



## Influence of the compressive stress on the infrared absorption of s p 2 -bonded boron nitride in cubic boron nitride thin films

Hangsheng Yang, Yan Zhang, Xiaobin Zhang, and Yabo Xu

Citation: Applied Physics Letters **91**, 061907 (2007); doi: 10.1063/1.2768199 View online: http://dx.doi.org/10.1063/1.2768199 View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/91/6?ver=pdfcov Published by the AIP Publishing

## Articles you may be interested in

Residual compressive stress induced infrared-absorption frequency shift of hexagonal boron nitride in cubic boron nitride films prepared by plasma-enhanced chemical vapor deposition J. Appl. Phys. **112**, 053502 (2012); 10.1063/1.4749805

Functionalization of cubic boron nitride films with rhodamine B and their fluorescent properties Appl. Phys. Lett. **99**, 063103 (2011); 10.1063/1.3619837

X-ray absorption studies on cubic boron nitride thin films J. Appl. Phys. **101**, 013710 (2007); 10.1063/1.2405717

Bonding characterization, density measurement, and thermal diffusivity studies of amorphous silicon carbon nitride and boron carbon nitride thin films J. Appl. Phys. **92**, 5150 (2002); 10.1063/1.1512966

Infrared ellipsometry on hexagonal and cubic boron nitride thin films Appl. Phys. Lett. **70**, 1668 (1997); 10.1063/1.118655



## Influence of the compressive stress on the infrared absorption of $sp^2$ -bonded boron nitride in cubic boron nitride thin films

Hangsheng Yang,<sup>a)</sup> Yan Zhang, and Xiaobin Zhang State Key Laboratory of Silicon Materials, Department of Materials Science and Engineering, Zhejiang University, Zheda Road 38, Hangzhou 310027, China

Yabo Xu

Department of Physics, Zhejiang University, Zheda Road 38, Hangzhou 310027, China

(Received 20 April 2007; accepted 12 July 2007; published online 7 August 2007)

Cubic BN films with a pure cubic phase upper layer were prepared by plasma-enhanced chemical vapor deposition. Infrared spectroscopy was applied to analyze the content of initial  $sp^2$ -bonded BN layer in cubic BN thin films under compressive stress. It was found that the peak intensity near 1380 cm<sup>-1</sup> attributed to the B–N stretching vibration of  $sp^2$ -bonded BN was suppressed by the compressive stress in cubic BN films. The deviation between the measured and calculated peak intensities was found to be linear with the compressive stress when the upper layer of the film is a pure cubic phase layer. © 2007 American Institute of Physics. [DOI: 10.1063/1.2768199]

Cubic boron nitride (c-BN) films have significant technological potential applications because of their excellent properties, such as high hardness, wide band gap, and p-/n-type dopability.<sup>1,2</sup> Recently, much effort has been made toward the improvement of c-BN films.<sup>3–9</sup> High energetic ion bombardment is still necessary for c-BN nucleation and growth, which induced high compressive stress accumulation up to several gigapascals in film.<sup>1</sup> Also, an  $sp^2$ -hybridized amorphous BN (a-BN) layer and a textured turbostratic BN (t-BN) layer are always deposited on silicon substrate before c-BN nucleation. The infrared (IR) spectroscopy is widely used to evaluate the content of  $sp^2$ -bonded BN layer in c-BN films. Quantitative determination of the  $sp^2$ -bonded BN by IR was found to be problematic. For example, the absorption coefficient of the  $sp^2$ -bonded BN in *c*-BN films was found to be much less than that predicted from the nearly singlecrystal properties, and the absorption coefficient of the  $sp^2$ -bonded BN peak near 1380 cm<sup>-1</sup> changed by a factor of 3 for a modest change in substrate bias during film preparation.<sup>10,11</sup> Recently, we have developed a c-BN film deposition process by which the upper layer of the c-BN film could be a pure cubic phase.<sup>12,13</sup> Therefore, it is possible to measure the *t*-BN content by cross-sectional high-resolution transmission electron microscopy (HRTEM).

With these as a background, in this letter, we studied the influence of the compressive stress on the IR absorption of the initial  $sp^2$ -bonded BN layer in *c*-BN films, and our results revealed that the B–N stretching vibration peak intensity near 1380 cm<sup>-1</sup> is suppressed by the compressive stress accumulated during film growth.

Cubic BN films were deposited on single-crystal silicon substrates by inductively coupled plasma-enhanced chemical vapor deposition.<sup>5,12</sup> The plasma was generated at 1 mTorr with an input power of 7 kW. After a series of pretreatments, the plasma gas composition was changed from pure N<sub>2</sub> to approximately 1.6% N<sub>2</sub>+98.4% Ar by adjusting the flow rates of N<sub>2</sub> and Ar to 0.3 and 18.0 SCCM (SCCM denotes cubic centimeter per minute at STP), respectively. Then, 10%  $B_2H_6$  diluted with He was introduced gradually from a water-cooling injection probe into the plasma up to 0.3 SCCM within a 2 min time span. After stabilizing the plasma at 1 mTorr, the substrate bias was reduced to a sheath potential of approximately 65–80 V for 3–10 min film deposition.<sup>6,12</sup> Samples were characterized using crosssectional HRTEM (JEM-4000 FX II and JEM ARM 1250) and nonpolarized Fourier transform infrared (FTIR) (JASCO FT/IR-700) with the transmission mode at normal incidence. The compressive stress accumulated during film growth was determined from the bending of the silicon substrate using the Stoney formula.<sup>14</sup> The stress induced bending of silicon substrate was measured by a tenchor profiler 10 (KLA-Tenchor).

Figure 1 shows a typical IR spectrum of a *c*-BN film and its curve fitting. In many cases, the IR peak position and intensity determination by the standard method, as the dash lines shown in Fig. 1, is interfered by the overlap with adjacent peaks. In this letter, therefore, the peak intensities and positions were determined by fitting IR spectra with pure Lorentzian-type peak functions. With a linear background, the spectrum is composed of five peaks. The peaks at 781.03 and 1380.78 cm<sup>-1</sup> are attributed to the B–N–B bending vibration and B–N stretching vibration of *sp*<sup>2</sup>-bonded BN. The



FIG. 1. (Color online) FTIR spectrum of a typical *c*-BN film. The spectrum is well fitted with five peaks; the dash lines show the traditional peak position and intensity determination method.

<sup>&</sup>lt;sup>a)</sup>Author to whom correspondence should be addressed; electronic mail: hsyang@zju.edu.cn.



FIG. 2. (Color online) HRTEM image of a typical *c*-BN with a pure cubic phase upper layer. The interface between the  $sp^2$ -bonded BN layer and *c*-BN upper layer and their layer thicknesses are also shown schematically.

peak around 1076.94 cm<sup>-1</sup> is the characteristic transverse optical phonon of *c*-BN, and this peak position was found to be located between 1060 and 1100 cm<sup>-1</sup> depending on the remaining compressive stress, and shifted to high wave number linearly with increasing compressive stress.<sup>15,16</sup> The weak peak at 1505.17 cm<sup>-1</sup> can be attributed to a twophonon peak.<sup>17</sup> For good curve fitting, an additional peak at 1234.22 cm<sup>-1</sup> is necessary; this peak is attributed to *y*-BN, which is not yet understood.<sup>18</sup>

Figure 2 shows HRTEM image of a typical *c*-BN film. An *a*-BN/*t*-BN/*c*-BN layered structure is clearly observed. The upper *c*-BN layer is a pure cubic phase layer; no *sp*<sup>2</sup>-bonded BN was detected on the film surface or on the grain boundary of individual *c*-BN nuclei. Note that, in many cases, *c*-BN films have a *t*-BN/*c*-BN mixture upper layer, therefore, determination of the *sp*<sup>2</sup>-bonded BN content and its initial layer thickness becomes difficult. Here, the interface between the *c*-BN and *t*-BN layers is discernible but not straight. In this study, the initial *sp*<sup>2</sup>-bonded BN layer thickness (*T*<sub>initial</sub>) is defined as the area of initial *sp*<sup>2</sup>-bonded BN layer divided by the length of the film/substrate interface in a cross-sectional HRTEM image. In this way, *T*<sub>initial</sub> of the film in Fig. 2 was determined to be approximately 7.8 nm.

Figure 3 shows the  $T_{\text{initial}}$  of six films and their measured peak intensities ( $I_{\text{measure}}$ ) near 1380 cm<sup>-1</sup> correspondingly. For comparison, a series of calculated peak intensities ( $I_{\text{calc.}} = I_{\text{lowest}}T_{\text{initial}}/T_{\text{lowest}}$ ) were also shown, where  $I_{\text{lowest}}$  and  $T_{\text{lowest}}$  are  $I_{\text{measure}}$  and  $T_{\text{initial}}$  of the sample with the lowest compressive stress (corresponding to *c*-BN peak position at 1073.75 cm<sup>-1</sup> in this study), respectively. The calculated intensities are based on the assumption that the intensity is simply proportional to the layer thickness. No obvious linear relationship between  $T_{\text{initial}}$  and  $I_{\text{measure}}$  is shown in Fig. 3,



FIG. 3. (Color online)  $I_{\text{measure}}$  near 1380 cm<sup>-1</sup> shows no linear relationship with its  $T_{\text{initial}}$ . The  $I_{\text{calc}}$  is also shown.



FIG. 4. (Color online) Deviation  $(I_{calc.}-I_{measure})$  of the peak intensity is found to increase with compressive stress; the inset shows the *c*-BN peak position increased linearly with the measured compressive stress.

which is considered to be due to the different compressive stresses in films, since films were deposited under different substrate biases and for different deposition times.<sup>10,19</sup> The stress conditions inside a c-BN film are complicated due to the Si/a-BN/t-BN/c-BN multilayer film structure.<sup>19,20</sup> For c-BN film direct deposition on the substrate without a buffer layer, in situ stress measurement revealed that the total compressive stress increases steadily from the deposition of the initial t-BN layer to the deposition of the upper c-BN layer, while within the *c*-BN layer, the instantaneous compressive stress remains largely constant.<sup>19</sup> In this study, we also deposited c-BN films directly on the silicon substrates without a buffer layer, which suggests that a compressive stress is accumulated in the *t*-BN layer.<sup>19</sup> For simplification, we studied the effect of the film apparent stress on the peak intensity  $I_{\text{measure}}$  near 1380 cm<sup>-1</sup> using the *c*-BN peak wave number as the indicator of the apparent stress in the film.

Figure 4 shows the relationship between the  $I_{calc.}$  – $I_{measure}$  and the film compressive stress accumulated during c-BN growth. The  $I_{calc.}$  and  $I_{measure}$  are distributed randomly due to the different  $T_{initial}$ . However, the  $I_{calc.}$ – $I_{measure}$  is found to increase linearly with the compressive stress, which indicates that the  $I_{measure}$  is suppressed by the compressive stress in the film. The inset shows the linear relationship between the apparent compressive stress and the c-BN peak position. Since samples were prepared under very similar conditions with similar nanostructures, it is reasonable to consider that the c-BN peak shift is induced by compressive stress only.<sup>15,21</sup> Figures 3 and 4 suggest that the  $T_{initial}$  of a c-BN film could be deduced from the  $I_{measure}$  of t-BN near 1380 cm<sup>-1</sup> and the c-BN peak position when the upper layer is a pure cubic phase layer.

The IR absorbance of a *c*-BN film is sensitive to and is often influenced by its composition and nanostructure, for example, the existence of *t*-BN in the upper *c*-BN layer and the *t*-BN basal plane (0002) orientation variation.<sup>1,10,13,16,22</sup> In this study, we found that the  $I_{\text{measure}}$  near 1380 cm<sup>-1</sup> is also a function of compressive stress. This could be one of the reasons that the measured absorption coefficient of *t*-BN in *c*-BN films under compressive stress was much less than that predicted from the nearly single-crystal properties.<sup>10,11</sup> According to the quantum theory of phonon excitation, the IR absorption coefficient should be proportional to the density of phonon final states (at the center of Brillouin zone) which is related to the phonon dispersion and can be influenced by the strain in a material. Further works to clarify the mechanism for the IR peak intensity suppression by compressive stress are underway.

In conclusion, the effect of the compressive stress on the IR peak intensity near 1380 cm<sup>-1</sup> attributed to the B–N stretching vibration of  $sp^2$ -bonded boron nitride in a *c*-BN film was investigated. The  $I_{\text{measure}}$  near 1380 cm<sup>-1</sup> is revealed to be suppressed by the compressive stress, at least for *c*-BN films deposited by inductively coupled plasma-enhanced chemical vapor deposition. Our findings also suggest that the influence of the compressive stress on the IR absorption should be taken into account when IR was used to quantitatively analyze the composition of films under compressive stress.

The authors acknowledge Toyonobu Yoshida at The University of Tokyo for sample preparation and TEM observation. This work was supported by the National Foundation of Zhejiang Province, China (Grant No. Y405051) and the Zhejiang Province Educational Department, China (Grant No. 20061365).

- <sup>1</sup>P. N. Mirkarimi, K. F. McCarty, and D. L. Medlin, Mater. Sci. Eng., R. **21**, 47 (1997), and references therein.
- <sup>2</sup>C. B. Samantaray and R. N. Singh, Int. Mater. Rev. **50**, 313 (2005), and references therein.
- <sup>3</sup>X. W. Zhang, H. G. Boyen, N. Deyneka, P. Ziemann, F. Banhart, and M.

- Schreck, Nat. Mater. 2, 312 (2003).
- <sup>4</sup>W. J. Zhang, I. Bello, Y. Lifshitz, K. M. Chan, X. M. Meng, Y. Wu, C. Y. Chan, and S. T. Lee, Adv. Mater. (Weinheim, Ger.) **16**, 1405 (2004).
- <sup>5</sup>H. S. Yang, C. Iwamoto, and T. Yoshida, J. Appl. Phys. **94**, 1248 (2003).
- <sup>6</sup>H. S. Yang, C. Iwamoto, and T. Yoshida, Diamond Relat. Mater. **16**, 642 (2007).
- <sup>7</sup>K. Nose, K. Tachibana, and T. Yoshida, Appl. Phys. Lett. **83**, 943 (2003).
  <sup>8</sup>K. Nose, H. S. Yang, and T. Yoshida, Diamond Relat. Mater. **14**, 1297 (2005).
- <sup>9</sup>K. Nose, H. Oba, and T. Yoshida, Appl. Phys. Lett. 89, 112124 (2006).
- <sup>10</sup>O. Tsuda, Y. Yamada, T. Fujii, and T. Yoshida, J. Vac. Sci. Technol. A 13, 2843 (1995).
- <sup>11</sup>S. Jager, K. Bewilogue, and C. P. Klages, Thin Solid Films **245**, 50 (1994).
- <sup>12</sup>H. S. Yang, C. Iwamoto, and T. Yoshida, Thin Solid Films **407**, 67 (2002).
- <sup>13</sup>H. S. Yang, C. Iwamoto, and T. Yoshida, J. Appl. Phys. **95**, 2337 (2004).
- <sup>14</sup>G. G. Stoney, Proc. R. Soc. London, Ser. A **82**, 172 (1909).
- <sup>15</sup>S. Fahy, Phys. Rev. B **51**, 12873 (1995).
- <sup>16</sup>S. Fahy, C. A. Taylor, and R. Clarke, Phys. Rev. B **56**, 12573 (1997).
  <sup>17</sup>P. J. Gielisse, S. S. Mitra, J. N. Plendl, R. D. Griffs, L. C. Mansur, R.
- Marshall, and E. A. Pascoe, Phys. Rev. **155**, 1039 (1967). <sup>18</sup>J. Ullmann, J. E. E. Baglin, and A. J. Kellock, J. Appl. Phys. **83**, 2980
- (1998). <sup>19</sup>G. Reisse, S. Weissmantel, and D. Rost, Diamond Relat. Mater. **11**, 1276
- (2002).
- <sup>20</sup>Y. K. Yap, T. Aoyama, Y. Wada, M. Yoshimura, Y. Mori, and T. Sasaki, Diamond Relat. Mater. 9, 592 (2000).
- <sup>21</sup>Y. N. Zhao, B. Zhao, and Z. He, Spectrosc. Lett. **31**, 945 (1998).
- <sup>22</sup>H. S. Yang, C. Iwamoto, and T. Yoshida, J. Appl. Phys. **91**, 6695 (2002).
- <sup>23</sup>G. Kern, G. Kresse, and J. Hafner, Phys. Rev. B **59**, 8551 (1999).