



Synthesis, characterization and nanostructuring of (a-C:H):Si and (a-C:H):Si:metal films

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Abstract

Structural properties of carbon–silicon composite films, grown by PE CVD technique on Si substrates, were examined using Auger electron spectroscopy (AES), X-ray diffraction (XRD) and scanning probe microscopy (SPM) before and after SPM tip-induced actions. Metal-free (a-C:H):Si films were found to be considered as a polymer-like material with either amorphous or nanocrystalline structure, consisting of hydrocarbon chains with different molecular masses and lengths. For Mo-doped films, a higher content of structurally ordered atomic groups was registered as compared to the metal-free films.

A new effect of nanostructuring, i.e. the formation of nanocones under the action of local electric field in the metal-free films, was observed. Evidence was obtained in favor of local recrystallization of the nanoscale regions of the amorphous material under the SPM actions.

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1. Introduction

Recently, scanning probe microscopy (SPM)-based nanostructuring of carbon films attracts permanently increasing attention of researchers. This interest is caused by the data obtained on nanoscale modifications of hard carbon materials—diamond and diamond-like carbon (DLC) films. Among nanotechnological methods, being currently used for this goal, one can distinguish the SPM processes, which occur locally in the material under the action of electrical field underneath the probe. In particular, the field-induced actions lead to the formation of insulating nanostructures at a hydrogen-terminated diamond surface [1] and highly conducting nanostructures in low-conducting amorphous DLC films [2,3], and also to topological modifications in the form of nanoprotusions or nanocavities [3–6]. It should be noted that similar processes are found to develop in polymer films [7–10] but up to now the problem of patterning for such kind of soft materials is mostly

attacked by either thermomechanics [11] or dynamic plowing methods [12].

In this work, we report on the synthesis, characterization and SPM-based nanostructuring of carbon–silicon composite films.

2. Experimental details

The original films were deposited on Si substrates by PE CVD method [13]. Briefly, during deposition a vapor of silicon-organic liquid-polysiloxane (PS) was injected into a plasmatron region of a vacuum chamber. The vapor was used as a plasma-forming substance. The films were doped with metals by magnetron sputtering of a metal target (Mo, Cr) during film deposition. In this process, a bias voltage (500 V) was applied to the substrate. The pressure in the vacuum chamber was 5×10^{-2} Pa; the plasmatron arc discharge current was about 6 A. The metal-free and metal-containing films are further called as (a-C:H):Si and (a-C:H):Si:metal films, respectively.

The deposition rate of (a-C:H):Si films was 40 nm/min and the deposition rate of (a-C:H):Si:Mo films was 65 nm/min.

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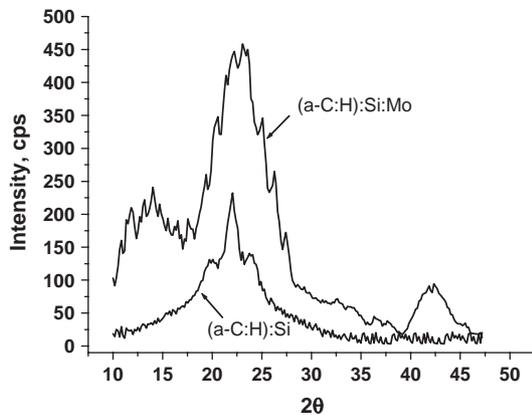


Fig. 1. XRD spectra of (a-C:H):Si and (a-C:H):Si:Mo films.

Details on the properties of (a-C:H):Si and (a-C:H):Si:metal films were reported elsewhere [13,14]. The thickness of the films used was up to 100 nm.

Structural characterization of the films was performed with X-ray diffraction (XRD) using a JDX-10P system (JEOL, Japan) with a $\text{Cu K}\alpha$ X-ray source.

The films of 100 nm thick were examined for the purpose of nanoscale modifications under the actions of local electrical field. The experiments were carried out in an air-operated SPM setup Solver P47 (NT-MDT Co., Russia) using Pt-coated cantilevers. The Pt-coated cantilevers were used as the probes for SPM actions in contact mode, and also for testing the samples before and after the actions. To induce the electric field underneath the probe, a series ($N=1-1000$) of rectangular voltage pulses with the magnitude U in the range from -10 V to $+10$ V and duration $\tau=1-1000$ ms were applied between the sample and the grounded probe at regular points of the scanned area. The exposure $T=N\tau$ was varied from 3 ms to 300 s.

In addition, both the original and SPM tip-treated (a-C:H):Si films were examined with a high resolution AES, ESCALab Mk2 VG Scientific, UK. The tested area was $1 \times 1 \mu\text{m}^2$. In order to reduce an influence of the initial electron beam on the film structure, the following measuring

conditions were provided: (i) the electron current was extremely lowered; (ii) the electron beam was directed obliquely to the sample surface; (iii) the only 230–260 eV energy interval for Auger electrons was registered; and (iv) the spectra acquisition took less 15 s. It should be noted that, in the case of carbon materials, the indicated energy interval is related to electron transitions via 2p-electron states of the valence band—it means that the observed spectra deviations can be associated with modifications of the valence band of carbon.

3. Experimental results and discussion

3.1. The original film structure

Fig. 1 demonstrates typical XRD spectra of the (a-C:H):Si and (a-C:H):Si:Mo films. As is seen from Fig. 1, the XRD spectrum for (a-C:H):Si films shows three broad diffraction peaks in the range of $2\theta=17-26^\circ$ (at the (002) graphite reflex position [15]) that indicates either amorphous or nanocrystalline structure of the (a-C:H):Si films tested. It should be also noted that the peak positions (at $2\theta \sim 20^\circ$, $\sim 22^\circ$ and $\sim 24^\circ$) are characteristic of different atomic groups (methenyl, methyl, methylene) in such hydrocarbon polymers as polyethylene and polypropylene [16]. The latter allows us to consider the a-(C:H):Si films as a polymer-like material.

In contrast, the presented XRD spectrum for (a-C:H):Si:Mo films exhibits numerous sharp diffraction peaks in the $17-26^\circ$ range. Being overlapped each other, these reflexes form an amorphous diffraction halo which can be associated with a higher content of structurally ordered atomic groups as compared to the (a-C:H):Si film structure. Besides, the spectrum shows two intensive peaks: (1) the peak at $2\theta \sim 42^\circ$ (interpreted as a reflex of graphite [15]) and (2) the peak at $2\theta \sim 14^\circ$ (non-identified). In main details, the XRD spectrum of the (a-C:H):Si:Mo film is distinctive for crystalline polymers, additionally containing both amorphous phase inclusions and graphite particles.

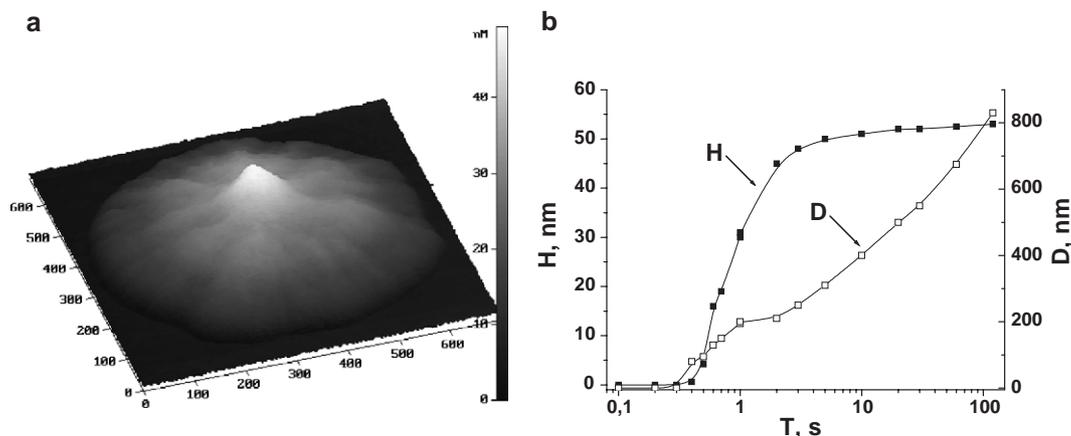


Fig. 2. Results of SPM actions on the (a-C:H):Si film ($U=10$ V): (a) cone-like nanoprotusion obtained at $T=8$ s and (b) the 'nanocone' height H and diameter D vs. exposure T plots.

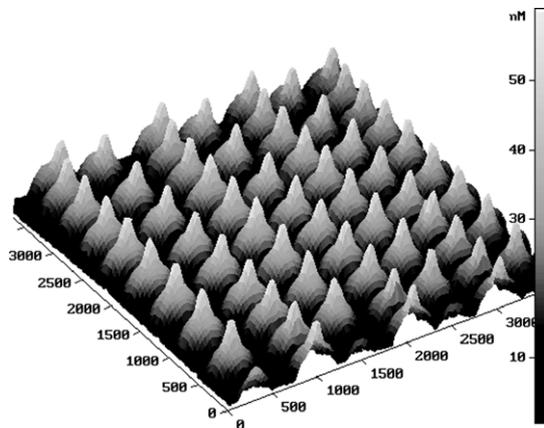


Fig. 3. Regular nanostructures (nanoproptrusions) array on the (a-C:H):Si film surface.

3.2. Scanning probe microscopy data

The SPM mapping over a scanned area of $1 \times 1 \mu\text{m}^2$ size reveals the film surface roughness of about 1 nm. Results of the SPM-actions can be summarized as follows.

3.2.1. SPM actions on the (a-C:H):Si film surface

First, it is found that no surface modification is observed under the action of voltage pulses of negative polarity. Second, it is established that, above $U \sim 5$ V, the positive pulse action at a given point reproducibly results in the growth of cone-like nanoproptrusions with the apex radius of $r \leq 5$ nm, as shown in Fig. 2a. The SPM-induced growth of the cone-like nanoproptrusions occurs when the exposure T reaches the threshold value T_C . The value of T_C is ~ 1 s at $U=10$ V and, at the low limit of the applied voltage, when $U \rightarrow 5$ V, the exposure should be very high, i.e. $T_C \rightarrow \infty$, in order to cause any measurable modification of the film surface. It is distinctive that the ‘nanoproptrusion’ height tends to saturation ($H \rightarrow H_{\text{max}}$) at high exposures, whereas its diameter (measured at the surface level of the original film) is constantly increasing with exposure, as demonstrated in Fig. 2b.

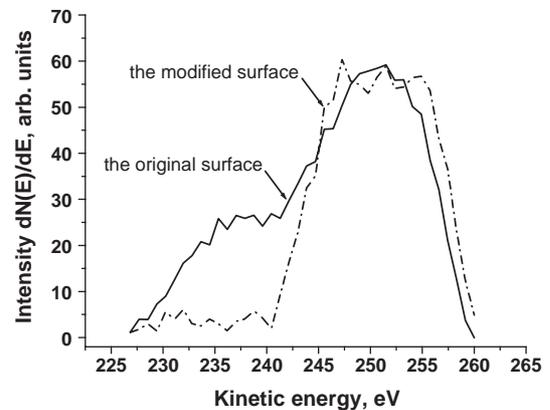
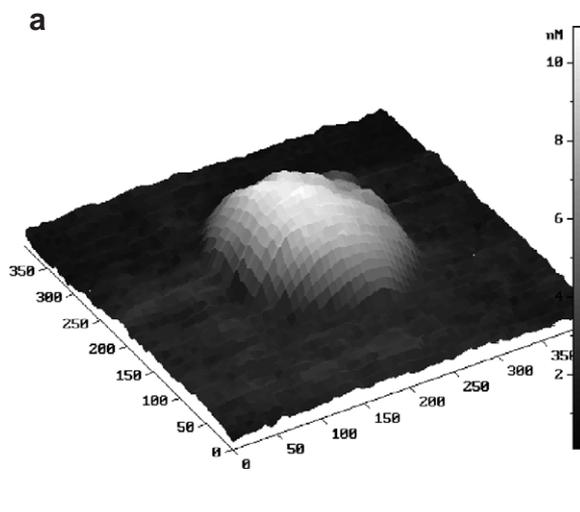


Fig. 5. Auger electron spectra of the (a-C:H):Si films before and after the SPM actions.

The developed SPM-based process is highly reproducible that allowed us to form the regular nanoproptrusion array with the surface density of $\sim 5 \times 10^8$ elements/ cm^2 (Fig. 3), thus realizing highly controlled nanopatterning of the (a-C:H):Si films.

3.2.2. SPM actions on the (a-C:H):Si:Mo film surface

In contrast to the (a-C:H):Si films, the SPM actions onto the metal-doped films result in the formation of hill-shaped nanoproptrusions, as shown in Fig. 4a. The nanoproptrusion appears under the action of voltage pulses of positive polarity when the pulse magnitude exceeds the value of ~ 4 V. No exposure threshold is registered in these experiments (Fig. 4b). It should be also noted that the SPM process is characterized by a relatively high disorder of $H(T)$ data at $T > 20$ ms (see the corresponding $H(T)$ plot in Fig. 4b).

3.3. High resolution AES data

Fig. 5 demonstrates the AES spectra of the original and SPM-modified (a-C:H):Si film surfaces (i.e. the latter was

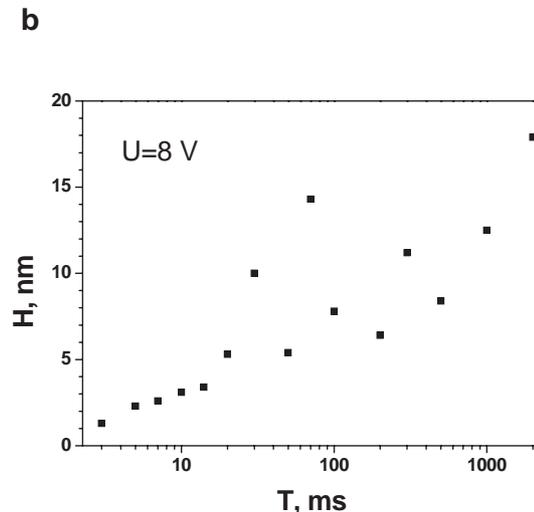


Fig. 4. Results of SPM actions on the (a-C:H):Si:Mo film ($U=8$ V): (a) hill-shaped nanoproptrusion obtained at $T=60$ ms and (b) the ‘hill’ height H vs. exposure T plot.

recorded from the region with an array of nanocones shown in Fig. 3). It is seen that the original film is characterized by AES spectrum taking up the whole energy range examined (see the solid line). Such a behavior can be associated with tailing of the valence band due to the amorphous structural state of carbon [17]. The main changes of the AES intensity at low kinetic energies is conventionally attributed to current structural models of a-C:H film as aromatic/graphitic clusters and olefin chains of sp^2 -carbon interconnected by hydrogen (or polymeric) sp^3 -regions and/or as hydrocarbon regions containing carbon–carbon double bonds with contiguous π bonds [18,19]. The observed decrease of intensity at the low kinetic energies (230–240 eV) for the modified film (see the dash-dot line) is referred to a lowered content of hydrogen, carbonization and appearance of carbon clusters with more perfect structures than that of amorphous network in the original film. During this rearrangement process, the initial structure is transformed to a more long range of clusters with sp^3 -bonded carbon.

4. Conclusions

In summary, we come to conclusion that the Mo-doping leads to drastic changes in the carbon–silicon composite structure. This circumstance strongly influences the SPM-based nanostructuring process. In the case of (a-CH):Si films, there is a latent period of SPM actions, on completion of which the electrical field induces the formation of new stable bonds accompanied by a decrease of the film density. It can be also proposed that the transformed polymer chains are mostly oriented along the electric force-lines, specifying the cone-like nanoprotrusion shape. Another mechanism dominates in (a-CH):Si:Mo films. Most probably, in this case, the field-induced structural rearrangement is negligible and the surface swelling observed is caused by local oxidation. More detailed investigations are needed to verify this hypothesis.

Acknowledgments

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