

Raman spectroscopy on the β - C_3N_4 structure formed by low-energy nitrogen ion implantation into a diamond surface

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Raman spectroscopy was employed to study the structure of the carbon nitride formed by low-energy nitrogen ion implantation into a diamond film. A series of narrow Raman peaks were observed in the range of 150–1500 cm^{-1} . These peaks match well with the calculated Raman frequencies of β - C_3N_4 , revealing the formation of the β - C_3N_4 phase. No Raman peaks were detected in this region when a graphite substrate was implanted under the same conditions, suggesting that the sp^3 -bonded carbon favors the formation of the sp^3 -bonded β - C_3N_4 . [S0163-1829(99)05619-2]

There has recently been considerable interest in the synthesis of carbon nitride thin films since Liu and Cohen proposed that a metastable phase of β - C_3N_4 , which has the same structure as β - Si_3N_4 , will have an exceptional hardness comparable to or greater than that of diamond.¹ This atomic coordination suggests that each sp^3 -hybridized carbon atom may be bonded to four nitrogen atoms in a distorted tetrahedral geometry and each sp^2 -hybridized nitrogen atom may be bonded to three carbon atoms in a trigonal planar geometry. This atomic configuration would produce an infinite three-dimensional covalent network with strong bonding in all directions. Subsequent calculations have shown that other crystalline C_3N_4 structures should have stabilities comparable to or greater than that of β - C_3N_4 ,² and that many of these structures should be quite hard. In addition, the energetically most stable material, rhombohedral C_3N_4 , which has a graphitelike structure, is expected to be quite soft. The local structural property that distinguishes potentially superhard and dense C_3N_4 structures from low-density, softer material is the carbon coordination: hard materials require sp^3 -bonded carbon in the C_3N_4 network, while sp^2 -bonded carbon will lead to much softer materials.

Extensive experimental effort has been made to prepare this theoretically predicted new material. Due to its high reactivity, atomic nitrogen is believed to play a major role in the synthesis of nitrides. Hence, nitrogen discharge assisted deposition has been widely used in producing carbon nitride thin films. Most films synthesized were found to be amorphous except that a few reports show the existence of crystalline β - C_3N_4 by presenting several electron diffraction rings from the tiny β - C_3N_4 grains embedded in the matrix of the films.^{3,4} However, as Hu, Yang, and Lieber mentioned in their paper, these diffraction data do not provide strong evidence for sp^3 -bonded β - C_3N_4 , and they observed a structural transformation from primarily sp^3 -bonded to sp^2 -bonded carbon as the nitrogen concentration increases from 11% to 17%.⁵

The ability of the ion implantation technique to modify materials far from equilibrium conditions makes it ideal for metastable material synthesis. It has been shown previously that nearly stoichiometric layers of β - Si_3N_4 can be prepared

by low- and high-energy nitrogen implantation into silicon. Attempts to introduce nitrogen into graphite or glassy carbon by high- or low-energy nitrogen implantation have been reported.^{6,7} In these experiments, in the N -implanted surface, carbon-nitrogen bonding states were formed, but no convincing argument for the β - C_3N_4 structure was presented.

To promote the formation of β - C_3N_4 , a substrate with the proper structure should be used. Since diamond is a material consisting of sp^3 -hybridized carbon versus the sp^2 carbon of graphite and the β - C_3N_4 phase is also sp^3 bonded, one can imagine that a diamond surface will favor the formation of an sp^3 -bonded β - C_3N_4 phase.

In this present work, the influence of the carbon bonding configuration of the substrate on the formation of the β - C_3N_4 phase was studied by low-energy nitrogen implantation into diamond and graphite surfaces. Raman spectroscopy was employed to obtain information about the structure of the carbon nitride layers formed.

The diamond thin film used in the experiment was deposited on a Si substrate by the hot filament chemical vapor deposition (CVD) method.⁸ The thickness of the diamond film is about 10 μm . The size of the polycrystalline diamond grains is between 0.1 and 1.0 μm . The Raman spectrum of the diamond film is shown in Fig. 1(a); a typical Raman peak at 1332 cm^{-1} was detected.

To generate an atomic nitrogen ion beam, a simple device using dc glow discharge was developed in our previous work. A very high ratio of N^+/N_2^+ , up to 5/1, was achieved. A detailed description of this beam source and the vacuum system can be found elsewhere.⁹ Briefly, the dc glow discharge was accomplished in a glass tube between a pair of electrodes consisting of a copper cylinder with an end plate and a tungsten wire. A pinhole, 0.1 mm in diameter, was drilled in the center of the 0.1-mm-thick end plate and was used as the nozzle for the nitrogen beam. The glass tube was mounted in a vacuum chamber. The base pressure in the vacuum chamber was about 1×10^{-4} Pa and the pressure was kept below 6×10^{-3} Pa during operation. The typical discharge voltage was about 450 V, and the discharge current used in the experiment was 4 mA. The time-of-flight (TOF) mass spectrum showed that under this discharge con-

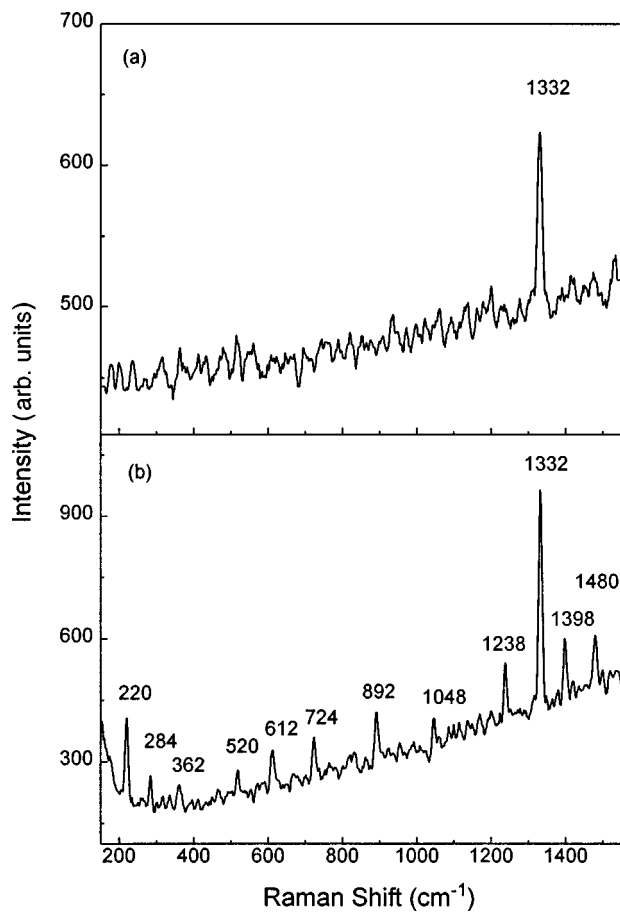


FIG. 1. The Raman spectra of the diamond film before (a) and after (b) low-energy nitrogen ion implantation.

dition the ratio of N^+ to N_2^+ was about 5/1.⁹ The diamond film was irradiated with this nitrogen ion beam in the vacuum chamber for two hours at room temperature. A bias voltage of 1.5 kV was applied to accelerate the nitrogen ions during operation.

In the study of carbon nitride films, a variety of techniques have been employed to analyze the nitrogen concentrations, the type of C—N bonds, the structure of the carbon nitride films, etc.

Information on both the stoichiometry and type of bonds present in the carbon nitride thin films can be obtained by x-ray photoelectron spectroscopy (XPS). So far a variety of XPS measurements have been reported.^{6,10,11} In those studied, sp^2 and sp^3 CN bonding configurations were assigned by deconvoluting the N 1s and C 1s peaks. However, these deconvoluted data and assignments from different groups are not always consistent with each other. The attributions of the obtained core level binding energies to values already known in literature are, in some case, quite questionable. For example, some authors have argued that very little charge transfer between C and N occurs in a covalent C—N bond,³ while others have reported a shift of about 3 eV in the binding energy of the C 1s core level due to the formation of such a bond.¹²

The Raman spectroscopy is sensitive to slight variation in the lattice symmetry. Hence, it is a useful tool to determine the structural quality of the film. The Raman measurements in our experiment were carried out using an Ar ion laser, and

TABLE I. Comparison of experimental Raman peaks with the calculated Raman frequencies.

Calculated ^a	Raman frequency (cm^{-1})	
	Observed	Difference (%)
206	220	6.8
266		
300	284	5.3
327	362	10.7
	520	
645	612	5.1
	724	
885	892	0.8
1047	1048	0.1
1237	1238	0.1
1327	1332	0.4
1343	1398	4.1
1497	1480	1.1

^aData from Ref. 15.

the scattered light was analyzed with a SPEX 1403 double spectrometer.

Most of the Raman spectra reported so far for synthesized carbon nitride films showed two main peaks, similar to that for amorphous carbon films, the so-called *D* (disorder) and *G* (graphite) bands approximately at 1375 and 1580 cm^{-1} , respectively.¹⁰ In contrast, Ren *et al.*¹³ reported a high peak at 2190 cm^{-1} and Bousetta *et al.*¹⁴ reported a peak at 1275 cm^{-1} attributed to carbon-nitrogen stretching modes. A major problem in the search for $\beta\text{-C}_3\text{N}_4$ is the structure characterization, in the absence of a reference sample, of the synthesized films. Since $\beta\text{-C}_3\text{N}_4$ was proposed to adopt the crystal structure of $\beta\text{-Si}_3\text{N}_4$,¹ Yen and Chou¹⁵ estimated the Raman peaks for $\beta\text{-C}_3\text{N}_4$ from the observed Raman frequencies of $\beta\text{-Si}_3\text{N}_4$ (Ref. 16) by correlating the stretching frequency for the carbon-nitrogen bond to the silicon-nitrogen bond. The 11 calculated Raman frequencies in the range of 150–1500 cm^{-1} are listed in Table I. In the Raman spectrum of their synthesized carbon nitride film, two prominent bands are detected at about 300 cm^{-1} . Three deconvoluted peaks at 266, 280, and 330 cm^{-1} match well with the calculated ones at 266, 300, and 327 cm^{-1} . However, our Raman spectrum, in the range of 150–1550 cm^{-1} , is entirely different from all those reported. A series of narrow peaks was observed. Figure 1 shows the Raman spectra measured before and after the low-energy nitrogen implantation of the diamond film. Before implantation, only one diamond peak at 1332 cm^{-1} was detected, while after irradiation with the nitrogen ion beam, 12 Raman peaks appeared. Ten of them match well with the calculated Raman peaks for $\beta\text{-C}_3\text{N}_4$ as listed in Table I. The Raman peak of $\beta\text{-C}_3\text{N}_4$ at 1327 cm^{-1} as calculated may be overlapped with the diamond peak at 1332 cm^{-1} . Since there are as many as ten peaks matching well with the calculated frequencies, which were directly deduced from the $\beta\text{-Si}_3\text{N}_4$ material, our Raman spectrum provides unambiguous evidence that the structure of our nitrated layer is similar to that of $\beta\text{-Si}_3\text{N}_4$, suggesting that the nitridation of a diamond surface can lead to the formation of the $\beta\text{-C}_3\text{N}_4$ phase.

To study the influence of the substrate, a graphite surface, which consists of sp^2 -bonded carbon, was irradiated with the

nitrogen ion beam under the same conditions. On the contrary, no Raman peak was detected in the same spectral region, although the nitrogen contents can also be found by mass spectrum or XPS measurements. This result supports our expectation that the sp^3 -bonded carbon favors the formation of the β -C₃N₄ phase.

Furthermore, after an air exposure for two months, we measured the Raman spectrum of the nitridated diamond surface again and the spectrum was exactly the same as that in Fig. 1(b), indicating that the carbon nitride layer formed was very stable.

In summary, nitridation of a diamond surface by low-energy nitrogen implantation can lead to the formation of the β -C₃N₄ phase which has a similar structure to that of β -Si₃N₄. The bonding configuration of the carbon in the

substrate is crucial to the structure of the carbon nitride produced. The sp^3 -bonded carbon favors the formation of sp^3 -bonded carbon nitride. The carbon nitride layer formed by nitridation of a diamond film is very stable. The physical and chemical properties of the nitridated diamond surface are being studied. The subsequent growth of a β -C₃N₄ film on such a modified surface by means of laser ablation deposition combined with a discharged nitrogen beam is also being studied.

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