Effect of Employing Chromium as a Buffer Layer on the Crystallinity of Hexagonal Boron Nitride Films Grown by LPCVD

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Abstract

Using chromium (Cr), which was deposited by radio frequency magnetron sputtering, as a buffer layer for synthesizing high-quality hexagonal boron nitride (hBN) films by low-pressure chemical vapor deposition (LPCVD) was demonstrated. The effect of growth temperature and annealing process on the quality of the Cr buffer layer was investigated. The characterization of the dependence of hBN film quality on growth temperature, substrate, and annealing process was discussed. All evidence shows that using a Cr buffer layer can significantly improve the crystalline quality of hBN. A DUVPD based on hBN film using Cr as the bottom electrode was fabricated with a small leakage current. The photocurrent is 3.5 nA at a bias of 500 V, and it exhibits good switching characteristics.

1. Introduction

In recent years, hexagonal boron nitride (hBN) has attracted extensive interest from researchers due to the application in deep-ultraviolet photodetectors which the corresponding intrinsic absorption edge is approximately 207 nm[1–3]. With a graphite-like structure[4, 5], hBN is composed of alternating boron and nitrogen atoms in a two-dimensional (2D) honeycomb structure and with van der Waals interactions between the layers[4–6]. As a wide bandgap semiconductor[7], hBN also has properties such as heat-resistant[8], high frequency[9], and radio resistance[10]. The exciting properties make hBN a prospective optoelectronics[11] and electronics material[12].

The conventional growth process for hBN is directly heteroepitaxy grown on a substrate such as sapphire[13], silicon carbide (SiC)[14], and silicon (Si)[15]. Still, it is difficult to produce high-quality and large-area hBN films due to large lattice mismatch and low nitrogen solubility [3, 16, 17]. Compared with a traditional substrate, transition metal substrates generally have a small lattice constant. So far, most studies on the growth of hBN films have used foil form of transition metals as substrate, mainly nickel (Ni)[18], platinum (Pt)[19], copper (Cu)[20]. However, it is hard to synthesize high-quality hBN films using metal foils as a substrate due to the uneven and rough surface of the foils[21–25]. Due to the strength and flatness of the foils and the difficulty of transferring hBN films when integrated with other silicon-based or sapphire-based devices, the use of transition metal foil to grow hBN still has certain limitations. In this paper, we proposed a novel growth method of hBN films on the transition metal chromium (Cr) buffer layer using low-pressure chemical vapor deposition (LPCVD)[26–28].

Using Cr as buffer layer for hBN growth has the following advantages: ☒) The lattice constants of hBN and Cr are 0.25 nm and 0.29 nm[29, 30], respectively, the lattice mismatch is only 3.3%. ☒) Nitrogen atoms are more challenging to adsorb on the substrate than boron atoms. Compared with the traditional substrate, the nitrogen atom has a higher solubility in the transition metals[31, 32], which should reduce nitrogen vacancies in the film. ☒) The metal buffer layer grown on traditional substrates has a smooth and uniform surface[33, 34] over the whole area, which is more suitable for the growth of high-quality hBN films.

2. Experiment

The deposition of Cr buffer layer: The Cr buffer layer was sputter deposited on sapphire (0001) substrates by radio frequency magnetron sputtering (RFMS)[35]. The sputtering chamber was pumped to a base pressure of 5×10^{-4} Pa, then filled with Ar at a rate of 80 sccm to the working pressure of 1 Pa. The Cr buffer layer was deposited at a sputtering power of 80 W for 60 minutes. The deposition temperature varied from 400 to 700°C. After the deposition process, the Cr buffer layer was annealing in situ at 850°C for 10 minutes.

The growth of hBN films: The hBN films were grown on the Cr buffer layer by a low-pressure chemical vapor deposition (LPCVD) system[36, 37]. The chamber was pumped to 7.5×10^{-4} Pa, and then the substrate was heated to 1450°C under nitrogen ambient with an N_2 flow rate of 100 sccm. The B and N source for the growth were boron chloride (BCl_3) and ammonia (NH_3) at flow rates of 10 sccm and 30 sccm, respectively. The samples were annealed at 1650°C for 10 minutes to recrystallize the hBN films.

Characterization of the Cr buffer layer and hBN films: The surface morphology and structure were investigated using field emission scanning electron microscopy (SEM; JSM-7500F). The crystal quality was characterized by an X-ray diffraction pattern (XRD; TTRIII, Rigaku) using Cu K α radiation. Raman spectra were acquired by LABRAM HR Evolution using a laser excitation wavelength of 532 nm. The sheet resistance of the Cr buffer layer was measured by a Four-Point Probe Meter (RTS-8).

3. Results And Discussion

A schematic diagram of the growth process of the hBN film was shown in Figure 1. Firstly, the Cr buffer layer was deposited on sapphire (0001) substrates by RFMS. Then, the hBN films were grown on the Cr buffer layer (Cr/sapphire) by LPCVD. The surface morphology of the substrates is one of the most critical factors that will limit the quality of hBN films. The crystal quality of the buffer layer obtained by RFMS seriously depends on the growth process and technological conditions. The surfaces of metal foils often have many grain boundaries and grooves or protrusions, which cause high-density defects during nucleation and growth of hBN film. Therefore, depositing a high-quality Cr buffer layer with a low density of grain boundaries is the key to synthesizing high crystalline quality hBN films. Consequently, we investigated the dependence of surface morphology and crystal quality of the Cr buffer layer deposited by RFMS on growth temperature and thermal annealing.

3.1 Growth of Cr buffer layer and characterization

To evaluate the sputtering temperature on the crystal quality of Cr, we deposited Cr buffer layer at various sputter temperature of 400°C, 500°C, 600°C, and 700°C. Figure 2(a) is the X-ray diffraction (XRD) pattern of the Cr grown on the sapphire substrates with different sputter temperature. Cr-I, Cr-II, Cr-III, and Cr-IV are corresponding to the sputtering temperature of the Cr buffer layer at 400°C, 500°C, 600°C, and 700°C, respectively. The (110) peaks of the Cr buffer layer at 44.4° are in good accordance with the standard

card (PDF#06-0694)[38]. However, the XRD peak of the Cr buffer layer is almost invisible at sputter temperature of 400°C(Cr-I), indicates that Cr has poor crystal quality at a lower temperature. However, with the increase of sputter temperature, the (110) peak of chromium gradually shifts toward the standard peak position. (The XRD peaks of Cr-II, Cr-III, Cr-IV are at 42.8, 44.53, 44.52, respectively). Peak positions not marked in figures are signals of the sapphire substrate. At the same time, the full width at half maximum (FWHM) of Cr (110) peak gradually decreases with the increasing of sputter temperature, and the FWHM varies from 1.0° (500°C) to 0.67 ° (700 °C). Figure 2(b) shows the XRD pattern in the θ -2 θ configuration of the Cr buffer layer grown at different temperatures after the [annealing process](#). The thermal annealing (TA) temperature of chromium is at 850°C. It can be seen that the Cr (110) peak of Cr-I appears after thermal annealing with a peak position of 44.63° and FWHM of 0.45°. The annealing process significantly improves the crystal quality of the Cr buffer layer, and the FWHM of Cr (110) peak reduces from 0.67 to 0.32 at a sputter temperature of 700 °C.

The surface morphology of the Cr buffer layer also depended on the sputtering temperature and annealing process. As shown in Fig.3, the surfaces of Cr buffer layers consist of regularly arranged and distributed nanocrystal grains. The average size of these grains varies from 70 nm to 120 nm, depending on sputter temperature and the annealing process. Fig. 3 (a)~(d) are SEM images of Cr-I, Cr-II, Cr-III, and Cr-IV, respectively. The nanocrystal grains are polyhedral structures composed of multiple edges for the Cr buffer layer deposited at 400 °C and 500 °C. As the temperature increases, the crystal domain becomes more extensive, and the grain boundaries become indistinguishable. Figures 3 (e)~(h) show that the surfaces of annealed Cr buffer layers in which grain boundaries are bonded, and the grains become denser than unannealed samples. Besides, the dimension of Cr grains increases with the increase of growth temperature after the thermal annealing process. This result is mainly due to the recrystallization of the Cr buffer layer after annealing. These indicate that the surface morphology of the Cr buffer layer improves significantly with the increase of the sputtering temperature and the application of the thermal annealing process.

To further determine the effect of sputter temperature and annealing process on continuity of the Cr buffer layer, the electrical property of Cr buffer layers is carried out by a square four-point probe measurement. Figure 4 shows the sheet resistances of the Cr buffer layer with different sputter temperatures and annealed at 850°C. As the sputtering temperature increases, the sheet resistances of the Cr buffer layer gradually decrease. After the annealing process, all the sheet resistances of the Cr buffer layer are reduced. The sheet resistance decreases to 0.7 $\Omega / \square$ for the sample deposited at a temperature of 700°C. The electrical characteristics of the Cr buffer layer are improved as the sputter temperature increases, and the thermal annealing process is applied.

The above experimental results show that the crystal quality, surface morphology, and electrical properties improve significantly with increasing sputter temperature and thermal annealing. The optimum deposition conditions of the Cr buffer layer by RFMS include a sputter temperature of 700 °C and an annealing temperature of 850 °C.

3.2 Growth of hBN films and characterization

Temperature is an essential factor in limiting the quality of the films deposited by physical vapor deposition and affects the quality of the films grown by CVD. To obtain high-quality hBN films, we synthesized hBN films under different growth temperatures by LPCVD. For comparison, hBN films were grown on sapphire substrates and Cr/sapphire substrates at 1200 °C, 1350°C, and 1450°C, respectively. Figure 5(a) shows the XRD patterns of hBN films synthesized on sapphire substrates. At the growth temperature of 1200 °C, no corresponding hBN diffraction peak is observed at the sample grown on sapphire substrates, while the hBN (002) diffraction peak could be found after increasing the growth temperature. Besides, as the temperature increases, the hBN (002) peak shifts toward the bulk hBN peak, which is centered at 26.7°, corresponding to the (002) plane[39, 40]. Figure 5(b) shows the XRD patterns of hBN films synthesized on the Cr-IV/ sapphire substrates. Similarly, with the increase of growth temperature, the hBN (002) plane peak shifts toward the standard peak position. The peak position shift indicates the crystal plane arrangement of films synthesized at higher temperatures is more regular. The FWHM decreases with increasing growth temperature and reduces to 0.67 ° at a growth temperature of 1450 °C. It is different from the sample grown directly on sapphire. The (002) plan peak appears when growing on the Cr buffer layer at the same growth temperature of 1200 °C. The diffraction peak is closer to 26.7°, and FWHM is narrower when the Cr buffer layer is applied. The results show that the hBN film has more excellent crystal quality on the Cr buffer layer than the direct growth on the sapphire substrate. Therefore, we get the best crystalline quality hBN films at the growth temperature of 1450 °C.

Furthermore, we investigated the effect of the quality of the Cr buffer layer on the crystal quality of hBN films. Figure 6(a) shows the XRD patterns of hBN films synthesized at a growth temperature of 1450 °C on sapphire substrate and the Cr buffer layers deposited at different sputter temperatures. Fig. 6(b) shows the XRD patterns of hBN films grown on a thermal annealed Cr buffer layer under the same sputter temperature. The position of (002) peak and FWHM of hBN films growth on Cr buffer layer are described in Fig. 6(c). The hBN peak gradually shifts toward the standard peak position, and the FWHM decreases from 0.654° (400°C) to 0.619° (700 °C) as the sputtering temperature of the Cr buffer layer rises. Compared with the hBN films grown on the unannealed Cr buffer layer, the hBN grown on the annealed Cr buffer layer resulted in a narrower FWHM. As the quality of the Cr crystal increases, the FWHM changes from 0.617° (TA Cr-I) to 0.587° (TA Cr-IV). It is indicated that a significant improvement in the crystallinity of hBN films can be achieved by growing on the high-quality Cr buffer layer.

Raman spectrum was employed to identify the bonding states of hBN. The typical Raman spectrum of the bulk hBN shows a strong peak at about 1366 cm⁻¹, arising from the E_{2g} vibrational mode of hBN[41, 42]. Figure 7(a) shows the Raman spectrum of hBN films synthesized on sapphire and the Cr buffer layer of which was deposited at sputter temperature of 400 °C, 500°C, 600°C, and 700°C, respectively. The hBN film grown on sapphire has a broad and weak Raman peak at around 1377 cm⁻¹ with an FWHM of 69.5 cm⁻¹. However, the Raman spectrum of hBN films grown on the Cr buffer layer shows a narrower vibration peak. Along with improving the crystal quality of the Cr buffer layer, the FWHM of the Raman peaks of the

hBN films synthesized on the Cr buffer layer decreases obviously, and the vibration peak gradually shifts toward the standard peak position. Fig. 7(b) shows the Raman spectrum of hBN films grown on a thermal annealed Cr buffer layer. Fig. 7(b) shows that the Raman vibration peak is further close to 1366 cm^{-1} and the FWHM becomes narrower. The E_{2g} peak of the hBN films grown on the best quality Cr buffer layer (TA Cr-IV) shifts to 1370.5 cm^{-1} , and the FWHM falls to 45.5 cm^{-1} . This consequence agrees with the XRD measurement results, manifesting the effect of the high-quality Cr buffer layer on improving the crystallinity of the hBN films.

In conclusion, the crystal quality of hBN films depends on growth temperature and whether there is a high-quality buffer layer. The quality of hBN films can be improved by increasing growth temperature and improving the quality of the Cr buffer layer. Besides, hBN films grown on the Cr buffer layer have better quality than those synthesized directly on the sapphire substrate.

3.3 Thermal annealing of hBN films

According to the above Raman spectrum results, even the best-quality hBN film grown on thermal annealed Cr buffer layer, its vibration peak position still has an absolute blue-shift compare with single-crystal hBN. It indicates that there is residual stress in the lattice of hBN. The compression stress in hBN is induced by lattice mismatch or thermal expansion coefficient mismatch between the hBN layer and the supporting materials. To relax the residual stress, the hBN films were thermally annealed at a high temperature of $1650\text{ }^{\circ}\text{C}$. In the first place, XRD patterns were measured to identify the effect of the annealing process on the quality of hBN films. The results are shown in Fig. 8 (a) and (b). After thermal annealed at such high temperature, the peak intensity and FWHM of the (002) diffraction peaks for all samples have improved significantly. However, the FWHM of (002) diffraction peak for annealed hBN films visibly varies with the substrate. The FWHM value for TA hBN films grown on the Cr buffer layer is smaller than TA hBN/sapphire. In the meantime, the FWHM values decrease with the improving quality of Cr buffer layers. Compared with the unannealed samples, the FWHM values of TA hBN films further become narrow. For example, the FWHM value of hBN films grown on TA Cr-IV is significantly reduced from 0.587° before annealing to 0.422° after annealing. In Particular, the FWHM value of the hBN films synthesized directly on a sapphire substrate decreases to 0.517° after annealing treatment from 1.33° . By comparing the XRD results of all the samples, the hBN film with the best crystalline quality is the TA hBN/TA Cr-IV sample, which (002) diffraction peak is centered at 26.7° with an FWHM of 0.422° .

In the second place, the Raman spectrum of hBN films after annealing are shown in Fig. 8(c) and (d). It is similar to the results of XRD, the FWHM of Raman vibration peak for TA hBN films also depends on the selected substrate. The better the Cr buffer layer's quality, the better the crystalline quality of the hBN film grown on. Moreover, the Raman vibration peak continually shifts to the standard peak position (1366 cm^{-1}) to improve the quality of the Cr buffer layer. After annealing, the E_{2g} peak of the hBN/TA Cr-IV sample shifts to 1367.1 cm^{-1} from 1370.5 cm^{-1} , and the FWHM value correspondingly falls to 25.2 cm^{-1} from 45.5

cm^{-1} . The above results and discussions indicate that the residual stress in hBN films can be relieved by high-temperature annealing. The crystalline quality of hBN films can be markedly improved.

The effects of substrate and annealing process on the surface morphology of hBN films were investigated by SEM. Fig. 9 (a) and (b) were SEM images of unannealed and annealed hBN films grown on the sapphire substrate, respectively. The surface of the unannealed hBN film looks like grassland, and it shows inferior continuity. Although the continuity and uniformity of the hBN are improved by the thermal annealing process, the film surface creases or even cracks locally after annealing treatment, which may be related to relaxation of residual stress in hBN films. Fig. 9 (c) and (d) show the SEM images of unannealed and annealed hBN films grown on the thermal annealed Cr buffer layer (TA Cr-IV), respectively. The surface morphology of the hBN film grown on the Cr buffer layer significantly improved compared to the one directly grown on the sapphire substrate. It seems like the film is smoother, more continuous, and more uniform. After annealing, the hBN crystal domains become more significant. No crack is observed in the hBN films, attributed to the smaller lattice mismatch between hBN film and Cr buffer layer, resulting in less internal stress. High-magnification SEM images of hBN films from the inset of Fig.9 (c) and (d) show that the crystal domain of hBN films becomes more extensive and more uniform after annealing.

Figure 9(a) shows the UV-vis absorption spectra of the sample TA hBN/TA Cr-IV after transferring to a quartz substrate. The optical absorption edge was 217 nm, and the film has almost no absorption from the visible to infra-red (IR) wavelength. The optical band gap (OBG) was about 5.67 eV according to the Tauc plot, shown in figure 9(b). The value of the OBG was close to the reported value by CVD synthesized hBN films[43]. After deposited Au top electrodes on the film, we manufactured a deep UV photodetector (DUVPD). The bottom electrode of the device was led out through the part blocked during the growth (inset in Fig.9c). A 224 nm laser (Photon Systems: HeAg 70-224SL) and pen-ray lamp (UVP: 90-0020-01) were used to test the DUV excitation response of the DUVPD. When the device was irradiated with the 224 nm laser, no photoelectric response was recorded. Therefore, the I-V characteristics were performed using the pen-ray lamp. This lamp has an intensity of $\sim 55 \mu\text{W}/\text{cm}^2$ at a distance of 0.75 inch at the DUV wavelength of 184.9 nm. As shown in Fig.9(c), the device demonstrated a strong DUV response. Since the electrodes on both sides are not symmetrical patterns, the curve of the magnitude of the photocurrent with the bias voltage is not symmetrical about the origin. The maximum photocurrent is 3.5 nA at a bias voltage of 500 V. Fig.9(d) shows the photoresponse of the DUVPD at a bias voltage of 100 V, and it could be seen that the device can be readily switched between “on” and “off” states.

4. Conclusion

In summary, the synthesis of high-quality and wrinkle-free hBN films on the Cr buffer layer by LPCVD had been achieved. There is a clear correlation between the crystalline quality of hBN films and the substrates, growth temperature, and thermal annealing process. The crystallinity of hBN films grown on the Cr buffer layer superior to the one using a sapphire substrate, sputtering temperature, and annealing process also played a decisive role in improving the quality of the Cr buffer layer. Also, the crystallinity of hBN films

increases with the rising growth temperature, and the variation with temperature of hBN films is both applied to a sapphire substrate and Cr buffer layer. Lastly, the hBN films are recrystallized by annealing process at high temperature, and the quality of annealed hBN films (with a diffraction peak of 26.7°) further near the standard peak position. Compared with the sapphire substrate, the underlying Cr layer can improve the quality of hBN films due to the reduction of mismatch and the more considerable adsorption of the nitrogen atom. The results were mainly due to the increased Cr grains and improved crystallinity of the underlying Cr buffer layer. Moreover, thermal annealing at high temperatures will improve the quality of hBN films due to the recrystallization and relaxation of stress. Finally, a DUVPD based on hBN film using Cr as the bottom electrode was fabricated. The device has a small leakage current, the photocurrent is 3.5 nA at a bias of 500 V, and it exhibits good switching characteristics.

Declarations

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References

1. K. Watanabe, T. Taniguchi, H. Kanda, *Nat. Mater.* **3**(6), 404-409 (2004)
2. Y. Kubota, K. Watanabe, O. Tsuda, T. Taniguchi, *Science* **317**(5840), 932-934 (2007)
3. J. Li, R. Dahal, S. Majety, J. Y. Lin, H. X. Jiang, *Nuclear Instruments & Methods in Physics Research Section a-Accelerators Spectrometers Detectors and Associated Equipment* **654**(1), 417-420 (2011)
4. W. Gannett, W. Regan, K. Watanabe, T. Taniguchi, M. F. Crommie, A. Zettl, *Appl. Phys. Lett.* **98**(24), (2011)
5. C. R. Dean, A. F. Young, I. Meric, C. Lee, L. Wang, S. Sorgenfrei, K. Watanabe, T. Taniguchi, P. Kim, K. L. Shepard, J. Hone, *Nat. Nanotechnol.* **5**(10), 722-726 (2010)
6. I. Naumov, A. M. Bratkovsky, V. Ranjan, *Phys. Rev. Lett.* **102**(21), 217601 (2009)
7. A. Rubio, J. L. Corkill, M. L. Cohen, *Phys Rev B Condens Matter* **49**(7), 5081-5084 (1994)
8. Z. Liu, Y. Gong, W. Zhou, L. Ma, J. Yu, J. C. Idrobo, J. Jung, A. H. MacDonald, R. Vajtai, J. Lou, P. M. Ajayan, *Nat. Commun.* **4**, 2541 (2013)
9. J. Gaskell, L. Eaves, K. S. Novoselov, A. Mishchenko, A. K. Geim, T. M. Fromhold, M. T. Greenaway, *Appl. Phys. Lett.* **107**(10), (2015)
10. Y. Z. Duan Xiaoming, Wang Yujin, et al., *MATERIALS CHINA* (10), 001 (2015)
11. X. L. Ding, G. Q. Ding, X. M. Xie, F. Q. Huang, M. H. Jiang, *Carbon* **49**(7), 2522-2525 (2011)
12. A. Catellani, M. Posternak, A. Baldereschi, A. J. Freeman, *Phys Rev B Condens Matter* **36**(11), 6105-6111 (1987)

13. A. R. Jang, S. Hong, C. Hyun, S. I. Yoon, G. Kim, H. Y. Jeong, T. J. Shin, S. O. Park, K. Wong, S. K. Kwak, N. Park, K. Yu, E. Choi, A. Mishchenko, F. Withers, K. S. Novoselov, H. Lim, H. S. Shin, *Nano Lett.* **16**(5), 3360-3366 (2016)
14. W. Chen, K. P. Loh, M. Lin, R. Liu, A. T. S. Wee, *Physica Status Solidi a-Applications and Materials Science* **202**(1), 37-45 (2005)
15. C. Rohr, J.-H. Boo, W. J. T. S. F. Ho, *Thin Solid Films* **322**(1-2), 9-13 (1998)
16. T. C. Doan, S. Majety, S. Grenadier, J. Li, J. Y. Lin, H. X. Jiang, *Nuclear Instruments & Methods in Physics Research Section a-Accelerators Spectrometers Detectors and Associated Equipment* **783**, 121-127 (2015)
17. M. Chubarov, H. Pedersen, H. Högberg, A. Henry, Z. J. J. o. V. S. Czigány, S. Technology A: Vacuum, Films, *J. Vac. Sci. Technol. A* **33**(6), 061520 (2015)
18. W. Auwarter, M. Muntwiler, J. Osterwalder, T. Greber, *Surf. Sci.* **545**(1-2), L735-L740 (2003)
19. R. Simonson, M. Paffett, M. Jones, B. Koel, *Surf. Sci.* **254**(1-3), 29-44 (1991)
20. A. B. Preobrajenski, A. S. Vinogradov, N. Martensson, *Surf. Sci.* **582**(1-3), 21-30 (2005)
21. A. Goriachko, Y. He, M. Knapp, H. Over, M. Corso, T. Brugger, S. Berner, J. Osterwalder, T. Greber, *Langmuir* **23**(6), 2928-2931 (2007)
22. D. E. Starr, E. M. Pazhetnov, A. I. Stadnichenko, A. I. Boronin, S. K. Shaikhutdinov, *Surf. Sci.* **600**(13), 2688-2695 (2006)
23. F. Orlando, P. Lacovig, L. Omiciuolo, N. G. Apostol, R. Larciprete, A. Baraldi, S. Lizzit, *ACS Nano* **8**(12), 12063-12070 (2014)
24. A. Nagashima, N. Tejima, Y. Gamou, T. Kawai, C. Oshima, *Phys Rev B Condens Matter* **51**(7), 4606-4613 (1995)
25. N. Guo, J. Wei, L. Fan, Y. Jia, D. Liang, H. Zhu, K. Wang, D. Wu, *Nanotechnology* **23**(41), 415605 (2012)
26. Y. Shi, C. Hamsen, X. Jia, K. K. Kim, A. Reina, M. Hofmann, A. L. Hsu, K. Zhang, H. Li, Z. Y. Juang, M. S. Dresselhaus, L. J. Li, J. Kong, *Nano Lett.* **10**(10), 4134-4139 (2010)
27. K. K. Kim, A. Hsu, X. Jia, S. M. Kim, Y. Shi, M. Hofmann, D. Nezich, J. F. Rodriguez-Nieva, M. Dresselhaus, T. Palacios, J. Kong, *Nano Lett.* **12**(1), 161-166 (2012)
28. L. Song, L. Ci, H. Lu, P. B. Sorokin, C. Jin, J. Ni, A. G. Kvashnin, D. G. Kvashnin, J. Lou, B. I. Yakobson, P. M. Ajayan, *Nano Lett.* **10**(8), 3209-3215 (2010)
29. F. Zhou, J. Szczech, M. T. Pettes, A. L. Moore, S. Jin, L. Shi, *Nano Lett.* **7**(6), 1649-1654 (2007)
30. S. Kondratyuk, G. L'vova, I. Radomysel'skii, I. J. S. P. M. Shlyakhtich, M. *Ceramics*, **18**(6), 400-404 (1979)
31. V. A. Shabashov, L. G. Korshunov, V. V. Sagaradze, N. V. Kataeva, A. E. Zamatovskii, A. V. Litvinov, K. A. Lyashkov, *Physics of Metals and Metallography* **114**(8), 681-691 (2013)
32. M. G. Barker, P. Hubberstey, A. T. Dadd, S. A. J. J. o. N. M. Frankham, *J. Nucl. Mater.* **114**(2-3), 143-149 (1983)

33. J. A. Thornton, J. Tabock, D. J. T. S. F. Hoffman, *Thin Solid Films* **64**(1), 111-119 (1979)
34. J. J. Olaya, S. E. Rodil, S. Muhl, E. Sanchez, *Thin Solid Films* **474**(1-2), 119-126 (2005)
35. V. Guilbaud-Massereau, A. Celerier, J. J. T. S. F. Machet, *Thin Solid Films* **258**(1-2), 185-193 (1995)
36. T. Takahashi, H. Itoh, A. J. J. o. C. G. Takeuchi, *J. Cryst. Growth* **47**(2), 245-250 (1979)
37. M. D. Allendorf, C. F. Melius, T. H. J. M. O. P. L. A. Osterheld, *Mat. Res. Soc. Symp. Proc.* **410**, (1995)
38. S. Wang, C. Vipulanadan, *Cem. Concr. Res.* **30**(3), 385-389 (2000)
39. Y. Kobayashi, T. Akasaka, *J. Cryst. Growth* **310**(23), 5044-5047 (2008)
40. R. Lynch, H. J. T. J. o. C. P. Drickamer, *The Journal of Chemical Physics* **44**(1), 181-184 (1966)
41. X. K. Cao, B. Clubine, J. H. Edgar, J. Y. Lin, H. X. Jiang, *Appl. Phys. Lett.* **103**(19), (2013)
42. Z. Y. Zhao, Z. G. Yang, Y. Wen, Y. H. Wang, *J. Am. Ceram. Soc.* **94**(12), 4496-4501 (2011)
43. T. H. Yuzuriha, D. W. Hess, *Thin Solid Films* **140**(2), 199-207 (1986)

Figures

Figure 1

Schematic diagram of the growth process of the hBN films on Cr (110)/sapphire substrate.

Figure 2

XRD pattern of (a) Cr-I, Cr-II, Cr-III, and Cr-IV. (b) TA Cr-I, TA Cr-II, TA Cr-III, and TA Cr-IV.

Figure 3

SEM images of Cr buffer layer (a) with the sputter temperatures of 400°C, (b) 500 °C, (c) 600 °C, and (d) 700 °C. (e) after annealed at 850°C, when sputtering temperatures of 400°C, (f) 500 °C, (g) 600 °C, and (h) 700 °C.

Figure 4

The sheet resistance of the Cr buffer layer (a) with different sputter temperatures, (b) after annealing at 850°C .

Figure 5

XRD patterns of hBN films (a) grown on (I) sapphire substrate with the growth temperatures of 1200°C (II) 1350 °C, and (III) 1450 °C. (b) grown on TA Cr-IV/sapphire substrate at the same growth temperature, as shown in Figure 5(a).

Figure 6

XRD patterns of (a) hBN grown on sapphire and Cr-I, Cr-II, Cr-III, and Cr-IV (b) hBN grown on sapphire and TA Cr-I, TA Cr-II, TA Cr-III, and TA Cr-IV. (c) The 2 Theta (I, IV) and FWHM (II, III) of hBN films as a function of the different sputter temperature before (II, IV) and after (I, III) annealing.

Figure 7

XRD patterns of (a) hBN grown on sapphire and Cr-I, Cr-II, Cr-III, and Cr-IV (b) hBN grown on sapphire and TA Cr-I, TA Cr-II, TA Cr-III, and TA Cr-IV. (c) The 2 Theta(I, IV) and FWHM (II, III) of hBN films as a function of the different sputter temperature before (II, IV) and after (I, III) annealing.

Figure 8

XRD patterns and Raman spectrum of (a) and (c) TA hBN grew on sapphire and Cr-I, Cr-II, Cr-III, and Cr-IV. (b) and (d) TA hBN grew on sapphire and TA Cr-I, TA Cr-II, TA Cr-III, and TA Cr-IV.

Figure 9

SEM images of (a)hBN/sapphire (b) TA hBN/sapphire, (c) hBN/TA Cr-IV, (d) TA hBN/TA Cr-IV. The inset of Fig.8 (c) and (d) show high-magnification SEM images of hBN films.

Figure 10

(a) UV-visible absorption spectrum, (b) optical band gap analysis, (c) I-V characteristics of the DUVPD, the inset shows the schematic diagram of the device, (d) Photoresponse of the DUVPD under UV light illumination at a bias voltage of 100 V.