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In situ infrared spectroscopic study of cubic boron nitride thin film delamination*

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This paper investigates the procedure of cubic boron nitride (cBN) thin film delamination by Fourier-transform infrared (IR) spectroscopy. It finds that the apparent IR absorption peak area near 1380 cm^{-1} and 1073 cm^{-1} attributed to the B–N stretching vibration of sp^2-bonded BN and the transverse optical phonon of cBN, respectively, increased up to 195% and 175% of the original peak area after film delamination induced compressive stress relaxation. The increase of IR absorption of sp^2-bonded BN is found to be non-linear and hysteretic to film delamination, which suggests that the relaxation of the turbostratic BN (tBN) layer from the compressed condition is also hysteretic to film delamination. Moreover, cross-sectional transmission electron microscopic observations revealed that cBN film delamination is possible from near the aBN(amorphous BN)/tBN interface at least for films prepared by plasma-enhanced chemical vapour deposition.

Keywords: cubic boron nitride films, infrared spectroscopy, delamination, compressive stress relaxation

PACC: 7280E, 8115H, 4630J, 3220F

1. Introduction

Cubic boron nitride (cBN) thin films show excellent properties including ultrahigh hardness, optical transparency, wide bandgap, low dielectric losses, high thermal conductivity and chemical inertness, and thus have many technological potential applications.[1−4] Recently, significant progress has been achieved on the preparation of high quality cBN films.[5−15] However, compressive stress induced delamination of cBN films from different substrates is still frequently occurred. In the past two decades, much effort has been focused on the mechanism of cBN film delamination, the compressive stress and humidity are considered to be two main reasons.[16−19] And it was found to be possible to peel off films from inside the silicon substrate,[20,21] inside the turbostratic BN (tBN) layer,[19,22,23] or near the interface between the tBN layer and silicon substrate.[24] After film delamination, the infrared (IR) peak position near 1070 cm^{-1} attributed to the transverse optical phonon of cBN was revealed to shift to low wavenumber indicating the compressive stress relaxation.[16,17,25] However, the lack of enough information, particularly information of the film structure variation during delamination, delayed the establishment of a reasonable mechanism of cBN film delamination.

In this study, therefore, a Fourier-transform infrared (FTIR) spectroscope with a non-polarized beam is applied to investigate the IR spectra variation during film delamination. We found that the IR absorption of peak near 1073 cm^{-1}, together with the peak near 1380 cm^{-1} attributed to the B–N stretching vibration of sp^2-bonded BN, increased remarkably after film delamination. In addition, the behaviour of tBN layer recovery is found to be hysteretic to film delamination similar to that of a viscoelastic body.[26−28] And direct high-resolution transmission electron microscopic (HRTEM) observation found that cBN films prepared in this study are delaminated from near the aBN/tBN interface, where aBN is the abbreviation for amorphous BN.

2. Experimental details

Cubic BN films were deposited on silicon substrates by low-pressure inductively coupled plasma-

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enhanced chemical vapour deposition (ICP-CVD) using B_2H_6, N_2, He and Ar as reactant gases.[6] Plasma was generated at 0.13 Pa with an input power of 7 kW. At first, pure H_2 plasma and pure N_2 were generated for the removal of oxygen and presputtering of the silicon substrate surface, respectively. Then Ar plasma was generated and the substrate bias was set at –150 V during the introduction of He diluted B_2H_6 from a water cooling probe. The 10% B_2H_6 gas was increased from 0 to an appropriate value within 3 min, and then the substrate bias was continuously decreased to become a sheath potential of approximately 80 V in another 3 min, finally the substrate bias was kept constant for film deposition.[6]

Samples were characterized using non-polarized FTIR (JASCO FT/IR-700) with the transmission mode at normal incidence. Both aBN and tBN are sp^2-hybridized but having different structures, hereafter in this paper, we use "tBN" to represent the total amount of sp^2-bonded BN in IR measurements (our HRTEM observation found that the initial aBN layer in our films is thinner than 2 nm). For direct HRTEM (JEM-4000 FX II and JEM ARM 1250) observation of the interface where films delaminated, cBN films were also deposited on the edge of ultrathin silicon flake substrates.[29]

3. Results and discussion

Figure 1 shows the apparent IR spectra of a cBN film measured at the same position during delamination. From the IR spectrum before delamination, the film thickness was approximately 100 nm, and the remained compressive stress was approximately 1.7 GPa.[6,30] Because the remained compressive stress was not high, the film delaminated slowly, therefore we could measure the IR spectra at different delamination stages. The IR peak near 1073 cm^{-1} shifted to 1051 cm^{-1} after delamination is in good agreement with previous report.[16] Moreover, Fig.1 also shows that peak intensities near 1073 cm^{-1}, and 1380 cm^{-1}, together with the peak near 780 cm^{-1} attributed to the B–N–B bending vibration of sp^2-bonded BN, increased remarkably during film delamination. Since the intensities of two sp^2-bonded BN peaks kept constant by changing the IR incidence angles during IR measurements,[31] the influence of the incidence angle change of IR beam caused by delamination induced film shrinking is not the reason for the increase of these peak intensities.

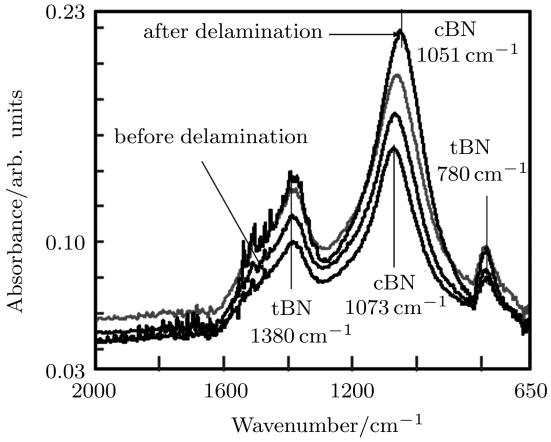


Fig.1. FTIR spectra change during a cBN film delamination. The spectra were measured at the same position. Film was prepared by continuously reducing the substrate bias from –150 V to –20 V for 5 min film deposition using gas flowrates of 1.0 sccm N_2 + 1.0 sccm H_2H_6 + 13.5 sccm Ar + 9.0 sccm He. The pressure during film deposition was 0.13 Pa and the substrate temperature was 300°C.

Figure 2 shows the pure Lorentzian-type curve fitting of an IR spectrum of the cBN film obtained after approximately 50% of the measured area peeled off from the substrate. With a linear background, the spectrum is composed of 6 peaks. Besides the well-known peaks near 780 cm^{-1} and 1380 cm^{-1} and 1073 cm^{-1}, the peak near 1505 cm^{-1} is attributed to a two-phonon peak,[32] the weak peak near 1210 cm^{-1} is often observed as the y-BN peak, though it is not yet understood.[33] The peak near 1051 cm^{-1} is attributed to the delaminated part of cBN. The inset is an image of the delaminating cBN film captured during IR measurement, the whole film peeled off from the substrate perfectly without being broken; and the bound between the delaminated part and undelaminated part of the film is clearly shown. The percentage of the delaminated area ($P_{1073-\mathrm{area}}$) measured from (1–Area_{1073}/ $\mathrm{Area}_{1073-\mathrm{initial}}$) is in agreement with delamination percentage (P_{picture}) evaluated from the inset picture, where the Area_{1073} and $\mathrm{Area}_{1073-\mathrm{initial}}$ are IR peak areas near 1073 cm^{-1} and Area_{1073} before film delamination determined by curve fitting, respectively. Figure 3 shows the details of apparent IR peak areas (near 1380 and 1073 + 1051 cm^{-1}, respectively) increasing with $P_{1073-\mathrm{area}}$. After the incubation period, the cBN peak area increased approximately linearly with film delamination percentage, while that of the tBN increased non-linearly. After the film is delaminated completely, the apparent cBN peak area

increased up to approximately 175% of the original area, and that of tBN increased up to approximately 195% of the original one.

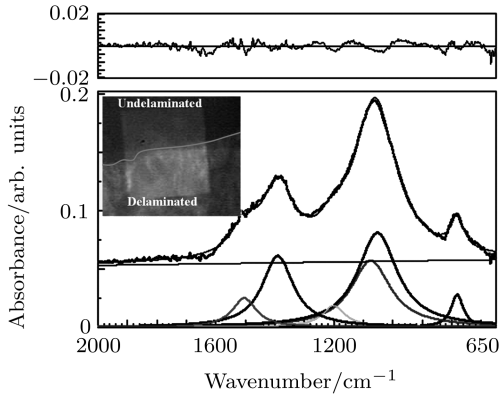


Fig.2. IR spectrum of the film when approximately 50% of the measured area delaminated from substrate and its curve fitting with pure Lorentzian-type peak functions. The inset shows the delamination conditions during IR measurement, and the square spot inside the inset is the area for IR measurement.

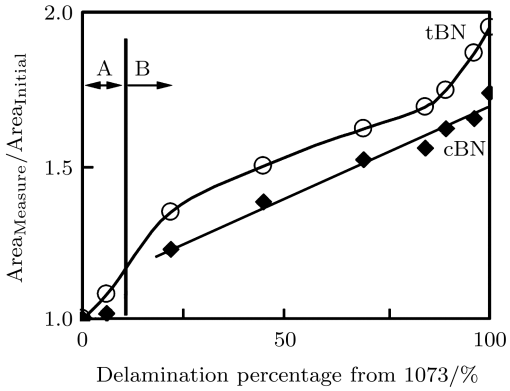


Fig.3. Area increase of apparent IR peaks near 1380 cm^{-1} and near 1073 + 1051 cm^{-1} during film delamination. (A) Incubation period of cBN layer delamination; (B) cBN layer has begun to delaminate.

Figure 4 shows the progress of film delamination calculated from the peak area/intensity variations near 1380 cm^{-1}, 1070 cm^{-1} and 1051 cm^{-1}, respectively. The delamination percentages evaluated from peak area near 1380 cm^{-1} ($P_{1380-\mathrm{area}}$) at time T were defined by (Area $_T$ – Area$_{\mathrm{initial}}$) / (Area$_{\mathrm{final}}$ – Area$_{\mathrm{initial}}$), and delamination percentage evaluated from peak area near 1051 cm^{-1} ($P_{1051-\mathrm{area}}$) were defined by Area $_T$/Area$_{\mathrm{final}}$, where Area $_T$, Area$_{\mathrm{initial}}$ and Area$_{\mathrm{final}}$ are peak area measured at time T, before film delamination, and after film delamination, respectively. The delamination percentage evaluated from the peak intensity ($P_{1073-\mathrm{intensity}}$, defined from its intensity similar to $P_{1073-\mathrm{area}}$) is in good agreement with $P_{1073-\mathrm{area}}$. Also, $P_{1051-\mathrm{area}}$ is consistent with $P_{1073-\mathrm{area}}$, however, it differs from $P_{1380-\mathrm{intensity}}$ (defined from its intensity similar to $P_{1380-\mathrm{area}}$) and $P_{1380-\mathrm{area}}$. Moreover, the tBN layer is found to delaminate faster than the cBN layer at the initial stage. This suggests that film starts to delaminate from the place near the tBN layer at the incubation period. The delamination of the tBN layer induces the cBN layer delamination. However, the nonlinear increase of the peak area near 1380 cm^{-1} suggests that the recovery of the tBN layer is still continued after the tBN peeled off from the substrate completely, similar to the hysteretic recovery of a viscoelastic body, thus the apparent delamination speed of tBN slowed down. This is in good agreement with our previous reports about the peculiar deformation behaviours of pure tBN films.[26−28]

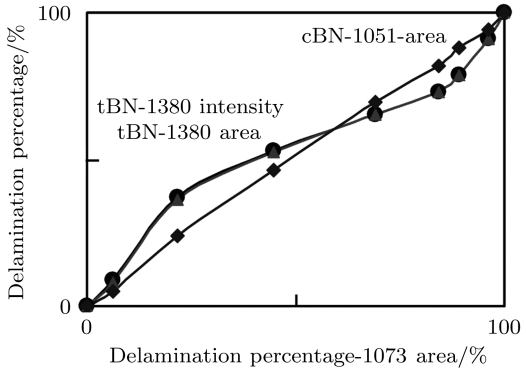


Fig.4. The progress of film delamination evaluated from the increase of peak area and intensity. The delamination percentage of the film at time T was defined as (Area $_T$–Area$_{\mathrm{initial}}$)/(Area$_{\mathrm{final}}$–Area$_{\mathrm{initial}}$) for peak near 1380 cm^{-1} and Area $_T$/Area$_{\mathrm{final}}$ for peak near 1051 cm^{-1}, respectively.

Figure 5 shows cross-sectional TEM images of cBN films delaminated from silicon flake substrate.[29] Figure 5(a) is an overview of a small part of a cBN film peeled off from the substrate. The relaxation of the film from compressive condition is clearly shown. Moreover, fragments of silicon substrate were found to be adhered on the delaminated film, it seems that cBN film is possible to delaminate from the place near the Si nanocracks. However, the HRTEM image in Fig.5(b) shows that the film peeled off from the place near the aBN/tBN interface. Although the film has delaminated, a typical layered-structure consisting of an aBN layer followed by a textured tBN layer and then a top cBN layer can still be observed.

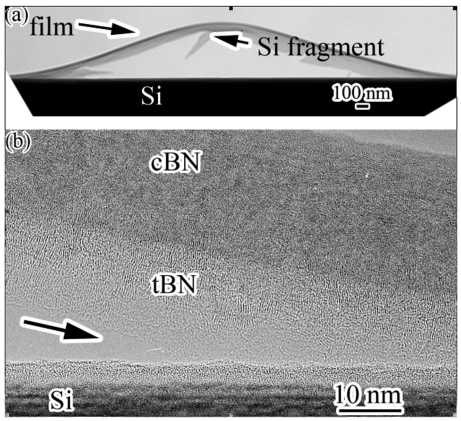


Fig.5. Direct TEM observation of cBN film delaminated from silicon flake substrate. (a) Overview of a cBN film delaminated from inside the silicon flake, the cBN film is peeled off perfectly, and some silicon fragments are still adhered on the film. (b) HRTEM image shows that the cBN is peeled off near the interface between the silicon substrate and the tBN layer.

Cubic BN films deposited on silicon substrates have typical Si/aBN/tBN/cBN layered structure, and delamination always occurs at the weakest part of the film. Cubic BN films were often found to be peeled off from inside the silicon substrate,[20,21] inside the tBN layer,[19,22,23] or near the interface between the tBN layer and silicon substrate,[24] which might be influenced by growth techniques. Recent results suggest that cBN prepared by ICP-CVD is nucleated and then grows on the top of the textured tBN layer, which suggests a good adhesion between the tBN layer and the cBN layer.[29,34,35] Therefore, the transition layer between the silicon and the tBN film seems to be the possible weakest part of a film, and the film is usually delaminated from aBN/tBN interface. The cBN film adhesion on silicon substrate could be improved partly by removing the initial aBN layer.[8] Meanwhile, pretreatment of the silicon substrate by heating or high-energy ion bombardment, at the same time, induces nanocracks into the near-surface of silicon, particularly for films on Si flakes; nanocracks are ready to be induced during silicon flake substrate preparation.[29] As a result, film delaminated from Si nanocracks is sometimes observed, as in the TEM image in Fig.5(a).

IR is widely used to quasi-quantitative determination of the content of sp^2-bonded and sp^3-bonded BN phases in cBN films. However, it was found that the absorption coefficient of the sp^2-bonded BN peak near $1380\,cm^{-1}$ changed by approximately a factor of three for a modest change in substrate bias during cBN film preparation.[36] Very recently, we also found that the tBN peak intensity near $1380\,cm^{-1}$ of cBN films is suppressed quasi-linearly by the remained compressive stress.[30] When the film is delaminated, the residual compressive stress is relaxed, and the IR absorptions of peak of tBN increases, as shown in Figs.1 and 3. In fact, from the difference between IR spectra before and after delamination shown in Refs.[23,37], the increase of IR peaks intensity after delamination is also discernible. Moreover, we also found that the IR peak intensity increase behaviour of the tBN layer is different from that of the cBN layer as shown in Figs.3 and 4, which indicates that the delamination behaviour of the tBN layer differs from that of the cBN layer. This can be explained by the different mechanical properties between cBN and tBN, cBN is the second hardest materials with ultrahigh elastic modulus, while tBN is one of the softest materials with low elastic modulus.[26−28] Recently, nanoindentation experiments also revealed that the recovery of tBN film after indentation is reversible and hysteretic, similar to that of a viscoelastic body, while no such behaviour is found for cBN film and silicon substrate.[26,27] Therefore, it is reasonable to consider that the viscoelastic recovery of tBN layer after film delamination is the reason for its nonlinear IR peak area variation.

Based on the above findings, we propose a possible cBN film delamination procedure as shown in Fig.6. Due to the high compressive stress, the as-deposited cBN film is under a metastable condition, and the cBN coated substrate is bent (Fig.6(a)). At this stage, any disturbance will induce the stress relaxation which results in the film delamination, such as atmospheric pressure change during opening the deposition chamber, reaction between boron and nitrogen dangling bonds with H_2O in air and so forth.[17−19] Usually, the silicon substrate is much thicker than the deposited cBN film, the recovery of silicon substrate occurred at first (Fig.6(b)). After part of the tBN layer is peeled off from the silicon, recovery of tBN layer begins and the IR peak near $1380\,cm^{-1}$ begins to increase, which also induces the delamination of the upper cBN layer (Fig.6(c)). Because tBN layer shows viscoelastic behaviours, its recovery does not finish immediately, but is continued after film delamination (Fig.6(d)).[27,28] Therefore, IR peak intensity of tBN is found to increase nonlinearly as film delamination is going on, despite the fact that the peak intensity of cBN increases linearly. Note that, when the remained compressive stress is too high, film delaminates and cracks into pieces quickly.

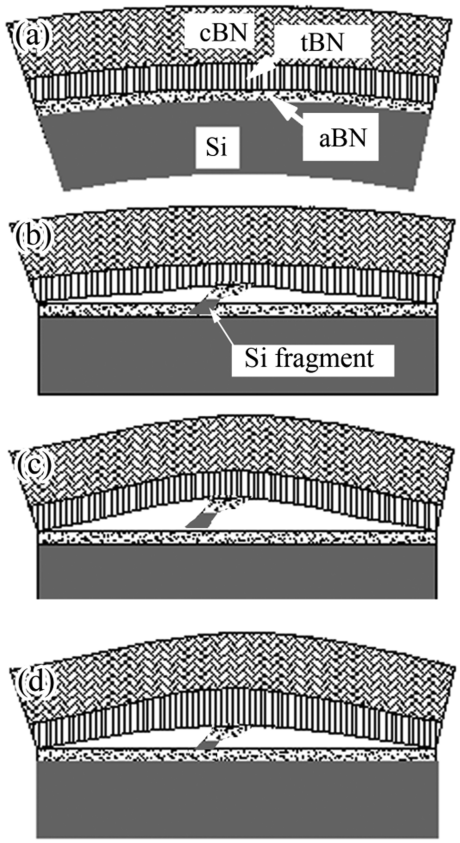


Fig.6. Schematic diagram of the procedure of cBN film delamination: (a) a cBN film before delamination, the film is bent with the substrate under high compressive stress; (b) recovery of the silicon substrate occurred first, which induced part of the tBN layer peeled off from the substrate; (c) recovery of the tBN layer induced the quick delamination of cBN layer, and IR peak near 1073 cm^{-1} increased drastically; (d) after film delamination, recovery of the tBN layer still continued like a viscoelastic body.

The reasons for the IR absorption variation of cBN films caused by stress relaxation are still open for discussion. The difference in preferential orientation of the tBN basal plane induced by stress was considered as one of the reasons, since a preferential orientation of the tBN layer has been frequently observed by TEM.[2,3,38,39] Thus if the degrees of the orientation are changed during film delamination, the absorption coefficients may appear different because IR absorption of tBN is anisotropic due to anisotropic lattice vibrational properties. Furthermore, according to the quantum theory of phonon excitation, the IR absorption coefficient should be proportional to the density of phonon final states (at the centre of the Brillouin zone) which is related to the phonon dispersion and thus can be influenced by the strain in a material.[40] The IR peak intensities increased after delamination induced stress relaxation provides a further evidence that the IR absorption can be suppressed by stress.[30] And this could be a possible reason that the measured absorption coefficient of tBN in cBN films under compressive stress was much less than that predicted from the nearly single-crystal properties.[36,41] Further works to clarify the mechanism for the IR peak intensity suppression by compressive stress are underway.

4. Conclusions

In summary, we found that the IR peak areas of sp^2-bonded and sp^3-bonded phases of boron nitride in a cBN film increased up to 195% and 175% of the original area respectively due to the compressive stress relaxation after film delamination. cBN film is found to be peeled off from the interface near the silicon substrate and the tBN layer or inside the silicon substrate. The recovery of the tBN layer during film delamination is hysteretic similar to that of a viscoelastic body. The present study provided primary information for a better understanding of the mechanism of cBN films delamination from silicon substrates.

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