Ceramics International **21** (1995) 399–401

Structure Modelling of DLC-Films Formed by Pulsed Arc Method

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(Received 11 November 1994; accepted 2 February 1995)

Abstract: Reported here is the continuation of the structure characterization of carbon thin films produced by a pulsed vacuum arc plasma source. Hydrogen free carbon films with thickness up to 3 μm were prepared with average deposition rate of 5 μm/h onto various substrates. It was found that these carbon films are not quite amorphous and can be described by modelling the clustered structure with different $sp^3/sp^2/sp$ bond ratios depending on deposition conditions. Results of the experimental investigations and numerical modelling of the films structure are presented.

1 INTRODUCTION

In recent years, a number of pulsed methods for preparation of diamond-like carbon films such as laser, laser-arc and arc were developed.[1–5] These methods are characterized by periodical incoming of plasma fluxes to the substrate, high pulsed deposition rates, suitable particle energies and their density in a plasma flow. Plasma has different particle energy distribution and films structure is defined by joint interaction of ions, atoms and molecules with the surface of growing layers.

The attraction of these methods is possibly to obtain exactly dosed thicknesses, dense and hydrogen-free hard carbon layers with good adhesion to different substrate materials and high percentage of sp^3 bonds. Collins *et al.*[1,2] have shown that up to 75% of atoms in the carbon films prepared by Nd-YAG pulsed laser are sp^3 bonded. These films were presented as 'amorphous diamond'. Structural elements of these films are clusters or nanocrystals with sp^3 bonds placed in a carbon matrix. Film densities up to 3·2 g/cm^3 were achieved. A high percentage of sp^3 bonds (up to 90%) was noted for carbon films deposited from pulsed arc discharge plasma in vacuum.[6]

It has been proved that pulsed deposition methods provide the high sp^3 bonds percentage in hydrogen free carbon films. On the other hand, the pulsed character of dense energetic plasma fluxes deposition can provide, in comparison with continuous methods, the nucleation mechanism changes and different carbon metastable phases formation. It takes detailed examination of kinetics and thermodynamics of pulsed deposition processes, to obtain information on structure of thin films.

This paper summarizes the results of detailed experimental and modelling investigations of carbon films prepared under the pulsed plasma vacuum arc deposition method to study general questions of carbon films structure formation under pulsed conditions.

2 EXPERIMENTAL

The pulsed plasma source described previously[4] was used to prepare carbon films. Films having thicknesses from several monolayers to 3 μm were obtained on Si, KCl, glass, stainless steel and some plastic substrates, placed on a grounded or electrically isolated holder. The deposition was carried out at a high vacuum of $p < 10^{-4}$ Pa, produced by an oil diffusion pump. High purity graphite was used as the starting material. Varying the deposition conditions: peak voltage between the cathode and anode of source (90–500 V), substrate temperature (293–773 K), discharge

pulses repetition time (0·1–1 s), and substrates position, continuous hard layers were obtained with good adhesion to substrate.

To study the structure of deposited films the TED, TEM, XPS, EELS, AES and some other techniques were used. Results obtained by these methods were compared with those for crystalline diamond, graphite and carbyne. The $sp^3/sp^2/sp$ ratio was obtained from XPS and AES spectra,[7] and atomic density from EEL spectra.[8] Data from TED and TEM were used to estimate near-ordering areas sizes and build structure models.

3 RESULTS AND DISCUSSION

Deposited under conditions of large vapor oversaturation and low substrate temperatures, different carbon phases having sp^3, sp^2 and sp bonds can arise at the same time with high probability. In fact, the presence of all binding types in a different ratio are simultaneously identified in pulsed deposited films.

Obviously, the carbon films structure can hardly be described by a simple model and a number of investigative methods are needed to obtain detailed information. Two approaches for analysing carbon films structure were used. First, the results of deposited film examination were being compared with those obtained in the same conditions for bulk materials. Second, experimental results were being compared with those of numerical modelling.

In our previous paper[6] it was reported that pulsed arc deposited films show some features of crystalline carbon materials depending on the deposition conditions. These films are not quite amorphous but have some ultimate sizes of ordered structure fragments. Examination of films with TED shows a structure composed of small ordered areas with sizes of 0·5–3·0 nm. Crystalline inclusions of carbyne and lonsdaleite in film volume were found.

It was found that the main pulsed deposition parameters defining a films structure are peak voltage between cathode and anode of plasma arc source and substrate temperature. Duration and frequency of pulses has less effect.

General dependencies of cluster size, sp^3 bond concentration and film density versus main deposition parameters are shown in Fig. 1.

These dependencies can be explained as follows:

When the peak voltage of pulsed arc source is increased, average particle energy in a plasma flow and deposition rate are also increased. Average particle energy from 10 to 100 eV was found while peak voltage was varied from 100 to 500 V. It

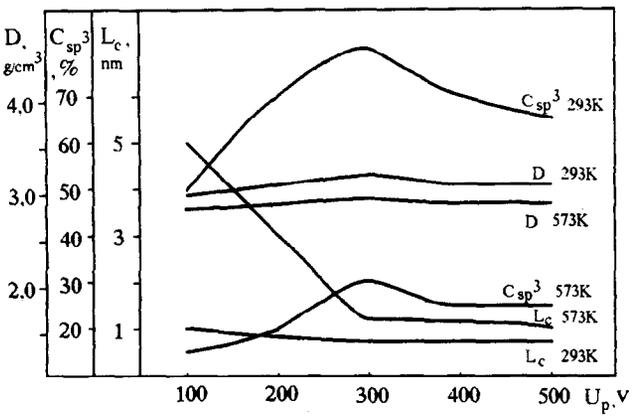

Fig. 1. Concentration of sp^3 bond, cluster size and film density versus peak voltage of the pulsed arc source and substrate temperature.

leads to more nuclei, increasing sp^3 bond percentage and also density of forming layers. Near the peak voltage of 300 V average particle energy is about 40–50 eV, which is more than the threshold of defect formation for graphite but less than that for diamond. When impinging particle energy is more than 60 eV (peak voltage more than 400 V), sp^3 bond percentage is decreased due to annealing and defect formation in diamond clusters. Increasing the substrate temperature leads to the formation of a higher equilibrium state of the deposition and increasing sp^2 bond percentage and cluster sizes occur. Also, three-dimensional ordering in sp^2 bonded clusters is experimentally observed with TED.

It is clear, that different models of film structure are possible for each set of deposition conditions.

As can be seen in Fig. 1, mass density of films calculated from bulk plasmon position of EEL spectra changes from 3·49 to 2·85 g/cm^3. This corresponds to atomic density changes from $1{\cdot}74{\cdot}10^{23}$ atom/cm^3 to $1{\cdot}42{\cdot}10^{23}$ atom/cm^3 (atomic density of diamond is $1{\cdot}77{\cdot}10^{23}$, graphite is $1{\cdot}13{\cdot}10^{23}$ atom/cm^3). These values characterize mass density in dominating clusters. Films mass density obtained by weighing substrates before and after deposition is about 10% less due to the presence of micropore and other defects. Tamor and Wu[9] calculated that defects in graphite could raise the density from 2·7 to a maximum of 2·9 g/cm^3 but no more. Therefore, pulsed deposited film structure can be predominantly formed by diamond clusters and highly defected graphite ones.

At the same time films have significant sp bond percentage.[6] This can be connected with polyenergetic plasma flow composition and high deposition rate. Due to this, vacancy concentration is increased and polyvacancies, which are a precursor of sp^2 and sp bonds, are formed.

These results were taken into account to choose modelling limits.

Structure modelling was carried out at the following:

— sizes of an ordered area are 0·5–4 nm;
— clusters are two- or three-dimensional and contain more than 20 atoms;
— clusters can contain defects such as embedded atoms and vacancies.

In particular, under these limits the interference intensity functions of electron scattering by carbon clusters were calculated.[10] Results of modelling were compared with those of TED and the above results and a good correlation was found, which confirms the above model suggestions. Thus, pulsed deposited carbon films can be described by models of ordered clusters with sp^3, sp^2 and sp bonds in a definite ratio. Deposition conditions define clusters structure, sizes, defects, and boundaries between clusters.

4 CONCLUSION

It is proved that the carbon films obtained by pulsed arc deposition method are not quite amorphous. Its models can be built on the basis of clusters of 0·5–4·0 nm in which structure, bonding type, shape and size depend on deposition conditions. Sizes of dominating clusters are quite uniform and are combined by interfacial layers. These layers contain the smaller clusters with all bonding types, defects such as vacancies, embedded atoms, and dangling bonds.

Results of theoretical and experimental examination show that at least three main models of film structure are possible defined by domination of sp^3, sp^2 or sp bonded clusters. The results above show some trends of pulsed deposited film structure formation and are aimed at understanding films growth mechanism under pulsed deposition conditions.

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