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Carbon nitride films on diamond layers and their thermal behavior

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A CN/diamond composite structure on silicon substrate was obtained by a two-step technique in preparing polycrystalline diamond layers by microwave plasma assisted chemical vapor deposition and then CN films by reactive rf magnetron sputtering. The samples were annealed at different temperatures in the range of 200 to 800 °C, respectively. All the as-grown and annealed CN films, which fully covered the diamond underlayer with the formation of a rather adhesive interface, exhibited amorphous nature uniquely. X-ray photoelectron spectroscopy and energy-dispersive x-ray studies both revealed that the nitrogen concentration of the films decreases after annealed at high temperature. Infrared spectra also suggested the thermal modifications on the content and structure of the CN films. The electric resistivity varies in a large range as the annealing temperature increasing, and confirmed the bonding configuration in favor of a graphite-like structure at high temperature. © *2000 Kluwer Academic Publishers*

1. Introduction

It is of great current interests to study on the synthesis and properties of carbon nitride (CN) films, see a recent review by Wang [1]. One reason is the theoretical prediction [2, 3] of the existence of a covalently bonded CN phase, β–C_3N_4, which should have a bulk modulus comparable to that of diamond. This suggested that CN films could be made for wear-resistant coatings with exceptional mechanical performance. Wu *et al.* [4] employed rf plasma-enhanced chemical vapor deposition (PECVD) to deposit polycrystalline CN films, which had the hardness up to 5100 kgf/mm^2. Sjöström *et al.* [5] prepared CN films by magnetron sputtering, and their nanoindentation tests showed a hardness as high as 60 GPa, and an elastic recovery of 85%. The other reason which promotes the interests on CN materials is to synthesize variable band gap semiconductors. Han *et al.* [6] found the optical band gap of the CN film was dependent on nitrogen concentration, which could be tailored by simply varying the preparation parameter. Amorphous CN (a-CN) films have been successfully synthesized and intensively studied by many other groups [7–11], and exhibited interesting electric, optical, and thermal properties which varied in a large range.

Now that diamond with excellent properties has been synthesized and widely used, it is attractive to combine the novel properties of CN with the successful technology of diamond. The CN/diamond composite structure is expected to have improved properties than either of the single one. For example, diamond used as hard coatings of cutting tools has high hardness, but the crystal strength and fatigue resistance are not so optimal. Diamond underlayer with CN coating will have better performance because of the superhardness and ultra-high elasticity of the CN film [5]. Moreover, the high electric resistance and high thermal conductance of diamond, combined with the band gap variability of CN, signify the potential of this composite as a novel electric-optical material. The intensive study on CN/diamond composite structure will have a profound impact on the science and technology ranging from microelectronics to astronautics.

In this paper, a combined two-step technique was proposed for preparing CN/diamond composite, by which we prepared polycrystalline diamond layers on Si wafers by microwave plasma assisted CVD (MWCVD), and then grew a-CN films by rf magnetron sputtering. Afterwards we annealed the samples at different temperature, T_A, ranging from 200 °C to 800 °C respectively, to learn the thermal behavior of the a-CN films systematically. The nitrogen concentration, bond structure, and electric resistivity of CN films varied distinctly with T_A. Thus the composite materials, stable diamond layers covered by CN films with a series of interesting properties, were preliminarily studied.

2. Experimental

Single crystalline n-type Si (111) wafers with resistivity of 5 $\Omega \cdot$cm were used as the substrates. The wafers were first covered with polycrystalline diamond layers of about 3-μm-thick in an MWCVD apparatus (ASTeX 2115). The layers were demonstrated to be high-quality pure diamond by Raman spectroscopy and x-ray diffraction (XRD) analyses.

Then the diamond layers were covered with CN films by rf magnetron sputtering of pure graphite in pure nitrogen plasma. The sample holder was fixed above the target at a distance of 55 mm, electrically grounded. Prior to the deposition, the vacuum chamber was evacuated by a turbomolecular pump to a base pressure of 3×10^{-3} Pa. During the whole 2-hour deposition, the working pressure was kept at a constant of 10 Pa by a mass flowmeter, and the sputtering power at 200 W by a power-coupling system. Without purposely heating the samples, a final temperature of about 100 °C was measured due to the energetic particle bombardment and plasma IR-radiation effects. The deposition parameters were selected in expectation to maximize the nitrogen concentration of the CN film, and to obtain a dense structure and an adhesive interface with the underlying diamond. The as-deposited CN film was about 3.5-μm-thick as given by cross-sectional analyses of scanning electron microscope (SEM). The samples were annealed in nitrogen ambient for two hours at different T_A ranging from 200 °C to 800 °C, respectively. The heating rate was constantly at 0.3 K/s.

XRD was performed on a Rigaku D/max-2400 x-ray diffractometer using Cu K_α radiation. Morphology observation was carried out by a Hitachi S-4200 scanning electron microscope, and energy-dispersive x-ray (EDX) analyses by an Oxford-6566 instrument installed on the SEM. Infrared (IR) transmittance was measured on a Perkin-Elmer 983G infrared spectrophotometer, and x-ray photoelectron spectroscopy (XPS) on an Escalab 5 spectrometer using the Mg K_α line of 1253.6 eV. The electric resistance were measured by a KEITHLEY 2400 sourcemeter using fourprobe method.

3. Results and discussion

Fig. 1 is the XRD spectrum of the as-deposited sample. The crystallinity of the composite structure is identified as amorphous CN film on polycrystalline diamond layer by one broad feature at around $2\theta = 22°$ of the CN film [12] and the distinct diffraction peak of the diamond (111), (220), (311) faces, respectively. In our experiments, all the as-deposited and annealed samples give similar diffraction patterns, suggesting that the CN films are uniquely amorphous even when $T_A = 800$ °C. These results are consistent with the experiments of McCulloch *et al.* [13], who annealed a-CN films and took *in situ* analyses in transmission electron microscope. They observed a few of graphite crystallites formed only when T_A is beyond 800 °C.

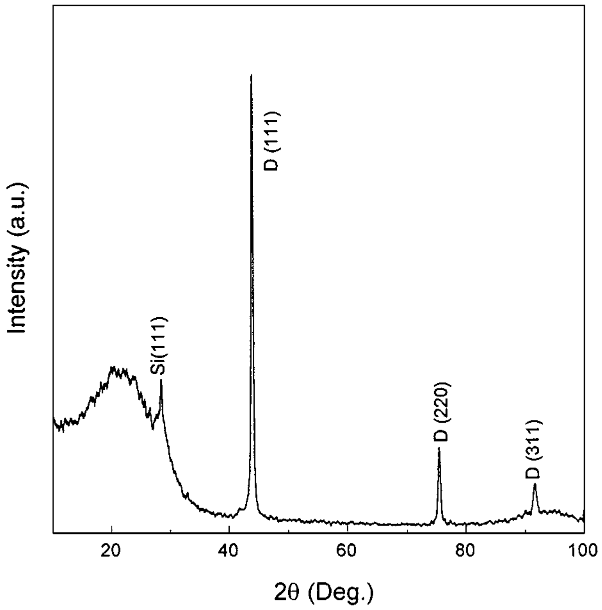


Figure 1 XRD spectrum of the as-deposited sample.

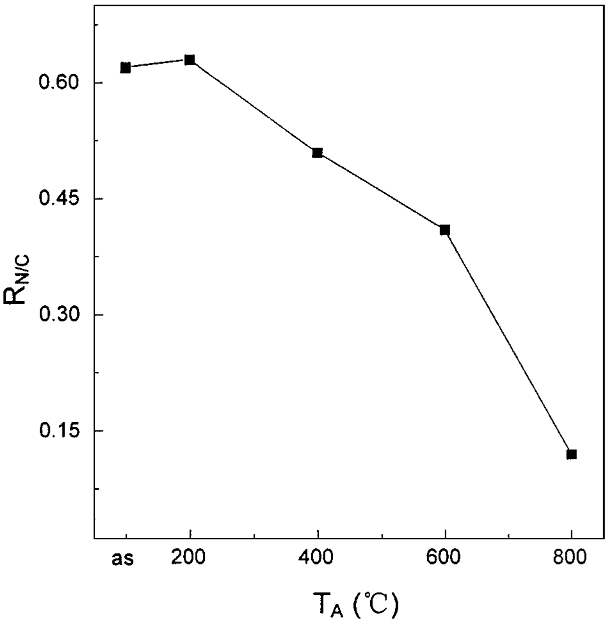
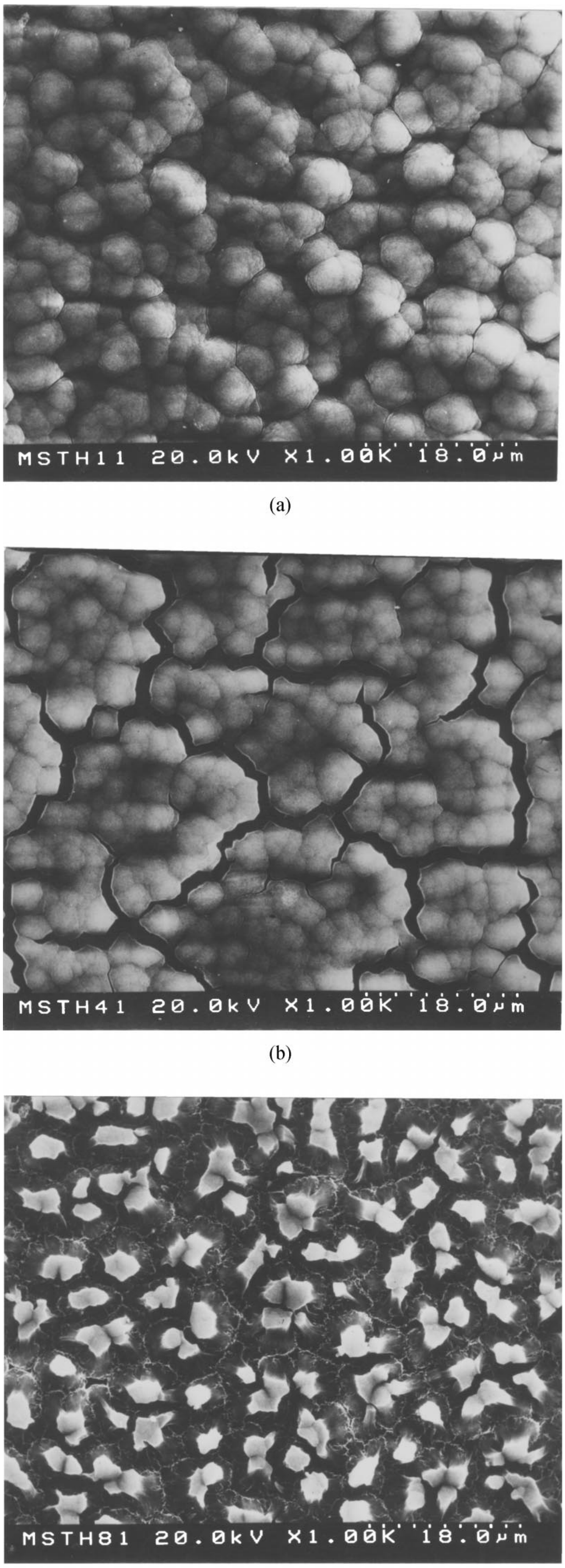


Figure 2 The $R_{N/C}$ dependence of the CN films upon T_A.

The CN film composition is determined by XPS and EDX analyses. Fig. 2 shows the N/C atomic ratio, $R_{N/C}$, of the CN films with different T_A as calculated from XPS spectra. $R_{N/C}$ is 0.62 for the as-deposited film and almost unchanged when T_A is up to 200 °C. However it decreases with further increasing T_A, and falls to as low as 0.12 when $T_A = 800$ °C. The dependence of $R_{N/C}$ upon T_A is well consistent with the results of the EDX analyses, indicating the unstable character of nitrogen in the a-CN network, which enable us to tailor nitrogen concentration of CN films by thermal treatment.

Fig. 3 shows the surface morphologies of the as-deposited and the samples annealed at different temperature. As shown in Fig. 3a, the as-deposited CN film is quite dense and uniform, composed of many hillock-like units with similar shape and dimension. When T_A increases up to 400 °C, cracks arise in the CN films, which are probably caused by the thermal stress relaxation. But with further increasing T_A, the film surface seems to be reconstructed and the cracks tend to heal up. And after annealed at 800 °C, no apparent cracks are found on the film surface. In such a way, we get the thermal stress in the CN film released without breaking the film structure. Considering the decrease of nitrogen concentration, it is reasonable to assign the morphology evolution to the migration and diffusion of the carbon and nitrogen atoms, which become mobile at high temperature.



(a)

(b)

(c)

Figure 3 SEM images of the surface morphology of the as-deposited sample (a), and the annealed samples at $T_A = 400°C$ (b) and $800\,°C$ (c), respectively.

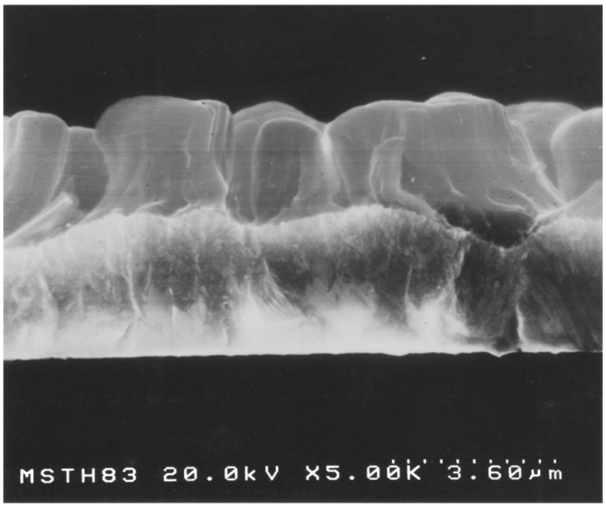


Figure 4 SEM cross-section image of the sample annealed at $800\,°C$.

Cross-sectional morphologies of all the as-deposited and annealed samples were also observed in SEM. Within our temperature range, the CN film closely covers the diamond layer with the interface unchanged, suggesting that the CN film is rather adhesive onto the diamond surface even at high temperature. Coincident with the nitrogen loss, the thickness of the CN film decreases slightly with the increase of T_A, resulting in the film with little mass density change. Fig. 4 is the cross-sectional SEM image of the sample with $T_A = 800\,°C$. It is noted that the continuity of the CN film is maintained after the thermal stress released, although the surface becomes relatively rough.

Fig. 5 is the XPS spectra of C 1s and N 1s electrons of the as-deposited and annealed samples. It is shown that with T_A increasing, the peaks of C 1s spectrum shift towards lower binding energy (BE) with the intensity enhanced. For N 1s state, the peak also shifts toward lower BE, but becomes flat and more asymmetric. The BE shifts of both C 1s and N 1s spectra are assigned to the charging effect during analyses [14], and the dependence upon T_A suggests the conductance of CN film varied after annealed at different temperature.

Some authors [14–18] deconvoluted the XPS spectra of CN films and assigned the components to different chemical states. In our case, it is complicated due to the disordered structure and low conductance of the obtained a-CN films which broadened the lines seriously. But the bond structure change with different T_A can be safely distinguished by fitting both of the C 1s and N 1s spectra with Gaussian peaks after Shirley background subtraction, respectively. It is found that in the as-deposited film, carbon and nitrogen atoms are covalently bonded. As T_A increases to $400\,°C$, the CN bonding states is rather stable. But when T_A further increases, the fraction of sp^3 CN bonds decreases accompanied by the film composition variation, suggesting the graphite-like structure is favored at high temperature.

Fig. 6 shows the IR spectra of the as-deposited and annealed samples. For the as-deposited sample, four absorption bands of the CN film are detected. The absorption at $\sim$3500-2800 cm^{-1} suggests the existence of NH and CH bonds. Hydrogen incorporated into the films although no H-containing precursors were used, because a certain amount of H_2O and H_2 remains in the deposition chamber due to the poor pumping efficiency of the turbo-molecular pump. The absorption at $\sim$2190 cm^{-1}

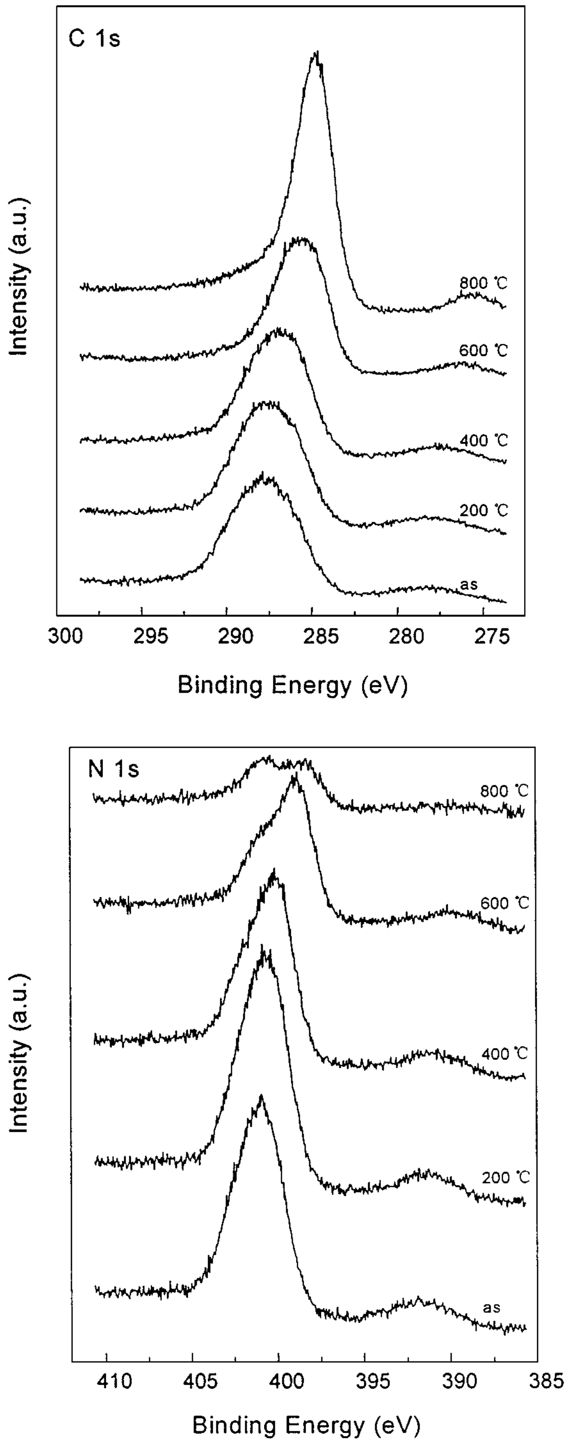


Figure 5 XPS spectra of the as-deposited and annealed samples with different T_A.

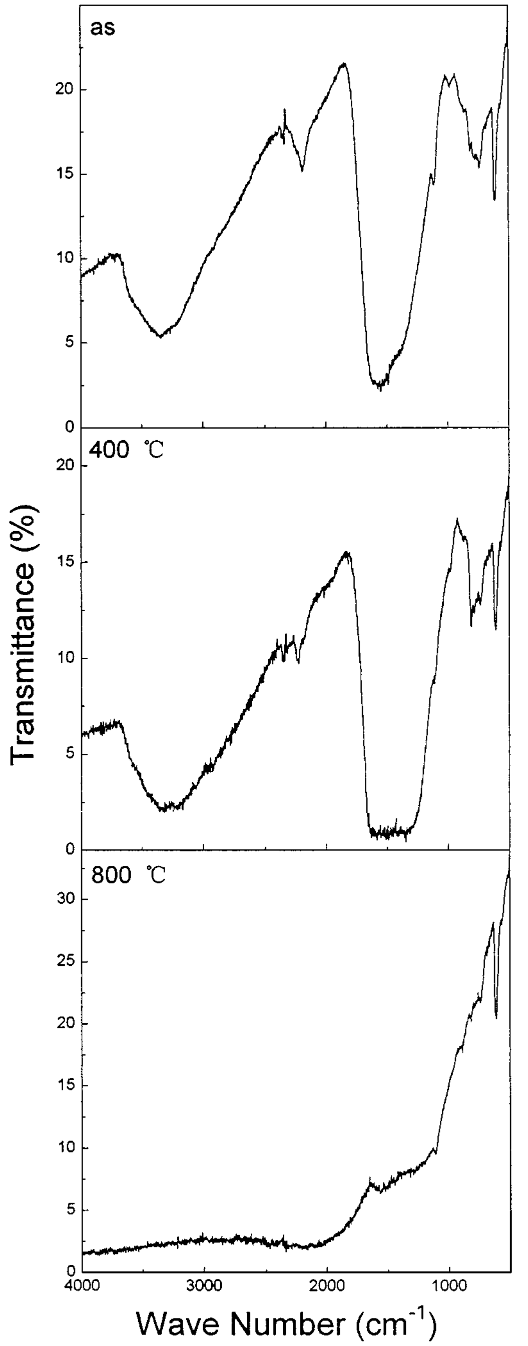


Figure 6 IR spectra of the as-deposited and annealed samples with different T_A.

is attributed to C≡N triple bonds. The broad absorption from 1600 to 1200 cm^{-1} corresponds to Raman active G and D bands, which present in IR spectra because of symmetry breaking due to the incorporation of nitrogen into the amorphous carbon network [19]. The absorption around 760 cm^{-1} is assigned to the polycondenced ring structure which becomes IR active because of the nitrogen incorporation. The Si substrate also gives two absorption bands at 1100 and 610 cm^{-1}, corresponding to the Si=O and Si—Si bonds. There is no prominent difference observed in the IR spectra after the sample annealed at 400 °C. But when $T_A = 800\,^\circ$C, the absorption bands of NH and CH bonds become undetectable, suggesting H or H-containing groups decomposed from the film. This is consistent with the high-temperature mass spectrometry analyses carried out by Matsumoto *et al.* [10]. The variation of the CN film properties is related to the decrease of H concentration [20]. The absorption bands at 1600–1200 cm^{-1} and ~760 cm^{-1} also become very weak, indicating the enlargement of pure graphitic domains after N and/or H decomposed. The sample with $T_A = 800\,^\circ$C has relatively low transmittance because of the rough surface.

Fig. 7 shows the resistivity of the CN films with different T_A. The resistivity of the as-deposited film is about 3×10^5 Ω·cm. With increasing T_A, it decreases monotonously, and falls to the value of 75 Ω·cm when $T_A = 800\,^\circ$C. The electric property of the CN film has been greatly modified after annealed at different

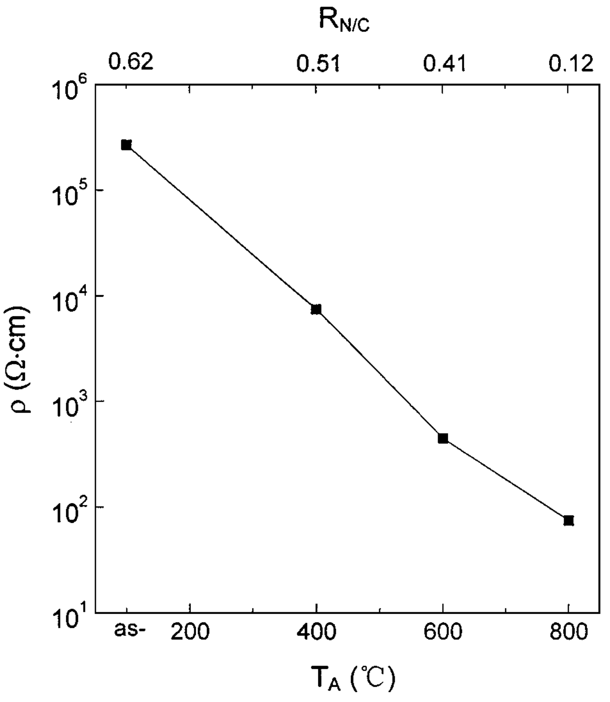


Figure 7 The electric resistivity dependence of the CN films upon T_A and $R_{N/C}$.

temperature. The correspondent $R_{N/C}$ of the film is also marked on the top axis, showing the relationship between the film composition and its electric resistance. Our electric measurements are consistent with the explanation of charging effect in XPS analyses, and confirm the graphitization tendency and the enlargement of the pure graphite domains in the films with T_A increasing.

In summary, the novel CN/diamond composite structure was obtained by a combined two-step growth technique of MWCVD and rf magnetron sputtering. The as-deposited CN film shows a dense and uniform surface, and an adhesive interface with diamond. Nitrogen atoms incorporate into carbon network by forming covalent bonds, with $R_{N/C} = 0.62$. Moreover, the composition, bonding configuration, and electric resistance of the CN film can be modified by thermal treatment. When T_A is elevated, the nitrogen concentration of the films decreases and the C—N bonding states tend to form sp^2 hybridization, resulting in a more graphitelike network with much lower electrical resistivity. The CN/diamond composite material presents brilliant prospects in industry applications.

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