boron nitride target in a mixture argon and nitride discharge.
2. A T(temperature) - V(negative bias) phase diagram was obtained.
3. It is firstly found that RIR peak position of c-BN is lower than TIR peak position of c-BN, this means that the compressive stress on the surface layer of c-BN film is smaller than that inside c-BN film.
4. Up to now, most lower peak position 1004.7 cm^{-1} accords well with the result calculated (1004 cm^{-1}) by Wentzcovith was detected, it is closes to the stress free value of c-BN.
5. The shift rate of IR peak position of c-BN in the films is about 3.8 cm^{-1}/Gpa.

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