Surface and electron emission properties of hydrogen-free diamond-like carbon films investigated by atomic force microscopy

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Abstract

In this study, we have deposited hydrogen-free diamond-like carbon (DLC) films by using DC magnetron sputtering of graphite target at various r.f. bias voltages. Surface and nanoscale emission properties of these DLC films have been investigated using a combination of atomic force microscopy (AFM)-based nanowear tests and conducting-AFM, by simultaneously measuring the topography and the conductivity of the samples. Nanowear tests show that these DLC films are covered with the thin (1.5–2.0 nm) graphite-like layers at surfaces. Compared to the film bulk structure, the graphite-like surface layers are more conductive. The graphite-like surface layers significantly influence the electron emission properties of these films. Low-energy carbon species can be responsible for the formation of graphite-like surface layers. Nanoscale electron emission measurements have revealed the inhomogeneous emission nature of these films. The low-field emission from these films can be attributed to the existence of sp2-configured nanoclusters inside the films.

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1. Introduction

The typical local electric field required for emission from solids is generally 1000 V/µm. However, field emission can occur at much lower applied fields of order of 10 V/µm in carbon-based materials, such as diamond [1,2], amorphous carbon [3–5], and carbon nanotubes [6]. This could increase opportunities for electronic devices, for example the field emission display or in areas in vacuum MEMS such as microwave amplifiers.

Extensive experimental work [3,7–9] has indicated the inhomogeneous and often ‘spotty’ emission properties of diamond and DLC films as a cold material in field emission display. The electron emission was proposed to originate from highly conducting inclusions of sp2-carbon in a matrix of insulating sp3-carbon. The surface structures of diamond and DLC films, such as hydrogen coverage, a graphite-like surface layer, surface morphologies, and damaged regions were found to have the effect on their electron field emission [2,8,10,11]. Despite these achievements, the microscopic field emission mechanism is far from being understood. The low-threshold is not the only requirement for application in displays: the key factors required are high emission site density and uniform distribution of emission current over the whole emission area.

In this study, we analyse the surface properties of a-C films deposited using DC magnetron sputtering of a graphite target at different r.f. bias voltages, such as surface roughness, the thickness of low-resistant layers at film surfaces, and surface structure. A conducting atomic force microscope (C-AFM) equipped with a conductive probe and a sensitive pA-preamplifier is used to measure the electron emission of a-C films simultaneously with topography at a nanoscale lateral resolution. We find that the graphite-like layer at a film surface is obviously conductive and electrons are easily delocalized within the graphite-like layer.

2. Experimental details

The DC magnetron sputtering of a graphite target for a-C deposition was described in detail elsewhere [12]. The Ar pres-
The film thickness was found to have an obvious effect on surface roughness. To investigate the effect of the bias voltage on film properties, we prepared a-C films at different bias voltages with an identical thickness of 150 nm. The film surface roughness and hardness showed a clear dependence on the applied bias voltage (Fig. 2). The RMS roughness decreased from 0.71 to 0.20 nm as bias voltage was varied from 0 to $-140$ V. The film hardness increased with the bias voltage. The best film with hardness up to 29 GPa was deposited at the bias voltage of $140$ V. Increasing bias voltage leads to an increase in the ion energy [17]. If the energy exceeds the critical value for atomic displacement in the structure, the ions can penetrate into the surface structure. The ion energy tends to be dissipated into the volume nearby. Thus, a denser, smoother, and higher sp3-content film is formed [12].

The wear tests were carried out at a given loading force for an increasing number of wear cycles, and the thickness of thin low-resistant layers at film surfaces was estimated by extrapolation [10]. The surface layer thickness as a function of bias voltage was shown in Fig. 3. The surface layer thickness did not show a clear dependence on the applied bias voltage. The thickness was typically in the range of 1.5–2.0 nm.

Graphite is composed of layers of carbon atoms that are arranged in six-membered, hexagonal rings. These rings are...
attached to one another at their edges. Carbon atoms in these ring arrays are in the sp²-hybridized state. Layers of fused rings can be modeled as an infinite series of fused benzene rings (Fig. 4). The carbon atoms in the first layer are located in precise alignment with the carbon atoms of the third layer. Correspondingly, the carbon atoms of the second layer are in alignment with the atoms of the fourth layer. This configuration is known as an “ABABAB” structure. The distance between any two adjacent layers is 0.335 nm [18,19]. These π electrons are not stationary, but are delocalized within adjacent π orbitals. Fig. 5 shows the AFM image and cross-sectional profile of one graphene layer obtained on a highly oriented pyrolytic graphite sample. The measurement shows an average layer-to-layer distance of 0.33 nm, which is well consistent with the value of 0.335 nm. The AFM can image the surface of the sample with sub-angstrom precision vertically.

Fig. 6 shows AFM images and cross-sectional profiles of the a-C films deposited at different bias voltages. The graphene layers can be observed at the surface of the a-C film deposited at bias voltage of 0 V (Fig. 6a). There are plenty of ‘holes’ surrounded by a graphene layer. The distance between two graphene layers is typically in the range of 0.4 and 0.6 nm. At a rough surface, the graphene layer can be highly stressed, and the layer-to-layer distance can be greatly increased. It is found that these holes...
are easily formed in the region of protrusions. The growth process of the graphene layer at film surface is illustrated in Fig. 7. The magnetron sputtering plasmas contain a large number of low-energy carbon ions, radicals and excited species. These low-energy carbon species (C\textsubscript{x} (x = 1–5)) have insufficient energy to break bonds at the surface. For these conditions, film formation is well described by standard nucleation and growth theories [20]. Atoms impinging on the sample surface either bounce off immediately or are adsorbed on the surface after a nearly instantaneous thermal accommodation with the substrate. The adsorbed atoms diffuse on the surface until either re-evaporation occurs or a permanent site (dangling bond) is found (Fig. 7). The bond energy (E\textsubscript{i}) in the cluster model of Walton and Rhodin as the sum of nearest neighbor bonds, each of energy (E\textsubscript{b}), for the most favorable configuration of atoms is expressed as [20]:

$$E_i = y_i E_b - x E_a$$  \hspace{1cm} (1)

where E\textsubscript{a} is the activation energy for monomer desorption, y\textsubscript{i} the number of interatomic bonds, and x is the number of atoms in the cluster. Inconsistent with the growth process of metal materials, the graphene layer-to-layer growth greatly contributes to an increase of the E\textsubscript{i} value. In this case, the cluster configuration is stable thermodynamically. A highly stressed cluster structure can be formed in the region of protrusions. The stability of a graphene layer may be greatly decreased. Plenty of holes can be observed at a relatively rough surface. Dislocations and minor defects can occur at the film surface. The growth of a graphene layer may be destroyed by the bombardment of some higher energy species. The bombardment of the surface by some energetic species may cause sputtering, displacement, and implantation. The coalescence process via the diffusion of adsorbed carbon species can often lead to the formation of a rough surface.

These 'holes' are not observed at the surface of the a-C film deposited at bias voltage of 140 V (Fig. 6b). Under the bias voltage, the carbon ions obtain high energy. The ion energy (E) is proportional to substrate bias voltage (V\textsubscript{b}) [17]:

$$E = k \frac{V_b}{P^{1/7}}$$  \hspace{1cm} (2)

where P is discharge pressure and k is a constant. Bombardment of the surface by energetic ions plays a crucial role in plasma–surface interaction. Backscattering, sputtering, and displacement take place when an energetic ion strikes a surface. The graphene layer at the surface can be destroyed by these energetic impacts. Incident ions can create dangling bands which act as chemisorption sites for deposited species [21,22]. The dangling bonds created by energetic impacts can contribute to the formation of a smooth surface. These energetic impacts are also important for forming a dense diamond-like phase. These impacts should provide the energy transferred into the subsurface layer and lead to the formation of a denser bulk structure.

Fig. 7. Growth of one graphene layer at film surface via surface diffusion and accommodation. Lower energy carbon species (C\textsubscript{x} (x = 1–5)) have insufficient energy to break the bonds at the surface and part of them are adsorbed on the surface. The adsorbed atoms diffuse on the surface until either re-evaporation occurs or a permanent site (dangling bond) is found.

Fig. 8. Topography (a) and simultaneously measured current image (b) at the region of wear marks with the wear depth of 1.5 nm. The protrudings are sp\textsuperscript{2}-rich nanoislands (a). The sp\textsuperscript{2}-rich nanoislands results in more localized current (b).
The topography (Fig. 8a) and current image (Fig. 8b) were simultaneously recorded at the region of wear marks with the wear depth of 1.5 nm. The 0.2 V tip voltage was kept for the current measurement. The characteristic shape of the wear marks was well consistent with the topography image. Compared to the region where the surface layer exists, the wear marks showed a higher threshold field. The Fowler–Nordheim (F–N) currents in a metal–dielectric–silicon capacitor can be written as [15,23–25]:

$$I = A_{eff} \frac{\Phi^2 E^2}{8\pi h \beta E} \exp \left( -\frac{8\pi \sqrt{2m_0 q \Phi}}{3h \beta E} \right)$$  \quad (3)

where $A_{eff}$ is the effective emission area of the conductive nanotip, $q$ the electronic charge, $h$ the Planck’s constant, $m_0$ the mass of the electron, $\beta$ the dimensionless field enhancement factor, $E$ the electric field across the dielectric, and $\Phi$ the barrier height.

The C-AFM measurements indicated the surface layer has a graphite-like structure. Electrons were easily delocalized with the graphite-like surface layer, which led to an increase in the nanotip emission area.

The microscopic $I$–$E$ curves obtained on the 150 nm thick DLC film at the locations with and with no graphite-like surface layer. The $I$–$V$ ramps were performed on the locations where the a-C film was covered with a continuous graphite-like surface layer (Fig. 9). The current varied linearly with the applied voltage, which suggested that the current flows along the subsurface layer and reaches the silicon substrate. The $I$–$V$ curves obtained
on the locations without the subsurface layer showed a relatively higher emission field (Fig. 9). These \( I-V \) curves followed the \( F-N \) field emission behavior [10]. However, these curves exhibited different threshold electric fields. The inhomogeneous electron emission can be primarily due to the existence of the conducting nanostructures inside the film.

The current images were obtained on the locations without the surface layer at a constant tip voltage. Fig. 10 showed the current images of films deposited at various bias voltages. There were a large number of localized conducting nanoclusters surrounded by a relatively insulating matrix. Inhomogeneous electron emission was formed due to the existence of these conducting nanoclusters. The sizes of conducting nanoclusters inside the film deposited at the bias voltage of 140 V were typically in the range of 4–8 nm. The contact radius of the nanotip was on the order of 2–8 nm [26]. The nanotip contact area can have an effect on the image resolution. The sizes of these clusters could be smaller than the contact area of the conducting tip. In this case, what was really being imaged was the tip shape, not the real shapes of the conducting nanoclusters [27]. The nanoclusters had very similar shapes, which also indicated an effect of a relatively large contact area on the image resolution. The sizes of these conducting nanoclusters increased with decreasing bias voltage. These clusters at the film deposited at the bias voltage of 0 V formed large conducting regions. An increase in the sizes of nanoclusters indicated the formation of graphite-like surface layers. Deposition of a-C films at low r.f. bias voltage is governed by the growth of graphene layers via the diffusion of adsorbed carbon species. When dislocations and minor defects occur at the surface, the growth process may lead to the formation of a-C films with rough surfaces. Nanoscale electron emission measurements have showed the inhomogeneous emission nature of a-C films. The low-field emission from a-C films can be attributed to the existence of \( sp^2 \)-configured nanoclusters inside the films. The sizes of these nanoclusters are well related to the film mechanical properties. The films covered with graphite-like surface layers exhibit a lower threshold field. Electrons are easily delocalized with graphite-like layers at film surfaces, which causes an increase of the nanotip emission area.

4. Conclusions

We have compared surface and nanoscale emission properties of hydrogen-free DLC films deposited using DC magnetron sputtering of graphite target at various r.f. bias voltages. AFM-based nanowear tests show that these DLC films are covered with thin (1.5–2.0 nm) graphite-like surface layers. Low-energy carbon species can be responsible for the formation of graphite-like surface layers. Deposition of a-C films at low r.f. bias voltage can be primarily due to the existence of the \( sp^2 \)-rich clusters inside a-C films can act as conducting nanostructures when a conducting nanotip is scanned along the film surface (Fig. 11). The localized conducting nanostructures establish a bridge between the silicon substrate and the conductive tip. Therefore, electrons are easily emitted from \( sp^2 \)-sites. Electrons are also easily delocalized inside a graphite-like surface layer, which may lead to an increase of the nanotip emission area.

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