Influence of oxygen on the growth of cubic boron nitride thin films by plasma-enhanced chemical vapour deposition*

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Cubic boron nitride thin films were deposited on silicon substrates by low-pressure inductively coupled plasma-enhanced chemical vapour deposition. It was found that the introduction of O_2 into the deposition system suppresses both nucleation and growth of cubic boron nitride. At a B_2H_6 concentration of 2.5% during film deposition, the critical O_2 concentration allowed for the nucleation of cubic boron nitride was found to be less than 1.4%, while that for the growth of cubic boron nitride was higher than 2.1%. Moreover, the infrared absorption peak observed at around 1230–1280 cm^{-1}, frequently detected for cubic boron nitride films prepared using non-ultrahigh vacuum systems, appears to be due to the absorption of boron oxide, a contaminant formed as a result of the oxygen impurity. Therefore, the existence of trace oxygen contamination in boron nitride films can be evaluated qualitatively by this infrared absorption peak.

Keywords: cubic boron nitride films, infrared spectroscopy, plasma-enhanced chemical vapour deposition

PACC: 7280E, 3220F, 8115H

1. Introduction

The unique properties of cubic boron nitride (cBN) film, including its high hardness exceeded only by diamond, good chemical inertness against ferrous metals and oxygen at high temperatures, high thermal conductivity and wide band gap with both p- and n-type dopability, make it an excellent material for applications.[1,2] For the past three decades, intensive studies have been focusing on cBN film synthesis,[1−5] and significant progress has been achieved,[6−15] although the deposition of high-quality and thick cBN films is still difficult. Very recently, it has been reported that the compressive stress of a cBN film can be reduced significantly by introducing O_2 into the deposition system, and oxygen-enriched cBN films with a thickness of over 2 μm were achieved with the assistance of a boron-rich adhesion-enhanced layer.[16,17] On the other hand, early research suggested that O_2 gas is detrimental to both cBN nucleation and growth.[18] Therefore, further study is needed to clarify the influence of O_2 on cBN nucleation and growth.

We have optimized the plasma-enhanced chemical vapour deposition (PECVD) technique for the preparation of high-quality cBN films with a very thin sp^2-bonded BN transition layer,[11,19] and have studied the influence of oxygen on the formation of the initial amorphous BN (aBN) layer.[7] In this study, the influence of O_2 on cBN nucleation and growth by PECVD is investigated. Also, the origin of the IR peak for cBN films frequently detected at around 1230–1280 cm^{-1} is found to be due to the boron oxide contaminations formed as a result of the oxygen impurity.

2. Experimental details

Cubic BN thin films were deposited on Si substrates by low-pressure inductively coupled PECVD.[19] The plasma was generated at a pressure of 1.33×10^{-1} Pa with an input power of 7 kW and substrate temperature of approximately 900 K. Details of the substrate bias and gas flow conditions for cBN deposition are shown in Fig. 1, under which the film growth rate was approximately 10 nm/min without the introduction of dry air. Samples were mainly characterized by Fourier transform infrared

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spectroscopy (FTIR) (JASCO FT/IR-700) with the transmission mode at normal incidence and by cross-sectional high-resolution transmission electron microscopy (HRTEM) (JEM ARM 1250) with an accelerating voltage of 1250 kV. The ultimate pressure of the ultrahigh vacuum (UHV) system used in this study is less than $\approx 1.06 \times 10^{-5}$ Pa, which enables us to study the influence of O_2 as an impurity on cBN film growth.

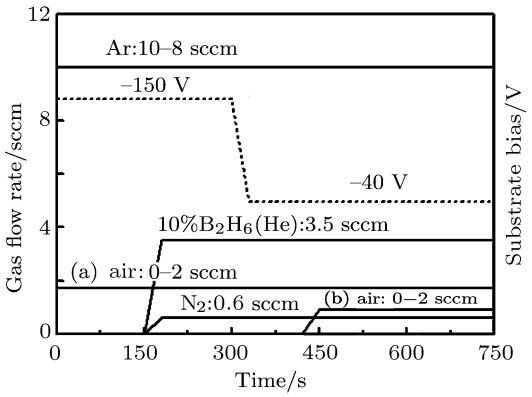


Fig. 1. Schematic diagram of parameters for deposition using Ar + dry air. Condition (a) dry air introduced into the chamber before cBN nucleation, and condition (b) dry air introduced after 2 min film pre-deposition. In both cases, the total flow rate of Ar + dry air was kept constant during the introduction of dry air.

3. Results and discussion

3.1. Influence of O_2 on cBN nucleation and growth

Figure 2(a) shows the IR spectra of BN films prepared with dry air introduced at the initial stage (condition (a) in Fig. 1). The IR peak at around 1080 cm^{-1} attributed to the transverse optical phonons of cBN is found to decrease markedly at a very low dry air concentration of 2.1% (corresponding to an O_2 concentration of approximately 0.4%), and no cBN could be detected when the dry air concentration exceeded 7.2% (approximately 1.4% O_2 concentration), resulting in the formation of only sp^2-bonded turbostratic BN (tBN) films. When the dry air flow rate was further increased, the tBN film growth rate also decreased, as shown by spectra 4 and 5. Figure 2(b) shows the change in IR peak intensity evaluated by Lorentzian-type curve fitting,[20] which clearly reveals the suppression of cBN formation by the introduction of dry air. The inset shows another series of experimental results (with the flow rate of Ar + dry air =15 sccm) showing the same trend. Our previous results indicated that the increase in N_2 concentration from 5% to 13% has very little influence on the cubic phase concentration and the film growth rate.[19] This suggests that the suppression of cBN formation for films as shown in Fig. 2 was caused by O_2 rather than N_2 in dry air.

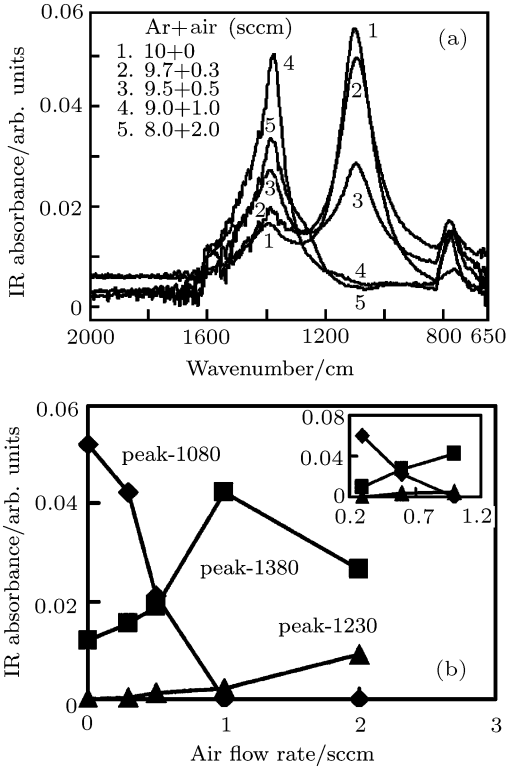


Fig. 2. (a) IR spectra of BN films prepared at dry air flow rate ranging from 0 to 2 sccm with dry air introduced initially. Detailed parameters are shown in Fig. 1. (b) The IR peak intensity at around 1080 cm^{-1} decreases with the dry air flow rate. The inset shows another series of experimental results at the flow rate of Ar+dry air=15 sccm.

Figure 3 shows the influence of dry air on the cBN growth after 2 min film pre-deposition before the introduction of dry air (condition (b) in Fig. 1). From spectrum 1, the thickness of the upper cBN layer of this film is evaluated to be approximately 10 nm after the 2 min pre-deposition. Figure 4 shows the HRTEM image of this film with the typical three-layered structure;[19,21] the upper layer is a 10-nm-thick pure cBN layer. This clearly indicates that dry air is introduced at the cBN growth stage for the films whose characteristics are shown in Fig. 3. Although the cBN growth rate is reduced by the introduction of dry air, similar to the results shown in Fig. 2, all the IR spectra in the inset of Fig. 3 show the existence of the cubic phase of BN in the upper layer of the film deposited in the presence of dry air, which indicates that cBN continues to grow at a relatively high dry air

flow rate after its nucleation. Accordingly, the critical dry air concentration allowed for cBN growth is 10.7% (approximately 2.1% O_2 concentration). Note that the flow rate of 10% B_2H_6 (He) is 3.5 sccm, corresponding to a B_2H_6 concentration of 2.5% in this study.

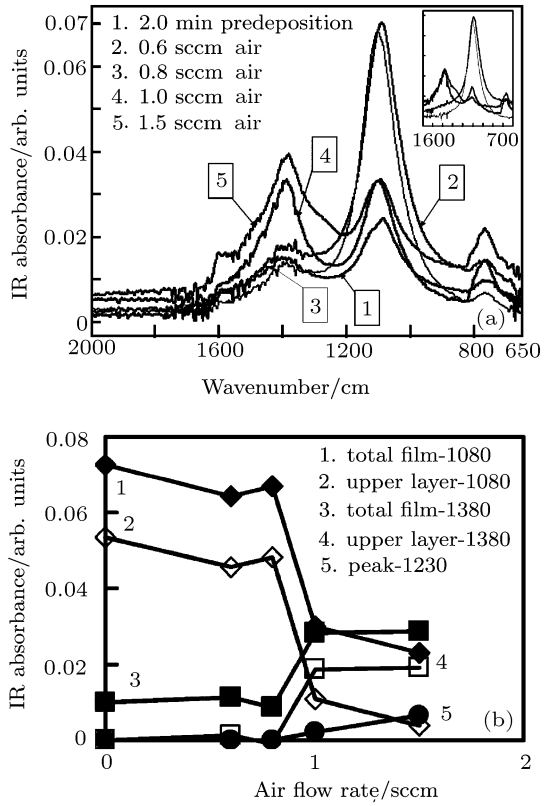


Fig. 3. (a) IR spectra of cBN films prepared with 2 min pre-deposition before the introduction of dry air, the inset shows the IR spectra of the upper layer of BN film deposited in dry air (obtained from the original spectra subtracted by spectrum 1). (b) Details of change in IR peak intensity versus dry air flow rate.

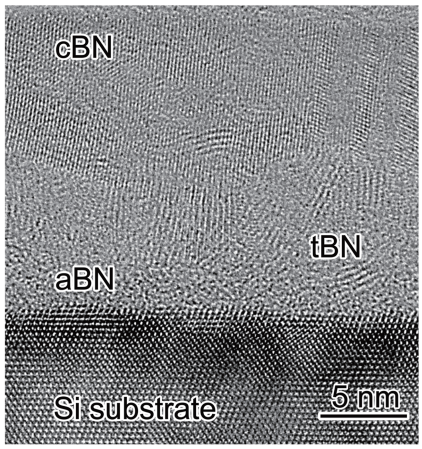


Fig. 4. HRTEM image of a cBN film grown with 2 min pre-deposition.

3.2. Influence of O_2 on IR spectra of cBN films

Figure 5 shows the detail of the IR spectra of BN films fitted with Lorentzian-type peak functions. For the cBN film deposited at a low base pressure of $\approx 1.06\times10^{-5}$ Pa, the IR spectrum is composed of four peaks, that is, the cBN peak at around 1080 cm^{-1}; peaks at around 780 cm^{-1} and 1380 cm^{-1} attributed to the B–N–B bending vibration and the B–N stretching vibration of sp^2-bonded BN, respectively, and a weak peak at around 1505 cm^{-1} attributed to a two-phonon peak.[20,22] When dry air is introduced into the chamber, as shown in the inset in Fig. 5, a new IR peak at around 1230–1280 cm^{-1} becomes discernible even from apparent IR spectra. Moreover, Figs. 2(b) and 3(b) clearly show that the intensity of this peak increases with dry air concentration, suggesting that the origin of this peak is caused by O_2 introduction. This is in good agreement with our previous results, showing that an additional peak at around 1230–1280 cm^{-1} is necessary for satisfactory IR spectra curve fitting when cBN films are deposited in non-UHV systems with a base pressure of approximately $\approx 5.3\times10^{-4}$ Pa.[23,24]

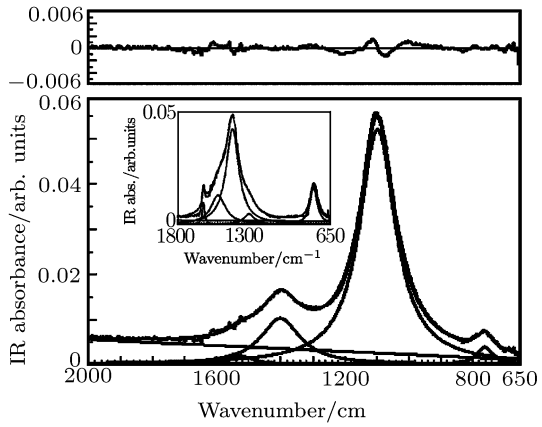


Fig. 5. Lorentzian-type curve fitting of typical IR spectra of cBN deposited in the UHV system without introducing oxygen. The parameters are shown in Fig. 1. The inset shows the Lorentzian-type curve fitting of spectrum 5 in Fig. 2(a) showing the additional peak at around 1230–1280 cm^{-1}.

3.3. Discussion

In high-pressure high-temperature cBN synthesis, the existence of oxygen is considered to cause a thermodynamical stimulation of the transformation from cBN to hexagonal BN (hBN).[25–27] The results of the

present study suggest that the introduction of oxygen also interrupts the nucleation and growth of the cBN film by producing a boron oxide contaminant. Moreover, Figs. 2 and 3 indicate that the cBN nucleation is more easily interrupted by the O_2 impurity than its growth due to the fact that cBN nucleation is more difficult to realize than the subsequent growth. For example, the threshold ion bombardment energy for cBN nucleation is approximately 20 eV higher than that required for its growth.[28] Unfortunately, in our deposition experiments with O_2, all cBN films began to peel off from substrates within 1 hour after being picked up from vacuum chamber, even with a film thickness as thin as several tens of nanometres. Moreover, by comparing the cBN peak position obtained from Figs. 2(a) and 3(a) and from cBN films with similar thickness without O_2 introduction, no tendency of cBN peak position shift can be found. It seems that the enhancement of film adhesion or the reduction of residual compressive stress, reported in recent papers,[16,17] have not been observed upon the introduction of dry air in this study, maybe due to the different deposition techniques and parameters used in other studies. For example, the substrate bias conducted in Refs. [16] and [17] were −300 V compared to a substrate bias of −40 V in this study.

A weak IR peak frequently detected at around 1230–1280 cm^{-1} for cBN films prepared in non-UHV systems is still not yet well understood, and has been considered to be due to the absorption of y-BN.[20,22−24] In this study, we found that this peak intensity is increased with O_2 concentration and that this peak can be removed by preparing films in the UHV system with a base pressure of approximately 1.06×10^{-5} Pa. According to Refs. [25]–[27], oxygen is soluble in cBN and hBN, and under B-rich conditions, such as plasma-enhanced vapour phase deposition of BN films, the O atom is energetically favoured to occupy the N position to form B–O bonding.[29] In addition, the antisymmetric B–O stretching vibration of the trigonal BO_3 group has an IR-active peak around this wavenumber.[30−32] It is, therefore, reasonable to conclude that the IR peak at around 1230–1280 cm^{-1} in cBN films is due to the absorption of boron oxide contaminant formed as a result of the oxygen impurity, rather than to a new BN phase. Accordingly, we will be able to use the peak intensity as a simple indication of O contamination in the film.

4. Conclusions

We have found that the introduction of O_2 suppresses both the nucleation and the growth of cBN in PECVD. It is, however, still possible to deposit cBN film at a relatively high O_2 concentration by predepositing a thin cBN layer before introducing oxygen. The critical O_2 concentrations allowed for cBN nucleation and growth are less than 1.4% and higher than 2.1%, at a B_2H_6 concentration of 2.5%. Moreover, the results of our study suggest that the active IR absorption frequently detected at around 1230–1280 cm^{-1} for cBN films prepared by conventional non-UHV systems is due to the absorption of the boron oxide contaminant formed as a result of the oxygen impurity, by which the existence of oxygen contamination in BN film can be detected qualitatively.

Acknowledgments

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References

[1] Yoshida T 1996 *Diamond Relat. Mater.* **5** 501
[2] Mirkarimi P B, McCarty K F and Medlin D L 1997 *Mater. Sci. Eng.* R **21** 47
[3] Samantaray C B and Singh R N 2005 *Int. Mater. Rev.* **50** 313
[4] Zhang X W, You J B and Chen N F 2007 *J. Inorgan. Mater.* **22** 385
[5] Yang H S, Nie A M and Zhang J Y 2009 *Acta Phys. Sin.* **58** 1364 (in Chinese)
[6] Matsumoto S and Zhang W J 2000 *Jpn. J. Appl. Phys.* (Part 2) **39** L442
[7] Yang H S, Iwamoto C and Yoshida T 2003 *J. Appl. Phys.* **94** 1248
[8] Zhang X W, Boyen H G, Deyneka N, Ziemann P, Banhart F and Schreck M 2003 *Nature Mater.* **2** 312
[9] Nose K, Yang H S and Yoshida T 2005 *Diamond Relat. Mater.* **14** 1297
[10] Nose K, Oba H and Yoshida T 2006 *Appl. Phys. Lett.* **89** 112124
[11] Yang H S, Iwamoto C and Yoshida T 2007 *Diamond Relat. Mater.* **16** 642
[12] Zhang W J, Bello I, Lifshitz Y, Chan K M, Wu Y, Chan C Y, Meng X M and Lee S T 2004 *Appl. Phys. Lett.* **85** 1344

[13] Yang H S and Xie Y J 2007 *Acta Phys. Sin.* **56** 5400 (in Chinese)
[14] Tian J Z, Lu F X and Xia L F 2001 *Acta Phys. Sin.* **50** 210 (in Chinese)
[15] Ma X Y, Yue J S, He D Y and Chen G H 1998 *Acta Phys. Sin.* **47** 871 (in Chinese)
[16] Ulrich S, Nold E, Sell K, Stüber M, Ye J and Ziebert C 2006 *Surf. Coat. Technol.* **200** 6465
[17] Lattemann M, Ulrich S and Ye J 2006 *Thin Solid Films* **515** 1058
[18] Zapien J A, Collins R W and Messier R 2002 *J. Vac. Sci. Technol.* A **20** 1395
[19] Yang H S, Iwamoto C and Yoshida T 2002 *Thin Solid Films* **407** 67
[20] Gielisse P J, Mitra S S, Plendl J N, Griffs R D, Mansur L C, Marshall R and Pascoe E A 1967 *Phys. Rev.* **155** 1039
[21] Yang H S, Iwamoto C and Yoshida T 2002 *J. Appl. Phys.* **91** 6695
[22] Ullmann J, Baglin J E E and Kellock A J 1998 *J. Appl. Phys.* **83** 2980
[23] Yang H S, Zhang Y, Zhang X B and Xu Y B 2007 *Appl. Phys. Lett.* **91** 061907
[24] Yang H S, Zhang J Y, Nie A M and Zhang X B 2008 *Chin. Phys.* B **17** 3453
[25] Turkevich V Z 1999 *Diamond Relat. Mater.* **8** 2032
[26] Hubert H, Gravie L, Buseck P, Petuskey W and McMillan P 1996 12*th Int. Symp. on Boron, Borides and Related Compounds* p56 Baden, Austria, August 25–30 1996
[27] Perevertailo V M, Smekhnov A A, Kuzenkov S P and Loginova O B 1994 *J. Superhard Mater.* **16** 18
[28] Amagi S, Takahashi D and Yoshida T 1997 *Appl. Phys. Lett.* **70** 946
[29] Orellana W and Chacham H 2000 *Phys. Rev.* B **62** 10135
[30] Pisarski W A, Gorvczka T, Wodecka-Dus B, Plonska M and Pisarska J 2005 *Mater. Sci. Eng.* B **122** 94
[31] Schneider J R and Shrader B 1975 *Mol. Struct.* **29** 1
[32] Nagai N, Imai T, Terada K, Seki H, Okumura H, Fujino H, Yamamoto T, Nishiyama I and Hatta A 2002 *Surf. Interface Anal.* **34** 545