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# AMORPHOUS CARBON NITRIDE FILMS: STRUCTURE AND ELECTRICAL PROPERTIES*

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The effect of deposition temperature and $N_2$ gas partial pressure on the morphology, structure, composition and electrical properties of $CN_x$ thin films was studied by HRTEM, EDS, STM and STS. Morphology ranging from homogeneous layers through spherical or cylindrical particles embedded into the films to low density globular deposit of $CN_x$ was observed as a function of the applied $N_2$ gas pressure. The N-composition was found between 1-20% and the structure varied from amorphous through fulleren-like to nanocrystalline diamond composed with amorphous $CN_x$ depending on the temperature and the plasma parameters.

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## 1 Introduction

The predicted $C_3N_4$ compound of high hardness and toughness [1] can be a promising candidate for hard coatings and tribological applications. Either the stochiometric form or various compositions of $CN_x$ thin films might be of high technological and scientific interest. These films were found to have distorted graphite-like structure constituted of buckled sp2-hybridized $CN_x$ planes cross-linked by sp3-hybridized bonds [2]. The buckling is attributed to the incorporation of pentagons in the basal planes of the graphite-like structure, due to the presence of N atoms. In our experiments $CN_x$ films were prepared by the interaction of carbon vapor and the nitrogen plasma generated by a DC arc between two graphite rods.

## 2 Experimental

$CN_x$ thin films were prepared in high vacuum by evaporation of C from a pair of graphite rods in a DC arc kept in $N_2$ pressures up to 1 mbar onto (100)Si, NaCl, HOPG and quartz platelets between room temperature and 800 °C. An additional DC plasma was ignited above the substrates in some experiments. The samples were characterized by transmission and high resolution electron microscopy (TEM and HREM), X-ray microanalysis (EDS) [3], scanning tunneling microscopy- and spectroscopy (STEM and STS) and electrical resistance measurements.

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## 3 Results and discussion

### 3.1 Influence of the $N_2$ pressure

Deposition at ambient temperature and below 0.05 mbar revealed a homogeneous amorphous structure. At 0.1 mbar $N_2$ pressure inhomogenities appeared in the form of a columnar structure. The column diameter was around 10 nm. Inside the columns a fringe like contrast of curved graphite like plates appeared. The estimated distance between these fringes is around 0.5 nm. The size of the ordered regions is smaller or the same as the column diameter. At 0.3 mbar $N_2$ pressure small (around 10 nm in diameter) balls and cylinders of $CN_x$ formed already in the atmosphere and fell onto the substrate embedding into the forming layer, creating a further morphological inhomogenity.

### 3.2 Influence of the deposition temperature

The films formed at room temperature are homogeneous, exhibit amorphous structure, while they have a transitional structure in the range of 200-600 °C substrate temperature and a structure containing fiber-like nanocrystals of 1 nm in diameter and about 10 nm in length formed at about 800 °C. In the last case the SAED pattern showed crystalline rings, corresponding to 111 and 220 reflections of diamond. The temperature dependence of the structure does not change strongly with the composition of the residual atmosphere during deposition ($N_2$ or air). The films prepared at 0.1 mbar $N_2$ pressure contained 5 at. % N, 1.5 at. % N and 1 at. % N when prepared at ambient, about 600 °C and about 800 °C substrate temperature, respectively.

Fig. 1 represents a HREM image of a fulleren-like $CN_x$ cylinder consisting of concentric multiwall tubes of bent graphite planes, which are typical beside bucky onions in films prepared at elevated $N_2$ pressures. The STM image in Fig. 2a shows spheres and cylinders of $CN_x$ of various heights assembled along a straight line. These objects are assumed to be responsible for the enhanced electron emission of $CN_x$ films measured by STS. I-V measurements revealed a band gap of 1 eV in a-$CN_x$ layers compared to 0.6 eV characteristic of the a-C films [4].

The electrical resistance measurements of the $CN_x$ films show Arrhenius type of temperature dependence. In Fig. 4 the TEM image and $\ln(R) = f(1000/T)$ plot of a pure carbon film is shown. As we can see on the TEM image the film is homogeneous, no remarkable defects related to the morphology were observed which means that zone of localized states must be narrow inside bandgap. This assumption is supported by the fact that only two regions on the Arrhenius plot can be separated - the first corresponding to the high- and the second corresponding to the low-temperature processes with activation energies 0.37 and 0.01 - 0.03 eV respectively. The first region is related to the excitation of charge carriers in zone of high mobility. The second region is related to the conduction by carriers in the localized states and characterised by activation energy of jumping from one defect to another in the nearest neighborhood.

In Fig. 5 the $CN_x$ film deposited at room temperature and 0.05 mbar $N_2$ pressure is shown. The N content of the film measured by XPS was about 5 at. %. The structure is amorphous but different from pure carbon film. In this film, as can be seen on the TEM image, large number of defects were observed due to columnar growth which means that localized states with wide range of energies must exist in the bandgap. Therefore the low-temperature region can not be interpreted so clearly. The high- temperature range as in the case of pure carbon film is related to

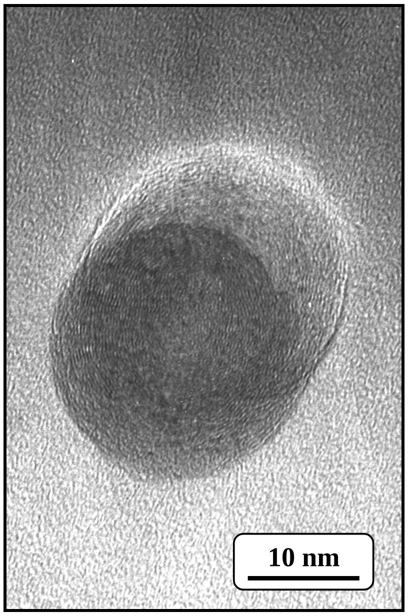



Fig. 1. HRTEM image of $CN_x$ film, deposited onto NaCl substrate at 0.1 mbar partial pressure of $N_2$ at ambient temperature.

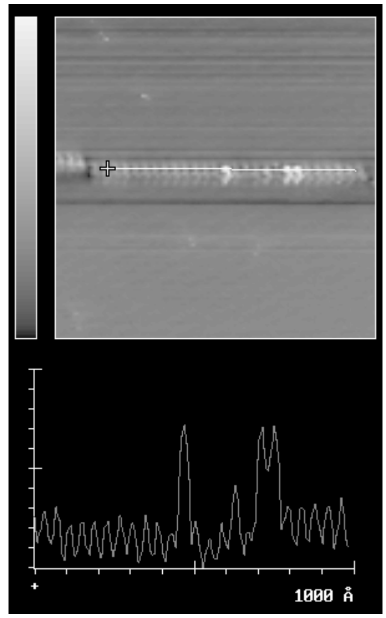



Fig. 2. STM image of $CN_x$ film deposited onto HOPG substrate at ambient temperature at 0.1 mbar $N_2$ partial pressure.

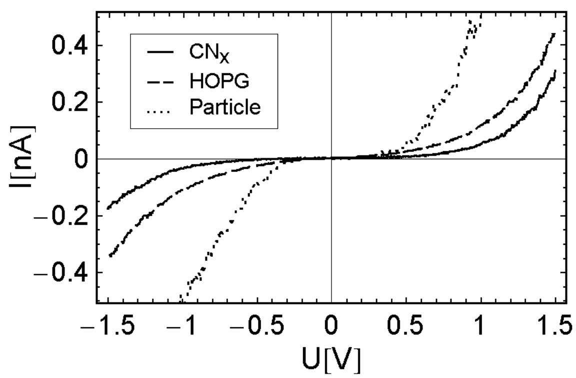



Fig. 3. STS I-V measurement of the film.

the conductance by carriers with energies in the high mobility zone. The activation energy 0.75 eV obtained from the plot in this case shows the mobility bandgap of the film which is different from density of states.

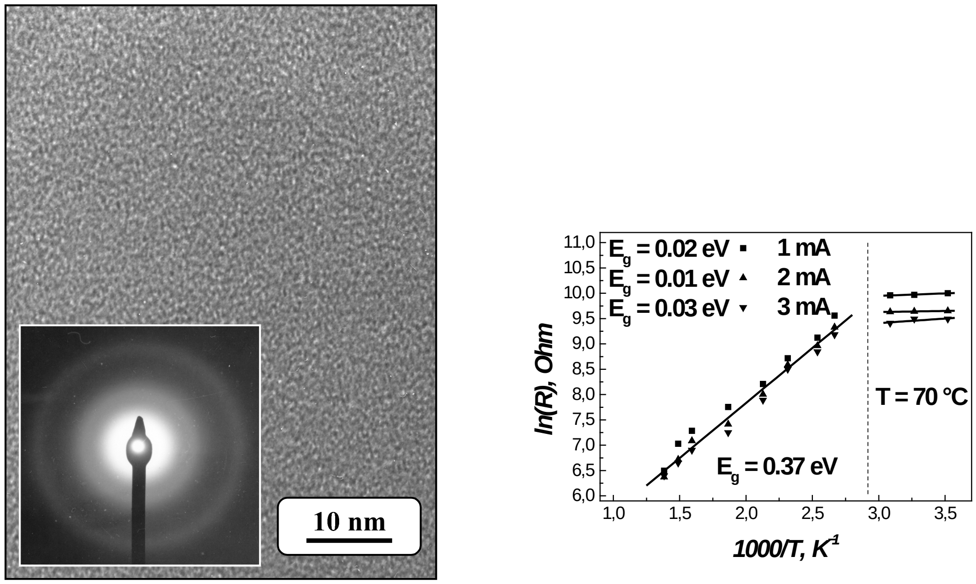



Fig. 4. Plan view bright field TEM image of 30 nm thick C film on NaCl substrate deposited at room temperature and temperature dependence of the electrical resistance of the film.

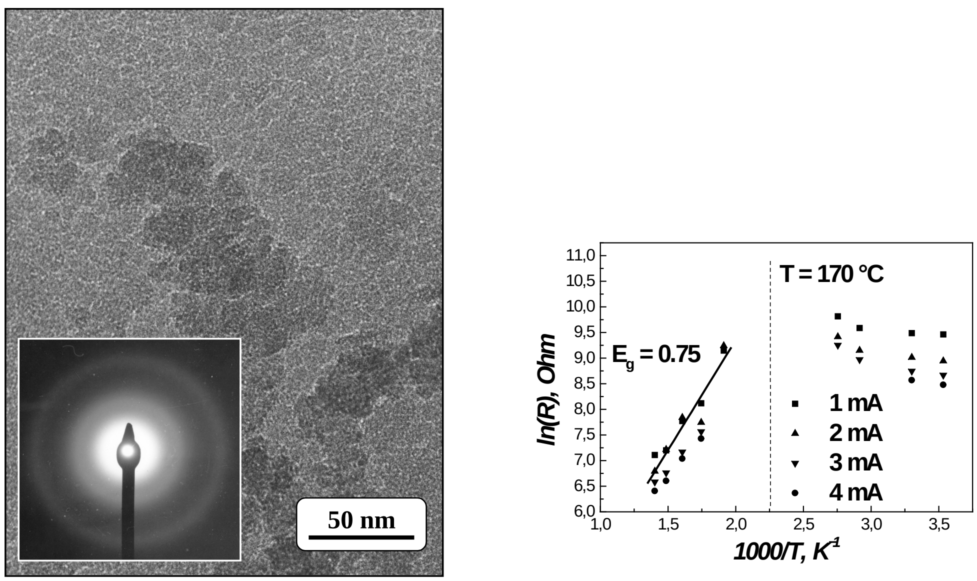
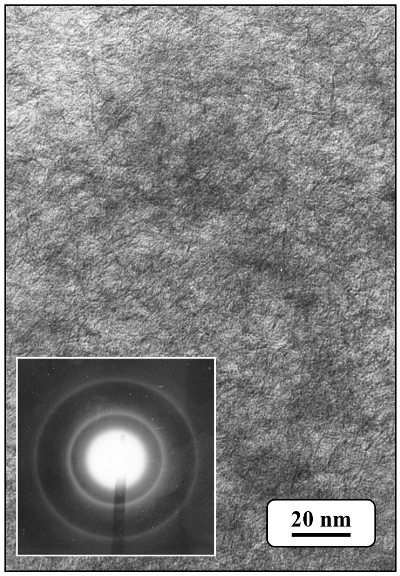



Fig. 5. Plan view bright field TEM image of 30 nm thick $CN_x$ film on Si substrate deposited at room temperature and $N_2$ pressure 0.05 mbar and temperature dependence of the electrical resistance of the film.



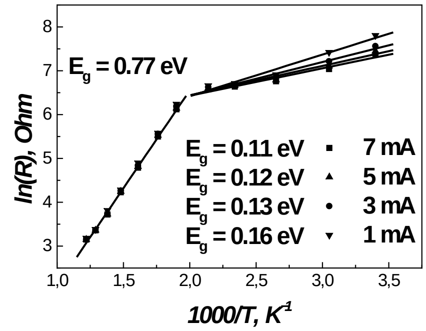




Fig. 6. Plan view bright field TEM image of 60 nm thick $CN_x$ film on Si substrate deposited at temperature 800 °C and $N_2$ pressure 0.05 mbar and temperature dependence of the electrical resistance of the film.

In Fig. 6 the $CN_x$ film deposited at temperature 800 °C and 0.05 mbar pressure is shown. The N content of the film measured by XPS was about 1 at. %. The film has a structure containing fiber-like nanocrystals of 1 nm in diameter and about 10 nm in length. In this case the SAED pattern shows sharper rings, corresponding to 111 and 220 reflections of diamond. Two regions can be separated on the plot of $\ln(R) = f(1000/T)$ - the first between room temperature and 230 °C with activation energy 0.11 - 0.16 eV and the second beetwen 230 °C and 550 °C with activation energy 0.77 eV. The activation energy in high temperature range as in previous two samples corresponds to the mobility bandgap.The activation energy measured at lower temperatures is sum of two values: energie of excitation of charge carriers in localized states and energy of jumping carriers between localized states. The last must be around kT which is in this range 0.02 - 0.04 eV. Therefore zone of localized states is about 0.1 eV.

## 4 Conclusions

Structures ranging from homogenous C films to isolated small spheres and cylinders of $CN_x$ were detected in the deposits, obtained at room temperature conditions and at different pressures of $N_2$. Up to 20 at. % N could be incorporated into these films. With increasing $N_2$ pressure during deposition the films become different from graphite like, and are light yellow, optically transparent, while their nanoscale structure becomes more ordered. We assume that multi-wall fullerene particles embedded into the $CN_x$ films can result in an enhanced electron emission compared to pure a-carbon layers.

Increasing the substrate temperature leads to further ordering and forming diamond nanocrystals of whisker like shape. The electrical resistance measurement results suggests the semiconductor like electronic structure with high density of localized states in $CN_x$ films.

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