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Formation of Nanocolumnar Structures under Magnetron Growth of Europium-oxide-doped Carbon Nitride Films

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Abstract

The atomic force microscopy is used to study surface morphology of carbon nitride CN_x and europium-oxide-doped carbon nitride $CN_x:Eu_yO_z$ films prepared by a direct-current magnetron. A clear correlation between the growth parameters and the resulting film structure is observed. It is established that the presence of a rare earth metal oxide leads to a structural ordering of the film surface. The self-organization processes within the films are investigated. Luminescence spectra and luminescence bands of europium-oxide-doped films are obtained.

Introduction

During the last decade a considerable attention has been directed at alloyed nanostructural materials, whose properties are defined by doping components as much as by their internal atomic patterns. As an example, the functional properties of carbonic materials depend on the specifics of "elementary blocks" (nanofibres, nanotubes, nanospheres), which build them on a mesoscopic level. An appreciable doping of such materials does not result in degradation of their nanodimensional structure. It does however lead to a superposition of the effects of alloying and spatial atomic organization. This makes it essential to investigate the mechanisms of their growth [1-3]. The study of such materials appears important both from fundamental and practical standpoints.

The desirable nanodimensional characteristics are usually attained by rather expensive and laborious lithographic methods such as the "e-beam" and the focusing ray lithography. It has been found that the synthesis of such nanostructures is essentially controlled by the growth conditions as well as by the substrate type and the utilized catalyst [4]. The use of catalytic metals (Ni, Co, Fe) is always crucial for the growth of carbonic nanomaterials (CNT/CNF). A catalyst is normally deposited on a substrate prior to the film growth and the diameter of the resulting nanotubes/nanofibres is directly related to the metallic layer width [2]. Under the described growth conditions the main function of the substrate is providing mechanical support for the nanostructure, although its interaction with the catalytic coating is also important. A careful balance between the processes of etching and growth was found to be crucial for preventing the damaging of lateral surfaces of the synthesized nanotubes/nanofibers and avoiding the formation of a continuous film [4]. Nanotubes/nanofibres may alternatively be prepared by non-catalytic methods. Magnetron sputtering exemplifies a method, which is compatible with semiconductor technologies and under certain growth conditions permits to obtain nanocolumnar arrays out of various materials (carbon, various metals etc.). It does not require any preliminary surface treatment, since the structure undergoes self-organization during the growth. Magnetron preparation of nanostructures has not yet been investigated in full detail.

The goal of this paper is to demonstrate the specifics and mechanisms of formation of nanocolumnar structures in magnetron-sputtered carbon nitride CN_x and rare-earth-doped carbon nitride (e.g. $CN_x:Eu_yO_z$) films.

Experimental

A direct current (DC) magnetron was used to prepare carbon nitride CN_x and europium-oxide-doped carbon nitride $CN_x:Eu_yO_z$ films through the sputtering of carbonic and combined carbonic-metal-oxide targets on gadolinium gallium garnet substrates in a N_2 atmosphere. The substrates were 0.5 mm-wide monocrystalline gadolinium gallium garnet plates with the (100) direction oriented normally to their surfaces. In our case the dopant impurity contained 40 atomic percent of europium (Eu_2O_3) and its concentration in the sputter target amounted to 6%.

The substrates underwent a preliminary two-stage cleaning by chemically pure ethyl and isopropyl alcohols as well as by isopropyl alcohol vapors. The final cleaning was accomplished immediately before the film growth by the argon glow-discharge plasma. No additional specific treatments of the substrates were performed.

The substrates were heated by a standard radiant heater in a multipurpose vacuum station VUP-5M and maintained at a constant temperature of 250°C. A DC planar magnetron with magnetic plasma confinement was used to sputter the targets. The magnetron power did not exceed 15-20 W and the pressure of the gas mixture amounted to 150 mTorr in all experiments.

3D AFM-images of the film surfaces were obtained by the NTEGRA Aura Scanning Probe Microscope (production of the NT-MDT Co., Zelenograd, Russia).

Luminescent-emission spectra of europium-oxide-doped films were obtained by a spectrofluorometer constructed on the basis of two MDR-2 monochromators.

Magnetron Sputtering of Nanostructured Films

It is well known that working pressures of the order of several tens of mTorr lead to growth of amorphous carbonic films, whereas the pressures ranging from 0.01 to 1 mTorr result in diamond-like polycrystalline films. These processes have been thoroughly investigated so we shall not dwell on them here.

When doped (under dopant concentration of several percent) carbonic films may lose their “diamond” bonds and undergo graphitizing, turning thus into metal-carbonic films with rather mediocre properties.

For this reason we have made an attempt to obtain and investigate the films under working pressure of approximately 150 mTorr. Some of the samples were doped so as to combine the structural properties of carbonic films and the dopant agent.

A planar DC magnetron utilized for the growth of the described samples is a constructionally simple system, featured by fairly complex physical processes occurring inside [5-13]. High working pressures lead to a longer lifetime of magnetron plasma and to a high concentration of the sputtered atoms in a rather narrow region of plasma localization. Under relatively low temperatures a sufficiently high atom density allows for formation of the chemical bonds. This gives rise to processes of self-organization so that the target material forms clusters within the plasma. Concurrently, the buffer gas is continuously pumped through the discharge zone. The flow rate of the buffer gas is small as compared to the thermal velocities of target atoms and buffer gas atoms and does not considerably affect the concentration and propagation of the sputtered atoms. Clusters formed from the target material and the products of chemical interaction between the target atoms and the buffer gas are deposited on the substrate.

It should be noted that the distance between the region of cluster formation and the substrate in a DC magnetron is several times bigger than the mean free path of both the buffer gas atoms and the target atoms. Hence the lifetime of clusters in a free state is substantial, which leads to an additional interaction between them and to a multitude of chemical reactions between the clusters and the buffer gas atoms.

The sizes of clusters and the density of their flow are determined to a large extend by the distance between the magnetron and the substrate. The cluster flows immediately above the magnetron and near the substrate surface may be substantially different.

During deposition the cluster flow passes through the high field region, where electrons captured by the magnetic field form a space charge of large magnitude. As a consequence thermal ions are drawn into this region and compensate electronic space charge. Due to interaction of the cluster flow with electrons and ions in the high magnetic field region, the clusters may acquire an electric charge.

This calls for an additional examination of magnetron deposition of nanostructural films and construction of new models of nanocolumn growth out of charged clusters. For instance, many features of the growth our film samples can be explained on the assumption of formation of nanocolumns out of charged clusters. We therefore assume that once the flow of dissimilarly charged clusters hits a relatively cold (with respect to the temperatures of plasma and clusters themselves) substrate, they undergo ‘solidification’ while their energy is transferred to the substrate [14, 15]. This is accompanied by formation of film nucleation canters, as observed in the AFM-investigations (Figures. 1, 2). On further deposition it becomes energetically favorable for clusters to attach themselves to oppositely charged nucleation sites on the substrate. Similarly charged clusters repel each other and deposit on the substrate forming thus new nucleation sites. Hence, the self-organization processes give rise to the growth of a nanocolumnar structure. The characteristic dimension of this structure is defined by temperature gradients of the deposited cluster flow, the buffer gas and the substrate as well as by their charge and cluster flow density, i.e. by the mass-transfer of the sputtered material. When sputtering a combined target or adding etching components directly the plasma it is necessary to account for their interaction with clusters in plasma and with the forming film, which may lead to a significant alteration of the film structure.

In view of the preceding, depending on the growth parameters (the nitrogen concentration in the buffer gas, the substrate heating temperature, the flow clusterization, the charging state of clusters, the substrate position with respect to the magnetron) the clusters may either become nucleation sites for nanocolumns growing perpendicularly to the substrate surface or may promote a globular character of the film growth [16-18].

In other words the growth conditions affect the non-catalytic self-organization of material upon a substrate.

The growth of europium-oxide-doped carbon nitride films is controlled by even greater number of parameters, which significantly expands the diversity of the occurring processes. One of the factors to be accounted for is the chemical interaction between the carbon and the europium oxide.

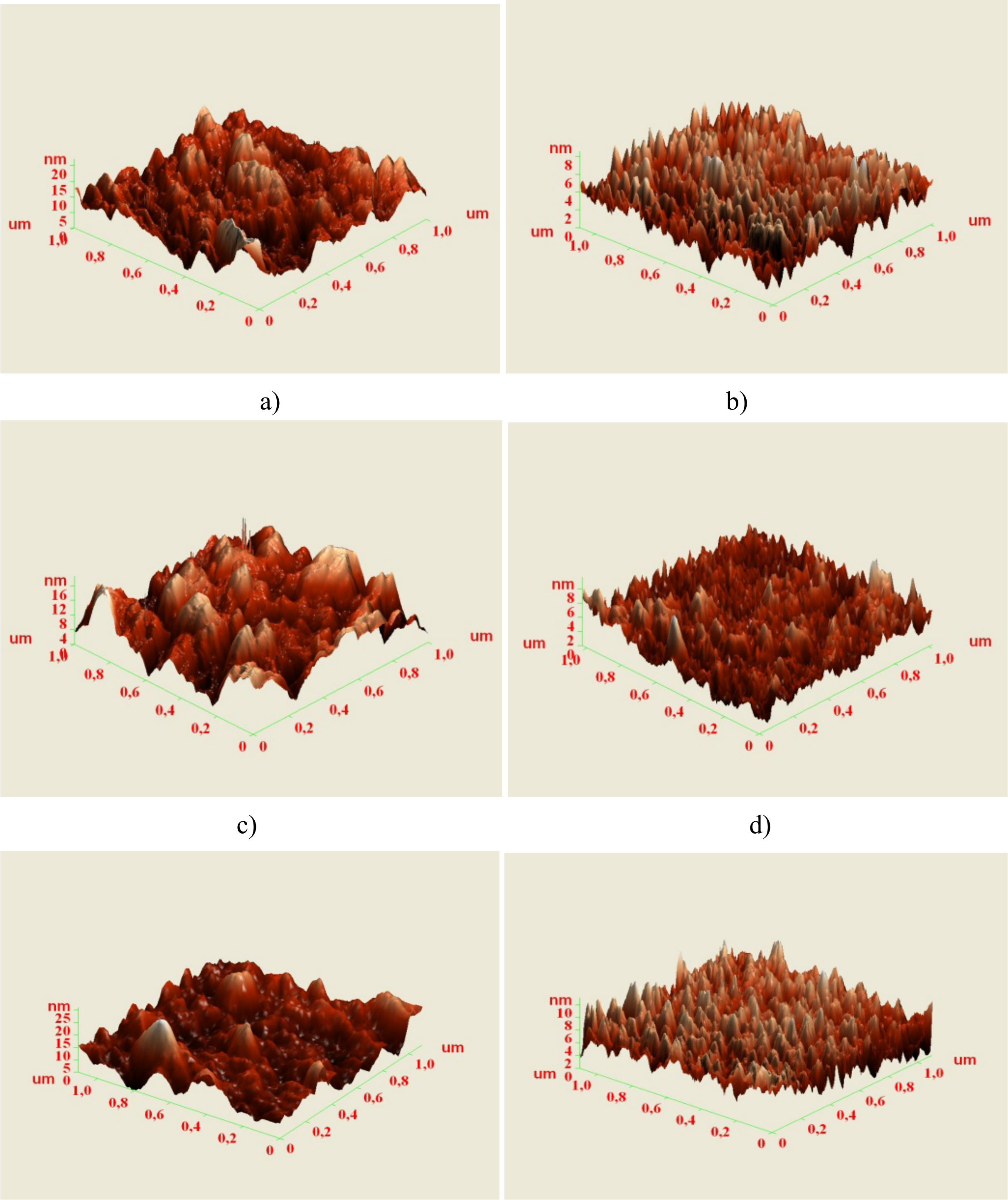
The energy of electronic impact is much bigger than the ionization energy of europium oxide molecules. There may arise europium oxide radicals, which in the course of carbon clusterization can trigger various chemical reactions. These are mainly the reactions of oxidation of target carbon by the dopant oxygen and the reduction of dopant oxide by the target carbon accompanied by formation of volatile products:

$$
\begin{aligned}
&Eu_2O_3 + C = (Eu_2O_2) + CO\uparrow \\
&\ldots \\
&Eu_2O_3 + 3C = 2Eu + 3CO\uparrow \\
&Eu_2O_3 + C = (Eu_2O_1) + CO_2\uparrow \\
&\ldots \\
&2Eu_2O_3 + 3C = 4Eu + 3CO_2\uparrow
\end{aligned}
$$

Despite the fact that the buffer gas is constantly pumped through the effective volume of the magnetron, the products of chemical interactions of the composite carbonic target may not be completely evacuated from this volume and may also interact with the forming carbonic clusters. The net effect of these interactions and reactions is the etching of carbonic clusters, which makes the cluster flow more uniform both in its cross-section and in cluster dimensions. This ultimately leads to a smoother surface of the growing film.

Figure 1 shows 3D AFM-images of the surfaces of CN_x (a, c, e) and CN_x:Eu_yO_z (b, d, f) films under various discharge powers. The film surfaces display a conspicuous needle-shaped structure formed of bundles of nanocolumns. Unalloyed films of carbon nitride are characterized by irregularly located large bundles of nanocolumns (as compared to smaller and more equally spaced bundles of europium oxide-doped films). It is readily seen that the conditions of uniformity are fulfilled for different magnetron powers and hence for different cluster flow densities. There is an evident etching effect of the dopant europium oxide manifested in comparatively small nanocolumn bundles of the alloyed films.

Luminescence spectra were taken for europium-oxide-doped samples (Figure 2).



a)

b)

c)

d)

e)

f)

Figure 1: 3D AFM-images of CN_x (a, c, e) and CN_x:Eu_yO_z (b, d, f) films grown during one hour for dopant concentration 3,2%. The magnetron current I and the discharge voltage U were I = 42 mA and U=350V (a, b); I = 53 mA and U = 425 V (c, d); I = 58 mA and U = 480 V (e, f).

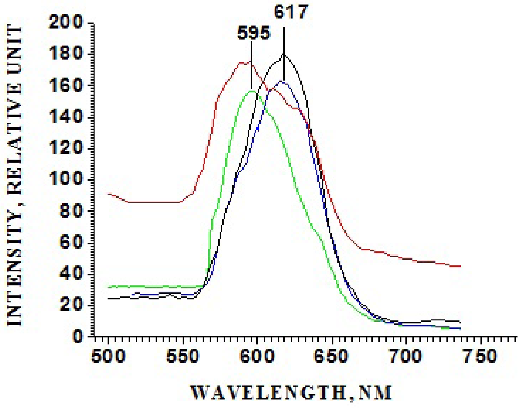


Figure 2: Luminescence spectra of CNx:EuyOz films grown during one hour for dopant concentration 3,2% and excitation wave length 296 ± 4 nm. The magnetron current I and the discharge voltage U were I = 53 mA and U = 425 V (red and green curves), and I = 58 mA and U = 480 V (blue and black curves).

The intensity of intracenter transitions in rare earths is usually defined by a number of factors, such as e.g. the optimal concentration of optically active centers, the transport of non-equilibrium charge carriers from the matrix to the rare earth, the excitation intensity and wave length and introduction of additional impurities, which favor formation of rare-earth ions with a big capture cross-section of charge carriers.

In materials possessing a nanostructure or nanostructural components no smaller part is played by the matrix nanostructure.

Taking into account that the film was alloyed by $Eu_2O_{3,}$ (not a pure Eu,) the excitation was transferred at the wave length 296±4 nm, which corresponds to the charge transfer band in Eu^{3+}-O^{2-} complex or to the oxygen adsorption band (Fisher band). Ions O^{2-}, which end up in the film upon decomposition of europium oxide play the role of an additional dopant, which promotes formation of rare-earth ions complexes with a big capture cross-section of charge-carriers.

Broad luminescence bands were registered with maxima at 595 nm and 617 nm, corresponding to $^5D_0$-$^7F_1$ and $^5D_0$-$^7F_2$ intracenter f-f transitions in Eu^{3+} ion respectively.

The broad luminescence bands are explained by the irregular nanostructure of carbonic films (which is evident in the above figures) and the uneven spacing of Eu^{3+} ions.
No other luminescence bands were registered.

The performed investigations permit to assert that alloying of individual bundles of nanocolumns (rather than doping of an entire film) by rare earth metals yields samples with essentially different properties. They can be used for creation of one-photon controlled nanolasers with wave-lengths determined by f-f transitions in the rare-earths, phase gratings with luminescent elements etc.

Technological usefulness of such systems can hardly be overestimated. Hence the necessity of further investigations into the processes of formation of nanocolumnar structures under magnetron growth of rare-earth-doped carbon nitride films.

Conclusion

Our study shows that formation of clusters in magnetron plasma is due to a sufficiently high gas pressure in the effective volume (of the order of 150 mTorr), and, hence, by a high plasma density in the discharge zone. This creates conditions for greater intensity of chemical reactions between the sputtering products, which can have a crucial effect on the final film structure. Under the magnetron operating pressure of about 150 mTorr there occurs a self-organization of nanocolumnar structures in carbon-nitride films. A nanocolumnar structure is formed through a non-catalytic process. Under magnetron growth of europium-oxide-doped carbon nitride films the nanocolumn bundles tend to be more regularly spaced and have a more uniform size distribution. This is due to the etching effect of europium oxide and of the products of chemical interaction between europium oxide and the target carbon. In europium-oxide-doped films CN_x:Eu_yO_z broad luminescence bands were observed with maxima at 595 nm and 617 nm. They correspond to $^5D_0$–$^7F_1$ and $^5D_0$–$^7F_2$ transitions in Eu^{3+} ion , respectively. Luminescence bands are manifestly dependent on the conditions of film preparation.

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