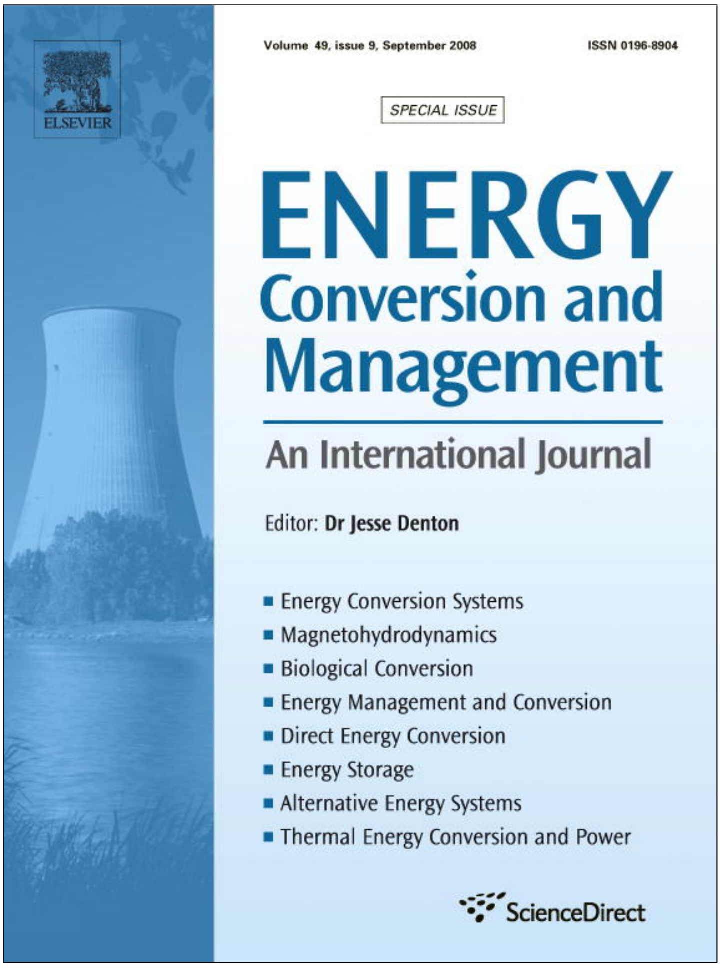
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Diamond-like carbon layers grown by electrochemical method–structural study

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ABSTRACT

A simple method of production of diamond-like carbon (DLC) thin films on various substrates by means of electrolysis of liquid hydrocarbons under ambient conditions is described in the paper. The amount of sp^3-hybridized carbon clusters within deposited films is a key parameter of their structural quality, and is investigated using scanning electron microscopy (SEM), and Raman spectroscopy. Obtained results indicate that although the electrolysis generally leads to granular DLC films contaminated with graphitic inclusions, providing current density larger than 520 mA cm^{-2} at 1700 V, sp^3-rich microcrystals with sharp edges can be found as well. Micro-Raman spectroscopic data strongly suggest that these microcrystals are minute diamonds, which eventually opens up a new perspective for a low-temperature synthesis of diamond-related materials.

1. Introduction

Diamond-like carbon (DLC) is a name first introduced by Aisenberg and Chabot [1] to describe a group of carbon materials containing significant fraction of tetragonally-hybridized carbon atoms as in diamond, although without any long-range periodicity. DLC does not exhibit any specific structure; it is rather a mixture of amorphous and crystalline carbon phases, properties of which strongly depend on deposition conditions. This kind of thin DLC films exhibit optical properties useful for, e.g. solar cells, providing antireflection coating on single crystalline "waste" microelectronic Si [2].

Apart from that, there are also DLC films that contain up to 50 at.% of atomic hydrogen within the structure, referred to as hydrogenated DLC (a-C:H), which are used, for example, as a surface source of H atoms on microcrystalline silicon solar cells. In such case, the DLC film deposition gives rise to increased short-circuit current, enhanced open-circuit voltage and increased fill factor as well. The latter is likely caused by passivation of recombination active centres on the surface and possibly by external gettering of defects and impurities from the bulk [2].

Since the first announcement of Aisenberg and Chabot [1], DLC films have been produced by a wide variety of deposition methods (chemical vapor deposition [3], physical vapor deposition [4], ion-sputtering [5] and others), among which electrolysis of liquid hydrocarbons has been the newest but reasonably successful so far [6–8]. Electrodeposited DLC films are distinguished by the lack of carbide interfacial layer that is inevitably formed on carbide-forming substrates at temperatures higher than 500 °C (silicon, titanium etc.), negligible thermal stresses due to the low deposition temperature (less than 100 °C), and very simple experimental set-up [9,10].

2. Experimental details

DLC films have been deposited by electrolysis of ethanol diluted with deionized water (alcohol concentration $[C_2H_5OH]/([C_2H_5OH]+[H_2O]) = 10–90$ vol.%). Graphite rod put together with a very thin platinum wire serves as an anode, whereas mirror-polished (100) silicon ($20 \times 10 \times 0.25$ mm^3) serves as a cathode. The distance between the electrodes is maintained at 3 mm, the DC voltage supplied may be adjusted from 1000 up to 2700 V, and the deposition temperature varies from 78 up to 100 °C depending on the boiling point of a given electrolyte. The deposition process is carried out for 5 h.

The sample morphology has been observed using Novascan 30 SEM microscope by Zeiss. Jobin-Yvone T64000 Raman system with additional microscopic adapter (Olympus) was used to measure Raman spectra of the films in the range from 1100 to 1800 cm^{-1} excited with a 488 nm line produced by an argon-ion laser.

3. Results and discussion

In Fig. 1 SEM images of the DLC films deposited by the electrolysis of the liquid mixture containing, respectively, from 10 up to 90 vol.% of ethanol (EA – ethanol content) using voltage $U = 1700$ V are shown. Previous observations proved that such

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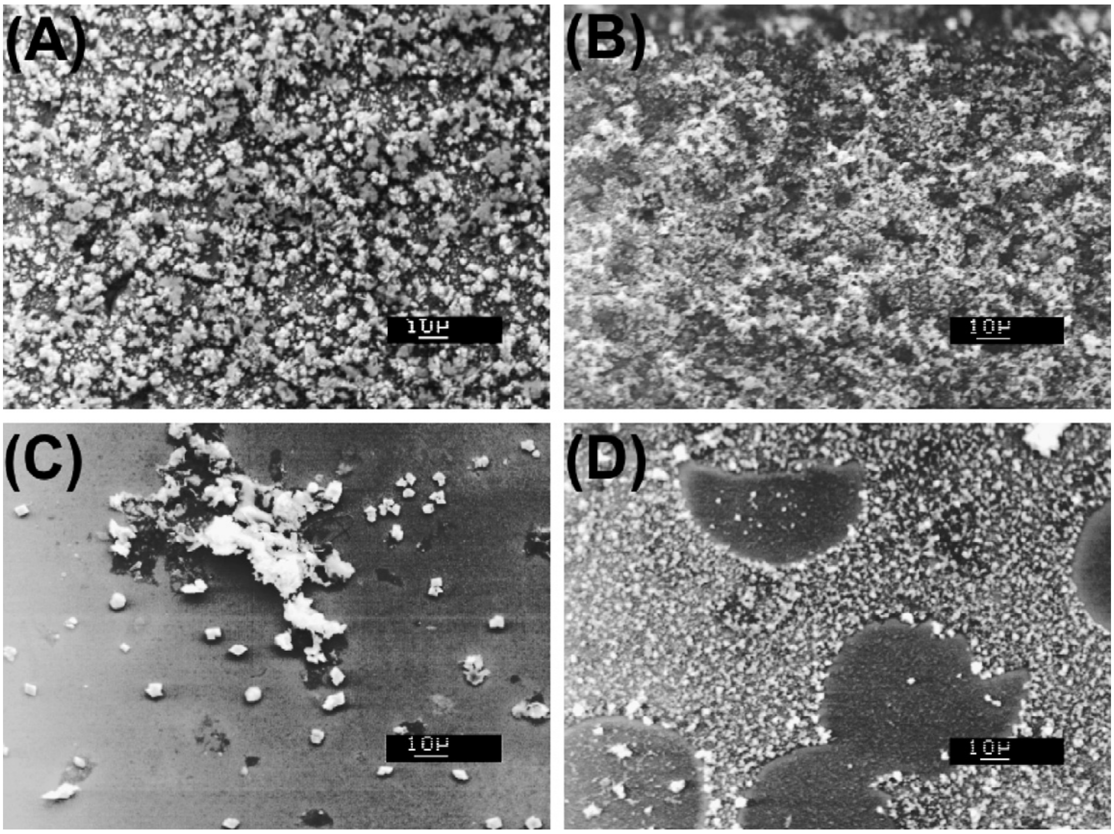

Fig. 1. SEM images of the carbon films obtained by electrodeposition method from a mixture containing, respectively: 10 (A), 50 (B), 66 (C), and 90 vol.% (D) of the ethanol.

films are composed mostly of sp^3-hybridized carbon atoms and are white in color [8]. In contrast, the structures discussed in the current paper are all black, which might indicate higher content of graphitic inclusions.

In Fig. 1A SEM topography of the film deposited from highly diluted electrolyte is seen (EA = 10 vol.%) The substrate is entirely covered by the deposit, and the structure obtained might be referred to as a cauliflower-like one with numerous lumps of the DLC spread randomly over elsewhere flat surface with a density as large as $7.5 \times 10^6\ \mathrm{cm}^{-2}$. The mean size of the lumps is around 5 μm, but the largest particles does not grow over 10 μm.

The film seen in Fig. 1B was made from the liquid mixture containing equal amounts of ethyl alcohol and water (EA = 50 vol.%) The film is closed as that in Fig. 1A, although the lumps are not so prominent. SEM micrograph exhibits a sponge-like structure, that is a rough film consisting of small carbon particles (around 1 μm in diameter) that form a system of hills and valleys and give rise to a highly extended surface.

In Fig. 1C a structure obtained from a mixture with EA = 66 vol.% is shown. In contrast to previous samples, the deposition process results in single, minute microcrystals left behind on the surface rather than any continuous film. The crystals vary in shape (rhomboidal, tetragonal, trigonal), but they all are about 5 μm in diameter, and have sharp, well defined edges. The particle density reaches $2.7 \times 10^5\ \mathrm{cm}^{-2}$ which is over a one order of magnitude smaller than that in Fig. 1A.

Finally, in Fig. 1D a film deposited by the electrolysis of a slightly diluted ethanol is presented (EA = 90 vol.%) SEM image exhibits structure with a heterogeneous morphology, i.e. a surface covered by small lumps of the DLC on one hand, and circular areas of the diameter of around 60 μm with hardly deposited carbon material on the other. The particles within the circular areas, that contribute to one third of the total surface area, are sparsely distributed with the density of $5 \times 10^5\ \mathrm{cm}^{-2}$, that is similar to that specific of microcrystals in Fig. 1C. In turn, the particle density in the area covered by the lumps reaches $2 \times 10^7\ \mathrm{cm}^{-2}$, and therefore 2 orders of magnitude higher.

Raman scattering measurements shown in Fig. 2 confirm structural heterogeneity of the films electrodeposited from ethanol. As a rule, two broad Raman features are observed, namely a line at around $1585\ \mathrm{cm}^{-1}$ characteristic of sp^2 inclusions and referred to as the G-line together with a line at $1355\ \mathrm{cm}^{-1}$ corresponding to tetrahedrally-bonded carbon atoms placed in the boundary between graphite microcrystals (D-line) [11]. Note that the spectra

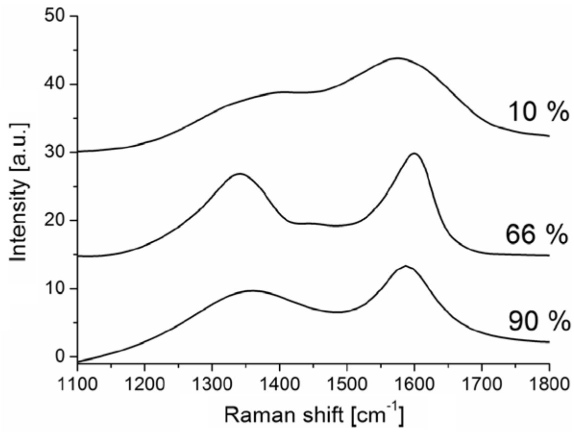

Fig. 2. Raman spectra taken from the DLC films deposited at, respectively, (from top to bottom): 10, 66, and 90 vol.% of ethanol.

recorded both in highly diluted and almost pure ethyl alcohol exhibit actually the DLC structure of the deposits due to their wide, overlapped D and G bands with almost no background luminescence. According to the model proposed by Rozploch co-worker [11] such a spectral shape follows from a structure which is a mixture of small sp^2/sp^3 carbon domains giving rise to interatomic bond distortion. On the other hand, micro-Raman spectrum taken from one of the microcrystals seen in Fig. 1C is similar to spectra observed in synthetic diamonds, namely two well defined 1332 and 1580 cm^{-1} peaks with a small shoulder in between, that corresponds to cage-like carbon structures (fullerenes that have not been fully accomplished yet).

4. Conclusions

Presented paper deals with the problem of low-temperature electrodeposition of DLC films from liquid hydrocarbon mixtures. In general, successful deposition of such films is demonstrated in the paper that results in structures of various surface topography depending on the electrolyte composition. As a rule, the films deposited from highly diluted and almost pure ethyl alcohol are continuous although rough and porous, whereas the structure deposited at moderate ethanol content exhibits single microcrystals left apart rather than any closed film. Raman spectroscopy data unambiguously proved that these microcrystals are minute diamonds, which might actually open up a new perspective for low-temperature deposition of this material. Apart from that, such DLC films with highly developed surface could be useful in many technological application, for instance, carbon-based capacitors, molecular sieves, adsorbing devices etc.

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