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In situ S-doping of cubic boron nitride thin films by plasma enhanced chemical vapor deposition

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Abstract

In situ sulphur doping of cubic boron nitride (cBN) films was investigated by adding H_2S into a plasma-enhanced chemical vapor deposition system. It was found that the nucleation of cBN was suppressed severely with a very low H_2S concentration, while cBN could be grown continuously even at a H_2S concentration as high as that of the boron source after its nucleation. Accordingly, S was incorporated into cBN films meanwhile keeping the cubic phase concentration as high as 95%. And a rectification ratio of approximately 10^5 was observed at room temperature for heterojunction diodes prepared by depositing S-doped cBN films on p-type silicon substrates, which suggests the possibility of an n-type-like doping. Moreover, 1500K post annealing of cBN films in H_2 atmosphere was found to be able to release the residual compressive stress evidently. Thus, film adhesion strength increased markedly, and cBN films reached a thickness over 200 nm without peeling off from silicon and quartz substrates in air after 9 months.

Introduction

Cubic boron nitride (cBN) films are of interest because of their excellent properties, which make them attractive for many potential applications. For example, cBN films show ultrahigh hardness only after diamond, chemical inertness against ferrous metals and oxygen even at high temperature, and high thermal conductivity, thus are superior candidates for hard coatings. Furthermore, the wide band gap in connection with *p*- and *n*- type dopability makes cBN films even excellent candidates for high-temperature and high-power electronic applications [1-4]. In fact, an ultraviolet light-emitting diode was prepared from a p-n junction of bulk cBN [5].

Recently, high-quality cBN films can be prepared routinely by a variety of chemical vapor deposition (CVD) and physical vapor deposition techniques with the assistance of energetic ion bombardment [6-8]. Primitive studies have found that the as-deposited cBN films usually exhibited p-type conductivity [9-11], and nanocrystalline p-type cBN/n-type silicon heterojunction diodes were revealed to have a rectification ratio as high as 10^4 at room temperature [10, 11]. Very recently, p-type and n-type doping of cBN films were realized by in situ Zn, Mg doping and post Si ions implantation [12-14], respectively. However, much more study is needed for further parameters optimization and mechanism clarification of the doping of cBN films.

We have developed a cBN film deposition process by which the upper layer of cBN films could be a pure cubic phase layer and the initial non-cubic phase transition layer thickness could be minimized to thinner than 3 nm even on Si substrate [6, 15, 16]. With these as a background, in this paper, the influence of H_2S on the nucleation and growth of cBN films for the possibility of in situ n-type doping of cBN film are studied. Also the effects of post annealing on residual compressive stress relaxation and film adhesion improvement are studied.

Experimental details

Cubic BN films were deposited on Si and quartz substrates by inductively coupled plasma-enhanced CVD [6, 15, 16]. The plasma was generated at 1 mTorr with an input power of 7 kW, and the substrate bias was controlled by an auxiliary rf power supply. The substrate temperature during film deposition was between 600 and 900 K heated by an electric heater from the back surface of substrate. The reactant gases during deposition were 10.0 sccm Ar, 0.6 sccm N_2, 3.5 sccm 10% B_2H_6 diluted in He, and 10% H_2S diluted in Ar was used as sulphur source.

Samples were mainly characterized by Fourier transform infrared spectroscopy (FITR) (JASCO FT/IR-700) with transmission and reflection modes at normal incidence, cross-sectional high resolution transmission electron microscopy (TOPCON EM 002BF) equipped with energy dispersion x-ray spectroscopy (EDX) operating at an accelerating voltage of 200 kV, and depth profile second ions mass spectroscopy (SIMS). TEM specimens were prepared by mechanical polishing to a thickness of approximately 100 μm and then ion slicing to a thickness sufficient for TEM observation. The I-V characteristics of cBN films were measured using a semiconductor parameter analyzer (Hewlett Packard 4156B). For I-V curve measurements, Ti dot electrodes with a diameter of 1 mm were fabricated on as-deposited samples by evaporation using a simple shadow mask, and Al was deposited on the back side of the Si substrate after mechanical polishing for Ohmic back contact [12].

Results and discussion

Figure 1 shows apparent transmission mode IR spectra of BN films prepared with H_2S introduced initially before cBN nucleation and growth. Three IR peaks are discernible at approximately 1380, 780 and 1100 cm^{-1}, attributed to the B-N stretching vibration, B-N-B bending vibration of sp^2-bonded BN, and cBN transverse optical vibration, respectively [3]. From IR spectra, cBN was found to be nucleated and then grown normally when H_2S flowrate was below 0.08 sccm, corresponding to an H_2S concentration of approximately 0.54% under the present deposition conditions; however further increasing the H_2S flowrate to 0.1 sccm (H_2S concentration of 0.67%) was found to suppress cBN formation drastically, resulted in a turbostratic BN (tBN) film growth, which suggests the suppression of cBN formation by H_2S.

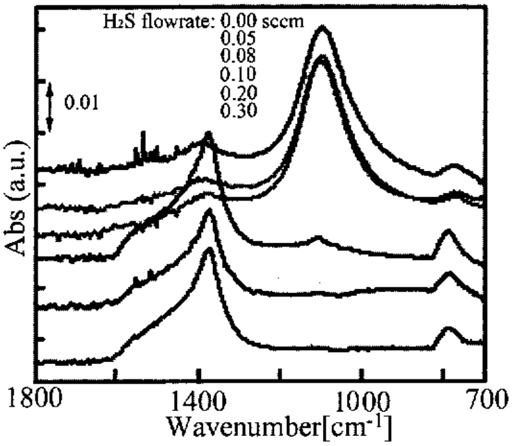

Fig. 1 IR spectra of cBN films with H_2S introduced initially.

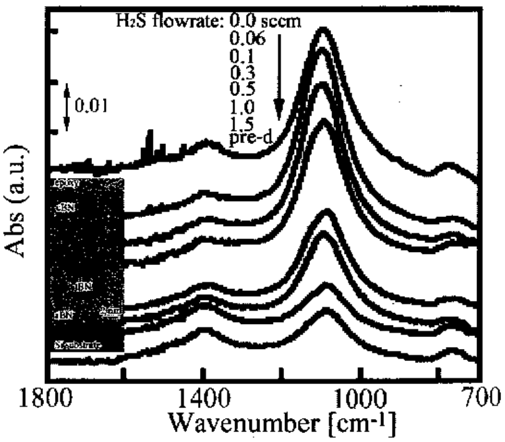

Fig. 2 IR spectra of films with a pre-deposition process before H_2S introduction.

Figure 2 shows apparent transmission mode IR spectra of BN films prepared with H_2S introduced after a 2-minute pre-deposition process without H_2S. For comparison, the IR spectrum of the cBN film stopped after the 2-minute pre-deposition process is also shown. The IR spectrum (pre-d) shows a strong peak near 1080 cm^{-1}, indicating the formation of cubic phase of BN. The inset of Fig.

2 is an HRTEM image of this cBN film showing a pure cubic phase upper layer. Therefore, H_2S was introduced in the cBN film growth stage in this series of experiments. It is evident that pure cBN film continued to grow under a H_2S flowrate of 0.5 sccm (approximately 3.4% H_2S), although, film growth rate decreased a little. Moreover, cBN films containing 50% cubic phase could still be prepared with a very slow growth rate even when the H_2S flowrate exceeded 1.0 sccm (approximately 6.7% H_2S). Note that the B_2H_6 flowrate in this series of experiments was 0.35 sccm. Therefore, cBN film continued to grow under conditions with S concentrations larger than those of B source concentration.

Figure 3 shows the depth profile SIMS of an as-deposited cBN film with 0.3 sccm H_2S flowrate. A high S atomic concentration was detected at the upper layer of cBN film, indicating the successful incorporation of S into the cBN film. The low concentration of S near the film surface is due to the surface contaminant. It is also shown that the S concentration is high near the Si side of BN/Si interface, which was possible due to the matrix effect and O_2^+ ion interference, resulting in an overestimation of the S concentration near the interface. Even though, a low S concentration is still confirmed near the film side of BN/Si interface, which is in good agreement with the application of the pre-deposition process without S introduction.

Figure 4 is a typical I-V curve measured from an S-doped cBN/p-type Si diode, a rectification ratio of approximately 10^5 was frequently measured at room temperature, which suggests the possibility of n-type-like doping of cBN films by S introduction. However, Hall measurement to confirm its carrier type is still a challenge at the present stage.

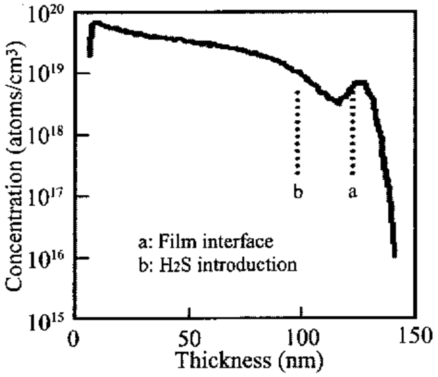

Fig. 3 SIMS of an S-doped cBN film without post annealing.

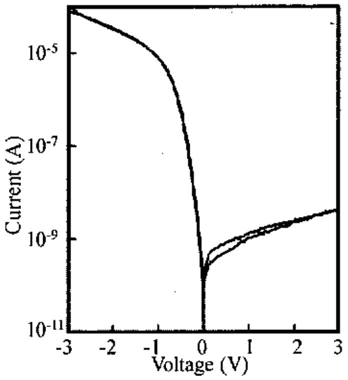

Fig. 4 I-V curve measured from an S-doped cBN/p-type Si substrate heterojunction diode at room temperature.

In situ doping of cBN films was found to be difficult since the nucleation of cBN is very sensitive to impurities. For example, the addition of Si, Zn, Mg and H_2 into the deposition system was found to suppress the cBN film nucleation and growth evidently [12, 14, 17-19]. It seems that there exists a threshold of impurity concentration allowed for cBN nucleation [4], similar to the sharp threshold of ion bombardment needed for cBN nucleation [20]. Our results, as was shown in Fig. 1, also suggest the existence of a sharp threshold of S concentration allowed for cBN nucleation. However, Fig. 2 indicates that the growth of cBN was less sensitive to S addition compared to its nucleation, and cBN grew continuously with an S concentration as high as that of B source, thus S was successfully incorporated into cBN films meanwhile keeping high cubic phase concentration unchanged.

The as-deposited S-doped cBN films also suffered ultra-high residual compressive stress. As a result, films began to peel off from substrates soon after been picked out from vacuumed chamber even with a thickness as thin as 100 nm. Therefore, post annealing was conducted for the possibility of film adhesion improvement in this paper. Figure 5 shows the change of IR spectrum of a cBN film by 120-minute post annealing at 1500 K in H_2 atmosphere. The cBN peak position shifted from 1106 to 1096 cm^{-1} after annealing, suggesting a compressive stress reduction of approximately 3.6 GPa [21, 22]. Moreover, in Fig. 5, two sp^2-bonded BN peak intensities near 780 and 1380 cm^{-1} increased after annealing, and the intensity of the cBN peak also increased evidently. The reason for these IR peak intensities change is still not yet understand. However, the intensity of sp^2-bonded BN peak near 1380 cm^{-1} was found to be suppressed by residual compressive stress in cBN film [22], and intensities of both cBN and sp^2-bonded BN peaks increased remarkably after film delamination induced compressive stress relaxation [23]. Therefore, the strong IR peak near 1380 cm^{-1} after post annealing shown in Fig. 5 is possible due to the absorption coefficient change or the increase of tBN crystallinity [24], but not due to the increase of sp^2-bonded BN concentration. After post annealing, cBN film adhesion increased markedly, as two images shown in Fig. 6, with the assistance of post annealing, cBN film thickness reached to approximately 200 nm without peeling off from Si and quartz substrates after been exposed in air for more than 9 months.

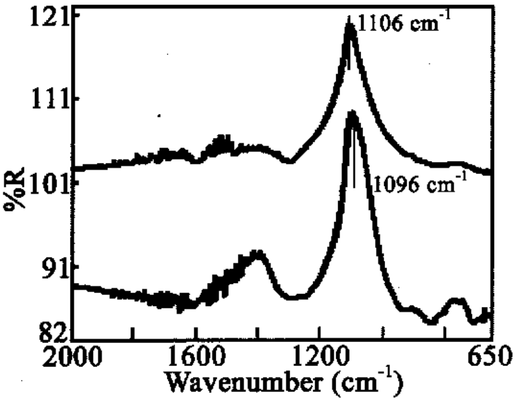

Fig. 5 FTIR spectrum measured from an as-deposited cBN (above) and the film after 1500 K post annealing (below).

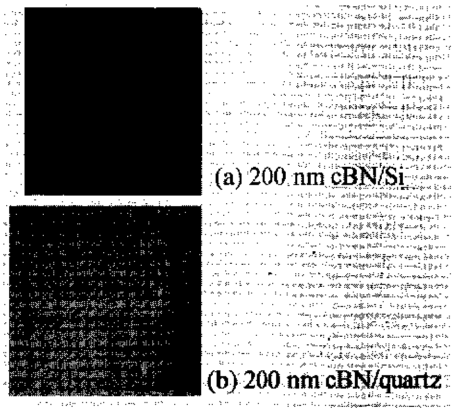

Fig. 6 Two images of post annealed cBN films on (a) Si and (b) quartz substrate, respectively, after 6 months.

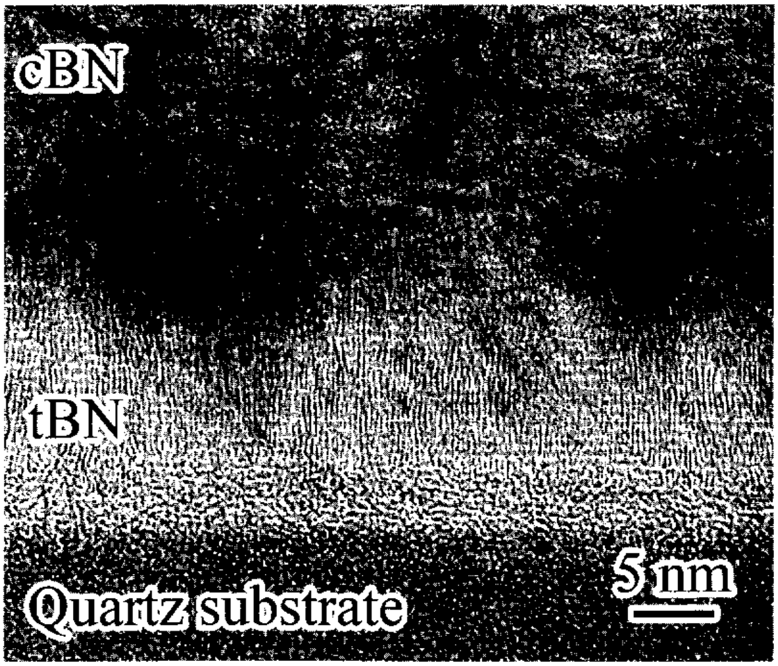

Fig. 7 HRTEM image of an S-doped cBN film deposited on quartz substrate after 1500 K post annealing.

Figure 7 shows the cross-sectional HRTEM image of a cBN film deposited on quartz substrate after post annealing. A typical three-layered structure was also found for the cBN film deposited on quartz substrates and the layered structure kept unchanged after 1500 K post annealing. Moreover, the initial sp^2-bonded BN transition layer thickness is as thin as 15 nm, and the upper layer is almost a pure cBN layer, indicating a high cubic phase concentration even doped with S.

In the past 3 decades, many techniques, such as the introduction of a buffer layer, post ion implantation, post annealing and so on, have been applied for cBN film adhesion improvement but with limited effects [3, 4]. Recently, it was found that the introduction of fluorine into the deposition system can improve the cBN film adhesion evidently [25]. However, for electronic applications, to improve cBN film adhesion without introducing any impurity is highly desirable. Although, only very limited effects was reported till now [26-31], post annealing has this advantage. In this paper, we found that, 1500 K post annealing of cBN films in H_2 atmosphere was effective for residual compressive stress relaxation and film adhesion improvement. Therefore, the present results provide a possible method for the preparation of thick and adherent cBN films with in situ S doping for their electronic applications. Further study to clarify the mechanism of cBN film adhesion improvement by 1500 K post annealing is underway.

Summary

Sulphur was in situ doped into cBN films during preparation by adding H_2S into a CVD system with the assistance of a pre-deposition process, and the as-deposited S-doped cBN/ p-type Si diodes showed rectification ratio of approximately 10^5 at room temperature. Moreover, 1500K post annealing of cBN films in H_2 atmosphere was found to be effective for the release of cBN film residual compressive stress without destroying film structure. Therefore cBN films reached the thickness of approximately 200 nm without peeling off from silicon and quartz substrates in open air for more than 9 months.

Acknowledgments

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