Laser-induced modification of carbon nitride thin films

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The results of experiments on local pulsed ultraviolet laser annealing of carbon nitride (CN_x) thin films are reported. It is shown that laser radiation can be used for efficient graphitization of CN_x thin films. The degree of local transformation of diamond-like sp^3 bonded CN_x compound films into graphite-like ones is dependent upon the radiation energy density. It is also shown that the electron field emission properties of the thin films can be modified by the laser treatment. © *2000 American Institute of Physics.* [S0021-8979(00)07324-2]

INTRODUCTION

The increased interest in carbon nitride materials is related to several factors. According to some theoretical predictions, a covalently-bonded, C_3N_4 crystal exhibiting characteristics comparable to or better than diamond should exist.[1] These characteristics include mechanical resistance, decomposition temperature, bulk modulus, thermal conductivity, electrical strength, and wide band gap. It was also established that incorporating nitrogen into the carbon matrix might result in a significant reduction of the electron field emission threshold, which makes CN_x compound films well suited for applications in high-resolution high-brightness displays.[2,3] Thus, investigating CN_x composites is motivated by the possibility of synthesizing new phases with new properties.

Various techniques have been employed so far for CN_x film deposition, including ion implantation,[4,5] carbon sputtering in a nitrogen atmosphere,[6,7] and hot filament[8] or electron cyclotron plasma deposition.[9,10] Recently, the growth of thin layers containing polycrystalline α-C_3N_4 and β-C_3N_4 phases was achieved.[11–15] More work is still required to improve the chemical composition and structure of these materials. To that end, various postgrowth modification techniques can be employed. One of the most powerful and sophisticated methods uses local laser melting/annealing of the film surface.

Laser irradiation is an effective method of modifying the properties of material surfaces. This is mainly connected with the factor of nonequilibrium processing with respect to conventional physical and chemical methods of surface treatment. At the present time the laser technique is known to be a promising tool for diamond and diamond-like film processing. Excimer lasers are preferred because their ultraviolet (UV) spectral range quanta, with energies higher than those of the material band gap, coupled strongly with the film surface. Lasers are known to be capable of locally transforming metastable carbon allotropes to graphite-like conducting phases.[16] We have also demonstrated laser induced enhancement of field emission properties of nanocrystalline diamond films.[17] The application of this technique to new types of materials may be of great importance to future microelectronic applications.

In this article the results of postgrowth laser annealing of 100–500 nm thick carbon nitride films are presented. CN_x films were grown on conductive silicon substrates by ion and plasma sources assisted physical vapor deposition techniques.[10] The structure, composition, and electronic properties of the films before and after irradiation were investigated and are presented below.

EXPERIMENT

A pulsed KrF excimer laser (248 nm, $h\nu = 5.0$ eV) was used as a radiation source with a pulse energy of up to 100 mJ, a duration of 20 ns, and a repetition rate of up to 100 Hz. Irradiation was performed in a high vacuum chamber pumped down to a base pressure of 10^{-8} Torr.

The film surface was maintained at room temperature. A two-lens optical projection scheme with an intermediate diaphragm was applied to provide uniform surface illumination of a ~ 1 mm^2 spot area. The intensity of the laser radiation was chosen to be below the value that led to visible alteration of the film surface.

Film structure and chemical composition were studied by using Raman spectroscopy (Jobin–Yvon S-3000) and x-ray photoelectron spectroscopy (XPS–VG ESCALAB MKII) setups. The XPS analysis was performed using Mg $K\alpha_{1,2}$ radiation. The photoelectron signal was recorded at 45° with respect to the surface. All spectra were recorded under a constant electron energy regime. The binding energies were calibrated with respect to the Au $4f_{7/2}$ line (83.8 eV).

The atomic composition was obtained by using sensitivity factors determined from Si_3N_4 reference samples, monocrystalline pyrolitic graphite, and SiO_2 film. The error in determining the concentration was estimated to be less than 20%. The ratio of sp^3 to sp^2 carbon bonds was determined by observing shifts of the carbon N $1s$ line.

Field emission characteristics were measured in a high vacuum chamber with a pressure below 10^{-7} Torr. Four

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TABLE I. XPS analysis of CN_x thin films at selected laser power densities.

Area No.	Pulsed fluence (mJ/cm^2)	sp^2-bonds fraction (%)	Nitrogen (%)	Oxygen (%)	N[1]/N[2] ratio	Si
1	initial surface	83	10–11	2	1.1	···
2	50	90	7–8	<1	0.7	traces
3	100	87	7–8	<1	0.3	···
4	200	95	5–6	<1	0.3	substantial

tungsten tip probes (anodes) with 20 μm radii were placed at a distance of 10–100 μm from the sample surface (cathode). A high dc voltage of up to 8 kV was applied between the sample and each probe separately to induce field emission. The measurement procedure included recording the emission current while the electric field strength was automatically cycled. The emission current density was calculated by dividing the measured current by the total surface area of the four tips used.

RESULTS AND DISCUSSION

The exposure consisted of 1000 laser pulses, with the exposures at different power densities. After irradiation, the samples were subjected to XPS analysis. The results of measurements on selected irradiated areas are summarized in Table I.

The C 1*s* and N 1*s* binding energies of the original film were determined. The shape of the C 1*s* line was found to be asymmetric without any visible multiplet structure (Fig. 1). The binding energies for the N 1*s* doublet peak (Fig. 2) were 398.2 eV (peak N[1]) and 400 eV (peak N[2]). The ratio of the peak intensities was close to unity for atomic nitrogen concentrations of 10%–11% and oxygen contamination up to 2%.

The laser irradiation effectively modifies the content of the CN_x films' surface layer. The nitrogen concentration decreases gradually as the laser fluence increases and, after irradiation with a maximum pulse energy density of 0.20 J/cm^2, is almost half the original value. This phenomenon is connected with the breaking of surface bonds and subsequent nitrogen desorption. At high laser fluences, the Si signal in the XPS spectra increases, which is evidence of severe thin film damage. The oxygen concentration in the modified layers did not exceed 0.3%—much less than that of the original surface—and remained the same even after long time exposure to atmosphere at room temperature.

The binding energy of the C 1*s* lines depends strongly upon the power density of the laser radiation, and shifts toward the values characteristic of graphite (284.1–284.3 eV).[18] This implies an increase of the sp^2-bonding fraction, or graphitization. As the laser radiation power increases this fraction grows up to 95% at 0.2 J/cm^2.

The intensity of the N[2] component of the N 1*s* line increases as well. This peak is attributed to nontetrahedral coordination of nitrogen atoms in CN_x film, while the N[1] peak, at an energy of 398.2 eV, corresponds to sp^3 hybridization of N–C bonds.[18] Figure 2 illustrates the gradual change in the form and position of the N 1*s* line.

Raman spectra of the films before and after laser irradiation are presented in Fig. 3. The Raman spectrum changes significantly after laser treatment. The spectrum after irradiation is similar to that of so-called glassy carbon (nanocrys-

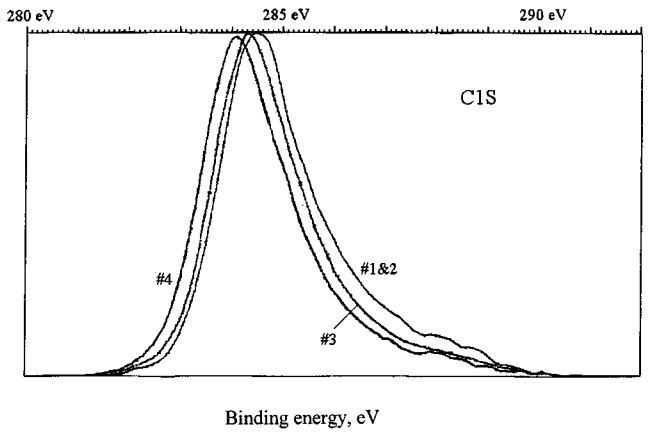

FIG. 1. The C 1*s* spectra from different areas of a CN_x film irradiated by an excimer laser at different power densities (see Table I for reference).

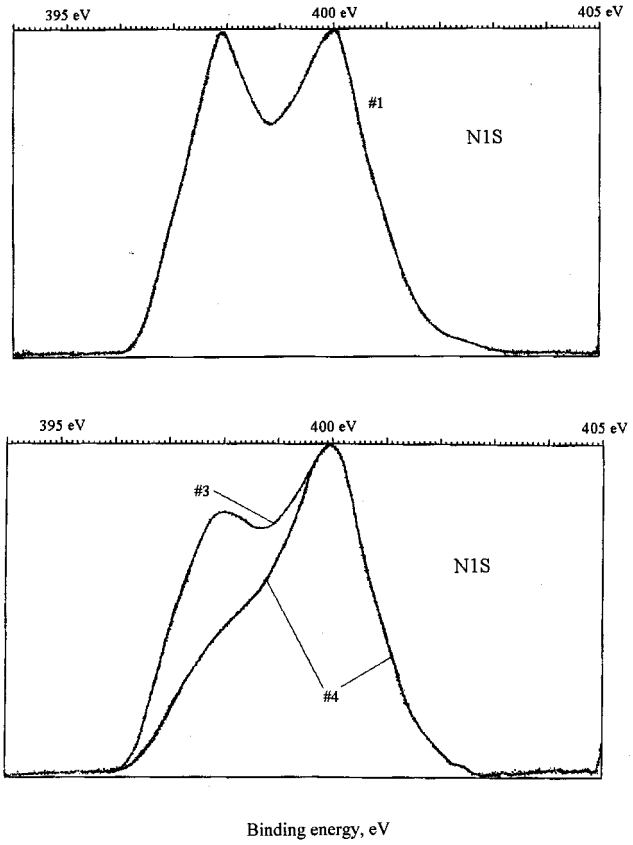

FIG. 2. The N 1*s* spectra from different areas of a CN_x film irradiated by an excimer laser beam at different power density (see Table I for reference).

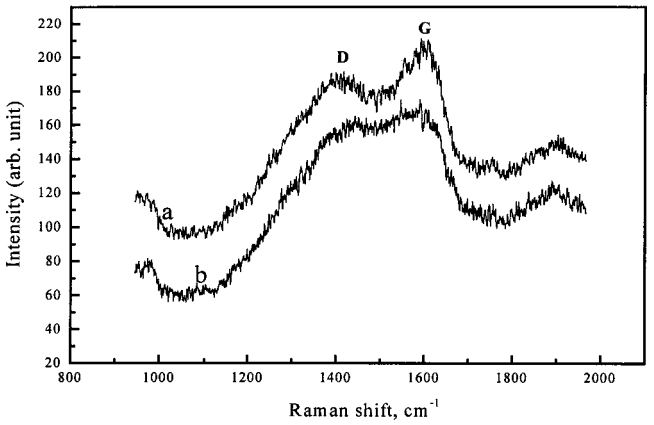

FIG. 3. Typical Raman spectra of a CN_x film before (a) and after (b) laser irradiation.

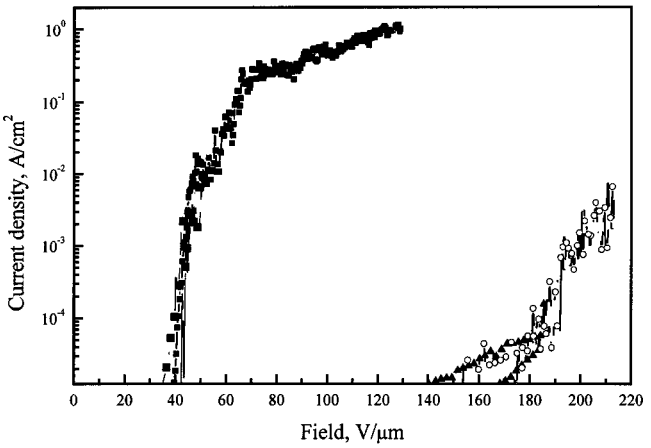

FIG. 4. The current–voltage characteristics of a CN_x film surface: before and after laser irradiation at different laser power densities: Initial surface (solid triangle), low energy irradiation (open circle), and high energy irradiation (solid square).

talline graphite), with characteristic D and G peaks at around 1400 and 1600 cm^{-1}, respectively.

The electron field emission from these films was tested in eight subsequent cycles. Measurements show that the effect of the laser irradiation on the film surface properties depends strongly upon the intensity of the laser pulses. The typical dependencies of the emission current on the field applied to the surface, before and after irradiation are shown in Fig. 4. The double curves represent the hysteresis behavior during increasing and decreasing fields. The initial threshold field is as high as 150 V/μm, with low emission current densities of about 0.1 mA/cm^2. Laser irradiation at moderate power densities ($<$200 mJ/cm^2) increases the maximum current density by 2 orders of magnitude, which could be connected with the change in the conductivity of the film due to the partial graphitization. The drastic decrease of the threshold field at a laser fluence of 200 mJ/cm^2 can be explained by the damaging action of the laser beam, which results in a partial denudation of the silicon substrate and/or the generation of a high density of defects in the films. This generally leads to surface electric field enhancement and improved electron transport, which provides for higher current densities (about 1 A/cm^2) and lower field emission thresholds (about 30 V/μm).

CONCLUSION

The results of local pulsed UV laser annealing of CN_x films show that laser radiation can be used for efficient graphitization of these films, i.e., for local transformation of diamond-like sp^3-bonded CN_x compound films into a graphite-like sp^2 one. The nitrogen content and the fraction of sp^3 C–N and C–C bonding diminish after irradiation. This effect is accompanied by changes in the electron field emission properties of the irradiated areas. The maximum carbon sp^2-bonding fraction (95%) corresponds to the lowest emission threshold.

The local modification of the electron emission properties of carbon nitride films can be used advantageously to improve the characteristics of current devices or design new concepts for lower cost field emission arrays (forming electrical conducting patterns in initially amorphous CN_x films characterized by dielectric rather than metallic properties).

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