Formation of oriented nitrogen-doped carbon films

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Oriented nitrogen-doped carbon films were obtained by the method of ion-assisted deposition of carbon in a nitrogen-containing glow discharge. Auger electron spectroscopy showed that the nitrogen content in the films ranges from 3 to 36 at. % with substrate temperatures from −20°C to +200°C. Nitrogen and argon were introduced into the chamber in a definite ratio up to the pressure $P = 10^{-1}$ Pa. The atomic and electronic structures of the carbon films were investigated by the methods of transmission electron microscopy, Auger electron spectroscopy, and Raman spectroscopy. Single crystals with a hexagonal crystal lattice with $a = 8.70$ Å were obtained at $T = 200$°C. © *1995 American Institute of Physics.*

Carbon clusters with a linear chain structure are obtained by thermal evaporation,[1] ion sputtering,[2] and laser evaporation of graphite (Ref. 3). Deposition of carbon clusters C_n can lead to the formation of films with different structures, which strongly affects the Raman scattering spectra of these films.[4]

In Ref. 5 we showed that when graphite is sputtered in the presence of ion irradiation, oriented carbon layers in which the carbon chains are oriented perpendicular to the surface of the substrate can be obtained. Crystals of carbon chains intercalated with atoms of these metals were also found to grow when impurities of some metals (K, Fe) were present.

In the present paper we report the results of deposition of thin carbon films by the method of ion-assisted deposition of carbon in a nitrogen-containing glow discharge. We show that oriented carbon films that crystallize in the presence of a nitrogen glow discharge can grow into well-faceted, hexagonal-type crystals ($a = 8.70$ Å).

The carbon films were deposited in a vacuum apparatus with a plasmatron. The apparatus was evacuated with a turbomolecular pump to a pressure of 10^{-7} Torr. After evacuation nitrogen and argon were introduced into the chamber in a definite ratio up to a pressure $P = 10^{-1}$ Pa. A high negative bias voltage was applied between the graphite target and the working chamber. As a result, the target was etched by argon ions in a nitrogen environment and partially etched by nitrogen ions from the gas-discharge plasma.

The method of ion-assisted deposition was employed in the experiments. In this method an additional negative bias voltage relative to the plasma could be applied to the substrate, and in the process the substrate was irradiated with slow argon and nitrogen ions. The bias voltage was varied from 0 to −200 V. The substrate temperature was

FIG. 1. Electron diffraction pattern from oriented close-packed carbon chains.

varied from −20 to +200 °C. In the course of a single experiment the gas mixture was introduced at a constant rate. Standard polished (100) silicon wafers were used as substrates for the Auger investigations of the films and NaCl crystals were used for Raman spectroscopy and electron microscopy.

The experimental results obtained by Auger electron spectroscopy show that the nitrogen concentration in the films depends strongly on the deposition temperature. The highest nitrogen concentration, equal to 36 at. %, was obtained in films on cooled substrates (down to −20 °C) and the lowest nitrogen concentration was 3 at. % (at 200 °C). We see that the nitrogen content in the films decreases substantially as the temperature increases.

To prevent the electron beam from destroying the films, the observations were performed with very low electron-irradiation intensities. This made it possible to record the true structure of the films. The diffraction patterns, obtained by the method of transmission electron microscopy, show that the carbon films deposited on cooled substrates have an amorphous structure. The structure of the films obtained at room temperature and higher temperatures corresponds to a carbon matrix consisting of two phases. The first phase gives a diffraction pattern consisting of six point reflections with interplane spacing $d = 4.39 \mp 0.05$ Å (Fig. 1). There are no higher-order reflections. This structure corresponds to close-packed carbon chains with cylindrical symmetry. The second phase (Fig. 2a), observed at temperatures $T > 180$ °C, consists of well-faceted hexagonal crystals with a diffraction pattern corresponding to a hexagonal lattice with the same interplanar spacing (Fig. 2b) $d = 4.39 \mp 0.05$ Å .

The Raman spectrum of the film with the minimum nitrogen content (3 at. %), obtained at $T = 200$ °C, is shown in Fig. 3. As one can see from the figure, a wide band with a maximum at $\nu_1 = 1580$ cm^{-1}, characteristic for the vibrational frequencies of the carbon framework of the chains, and a very strong peak at $\nu_2 = 2070$ cm^{-1} are present in

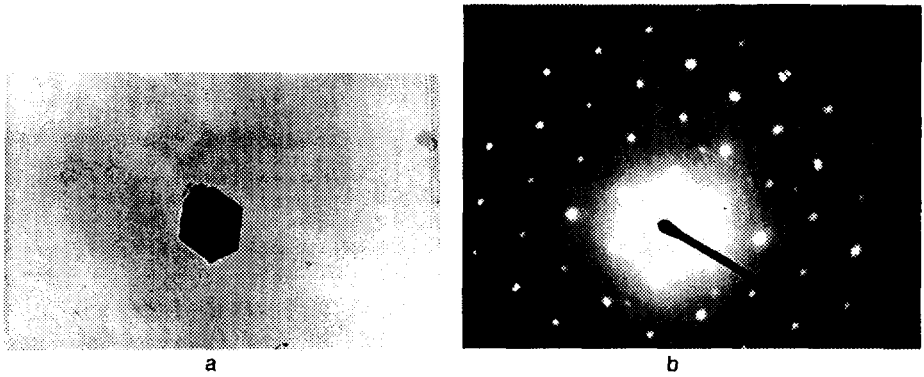

FIG. 2. a — Electron photomicrograph of a hexagonal crystal (×20 000); b — electron diffraction pattern from a hexagonal single crystal.

the experimental spectrum. The latter peak corresponds to the stretching vibrations of ketenimine =C=C=N.

The diffraction pattern from the carbon film (Fig. 1) was previously observed in ion-assisted deposition of oriented carbon film obtained by sputtering graphite with argon ions.[1] As was shown by means of Auger electron spectroscopy and electron diffraction, the film consists of linear carbon chains oriented perpendicular to the surface of the substrate. The crystals obtained in the present work at $T = 200$ °C (Fig. 2a) have the same

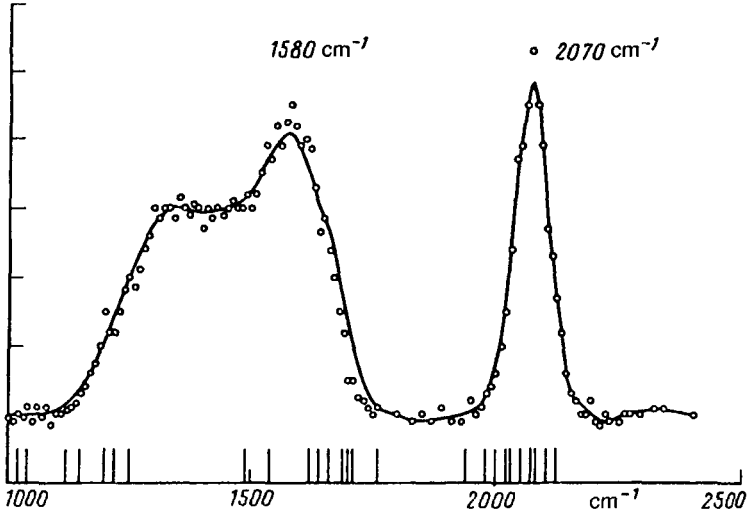

FIG. 3. Raman spectrum from an oriented nitrogen-doped carbon film (nitrogen concentration 3 at. %). The bars represent the computed vibrations of a 40-atom carbon chain containing periodic defects with a period of four atoms.

lattice parameter as the oriented film obtained at $T = 20°C$. These crystals demonstrate, therefore, that crystallization of these chains in a single crystal is possible in the presence of nitrogen and in the absence of metal impurities.

Our crystals had the same lattice parameter as the carbyne crystals obtained from graphite at high pressures and temperatures by Heimann,[6] who, in accordance with the model which he proposed, interpreted the first diffraction maximum as $d_{11.0} = 4.35$ Å of a hexagonal lattice, and thus he obtained $a = 8.70$ Å .

Since according to the Auger data the nitrogen content in the film is very low, corresponding to only several percent, the strong peak at $\nu_2 = 2070$ cm^{-1} in the Raman spectrum must be attributed to nitrogen arranged at the ends of rather long carbon chains (=C=C=N group). The same frequency also corresponds to vibrations of cumulene carbon chains =C=C=C=C=.

A possible model for the formation of a lattice of C:N crystals, which is in agreement with the Auger and Raman results, is based on close-packed C:N polymer chains. The formation of C:N polymers can be described as follows: At the first stage $-C\equiv N$ clusters are formed as a result of the interaction of carbon atoms with atomic nitrogen by sputtering graphite in a nitrogen-containing plasma. In our case the concentration of atomic nitrogen in the plasma was of the order of 50%. At the second stage, these clusters condense on the surface of the substrate, where a polycondensation reaction occurs. In this reaction the triple bonds are opened according to the scheme $(-C\equiv N)_n \rightarrow (=C=N-)_n$ and stable polycyan chains are formed. Oriented polymer chains with $sp1$-type hybridization of the carbon atoms are obtained at this stage. At high temperatures the nitrogen concentration decreases sharply. This can be explained by thermal desorption of N_2 molecules accompanied by the formation of longer rectilinear carbon chains with cumulated bonds, in which the nitrogen atoms play the role of stabilizing impurities.

In summary, it can be assumed that $sp1$-type hybridization of carbon atoms in a film is initiated by the atomic nitrogen in the plasma.

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