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Peculiarities of Field Electron Emission from CVD Diamond Films

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Abstract: Results are reported on characterization of the field electron emission from diamond films grown by dc arc discharge plasma CVD onto Si substrates from CH₄-H₂ gas mixtures. The field electron emission was observed at 15-20 V/ μ m. Emission current-voltage dependences were studied for films prepared at different CVD conditions and post-growth surface treatment/modification (ultrathin metal and metal oxide coatings, MW-plasma processing, laser-induced surface graphitization). Features of emission current versus applied field behaviour (including a hysteresis phenomenon, vacuum arc initiation) and ultralow (0.1-0.5 eV) values of effective work function derived from Fowler-Nordheim plot fitting are discussed. A high vacuum scanning tunneling-field emission microscope was applied for simultaneous mapping of field electron emission intensity, topography and work function to study electronic and structural properties of field emission centers.

1. INTRODUCTION

It was found that diamond and diamond-like carbon (DLC) materials may have excellent and stable field electron emission properties with high current densities at low electric fields [1-7]. The study of field electron emission for such materials was stimulated by the negative electron affinity of some diamond surfaces for which ultrahigh vacuum conditions are not required [8,9], making these materials candidates for vacuum micro-electronics applications including cold cathode flat panel displays. Field emission of electrons from polycrystalline diamond films was observed at fields as low as 3-5 V/ μ m [1,2], but more often fields of >20 V/ μ m are needed to obtain electron emission from diamond and DLC [3,4,7]. In this paper we report results on characterization of the field electron emission properties of diamond films grown by dc arc discharge plasma CVD onto Si substrates from CH₄-H₂ gas mixtures.

2. EXPERIMENTAL

The diamond films were prepared at various CVD conditions, including variation in i) CH₄/H₂ content from 2% to 30%, ii) deposition temperature, and iii) film thickness ranged from 0.2 to 12 μ m. The details of the film growth were reported in [10]. All samples were examined by Raman spectroscopy. Raman spectra displayed a band at 1332 cm⁻¹ corresponding to a coarse-grained diamond phase and a set of bands at 1140, 1480 and 1560 cm⁻¹, being characteristics of ultrafine sp³ and sp²-bonded carbon. The details of transformation of the Raman spectra depending on deposition conditions have been reported elsewhere [10].

For the field electron emission characterization, an experimental set-up with oil-free high vacuum pumping down to 10⁻⁷ Torr was used. In the vacuum chamber, four tungsten tip probes (anodes) with about 20 μ m curvature radius are placed at a distance of 10-100 μ m from the sample surface. A high dc-voltage (up to 8 kV) is applied between the sample (cathode) and each probe (anode) separately to induce field emission current. The values of the tip radius, the cathode-anode gap and applied voltage are used to calculate the electric field at the sample surface under the probes similar to that described in [11]. The maximum field on sample surface is located under the tip center and is perpendicular to surface. The value of the maximum field is taken hereinafter as the emission-induced field. Thus, the

field emission characteristics of local surface area down to 10 μm radius can be investigated. Three main parameters for emission characterization are studied:

- (a) local current (I) versus applied electric field (E) behaviour (I - E curves);
- (b) long-term stability of the current;
- (c) homogeneity of emission properties along the film surface.

3. RESULTS AND DISCUSSION

Typical I - E curves are shown in Fig. 1a for a 280 nm thick diamond film. Electron emission was observed at fields above 20 $\text{V}/\mu\text{m}$. Three main features in the emission I - E behaviour can be discerned. First, the emission current jumps from an undetectable value to a high value (of a few A) at arc-field E_{arc} and then decreases smoothly down to turn-off field $E_{\text{off}} < E_{\text{arc}}$ (a hysteresis behaviour). Second, the emission current increases smoothly (without jump) if the field is above E_{on} (turn-on field) and decreases almost at the same curve without hysteresis (see for example Fig. 2a). Third, both processes often exist, i.e., at first the emission current increases smoothly and reversibly and then the current jumps up at $E_{\text{arc}} > E_{\text{on}}$ ("before current jump" plot in Fig. 1a). Such a jump leads to a shift of increasing and decreasing branches of I - E curves to lower field values so a weak hysteresis develops. In the repeated I - E cycles the hysteresis almost vanishes (see "after current jump" plot in Fig. 1a).

Fig. 1. Field electron emission from 280 nm thick CVD diamond film: a) I - E plots, b) FN plots.

Fig. 2. Field electron emission from 4 and 12 μm thick CVD diamond films: a) I - E plots, b) FN plots.

For most of the films the turn-on and turn-off field emission processes (increasing and decreasing branches in I - E curves) showed hysteresis with the uncontrollable jump at the increasing branch, but during repeated cycles the hysteresis reduced. This emission behaviour with initial uncontrollable current jump called "vacuum arc initiation" was recently described for diamond and DLC films [12-14]. In these papers, protrusion-like damages of the sample surface were observed after vacuum arc initiation. A damaged surface areas were $>10 \mu\text{m}$. We also observed similar damages in rare cases of drastic

current jump. However, in most of cases of the current jump we did not find traces of the surface modification/damage after surface examination with optical microscope ($2\mu\text{m}$ resolution). Nevertheless, the presence of surface damage is not excluded in the case of the damaged areas of submicrometer dimensions. So it is thought that the hysteresis behaviour of the electron emission current accompanied by the current jump is a consequence of the field/current-induced modification of the diamond properties (e.g., a contamination removal or a formation of conductive channels either by electroforming processes or dielectric breakdown [12]) or/and geometric surface damage with protrusion formation. In contrast to submicron films (for which as a rule the current jump was observed, Fig.1a), the thick ($2\text{--}12\mu\text{m}$) diamond films often showed the I-E behaviour without a hysteresis (Fig.2a) and the emission-induced surface modification for these films was unlikely.

The I-E emission characteristics can be well fitted by Fowler-Nordheim (FN) plot for sections of I-E curves both before and after current jump (Figs.1b, 2b). The work function formally calculated from the FN-slope (neglecting field inhomogeneities and assuming the field enhancement factor to be close to unity) is of 0.18 eV before and of 0.13 eV after the jump. The difference in the work function values may indicate a modification in the film surface structure due to a field/current action at the moment of the current jump. Before the jump the emission properties of the film surface are reversible and homogeneous (see the straight fit on the "before..." plot in Fig. 1b). But after the jump a deviation from the straight FN-plot probably indicates an increasing inhomogeneity of surface emission properties. For the thick diamond films the work function (from FN analysis) is higher than for the submicron films (Fig.2b). The ultralow work function values formally derived here from FN plot fitting are not agreed with work function of 4 eV measured for diamond films by other methods [15,6]. One of the possible explanation of such difference may be a strong field enhancement on submicrometric surface features (surface nanoprotusions, sharp edges of diamond crystallites, thin conductive channels between crystallites etc).

The diamond films are characterized by the long-term stability of the emission current. The emission current is constant at different fields during at least 1 hour. The I-E curves are reproducible after many measuring cycles, after many hours and a day off. For the samples of glassy carbon and highly oriented pyrolytic graphite the field emission also shows hysteresis of the I-E plots and occurs at the same fields (about $30\text{--}60\text{ V}/\mu\text{m}$), but the emission current has a poor stability. A spatial homogeneity of the emission current for the diamond films is not excellent and values E_{off} may be different in 2 times for the same film.

The influence of the growth process parameters (variation of CH_4 content in $\text{CH}_4\text{--H}_2$ gas mixture, film thickness and substrate temperature) is illustrated in Fig.3. Direct correlations of the field emission properties with the film thickness (from 0.2 to $12\mu\text{m}$) and with the methane content were not found. To obtain the best emission properties, the diamond films of $200\text{--}400\text{ nm}$ thick grown at $\text{CH}_4/\text{H}_2 > 4\text{ vol.}\%$ are preferable. A correlation between field emission properties and electrical conductivity was also not detected for these films. To use low cathode-anode voltage more conductive thin films are needed because the voltage-drop over a semiinsulating diamond film can be as high as 500 V .

Some of diamond films were etched by a microwave plasma in different gas environment (H_2 , or O_2 , or Ar). A drastic change of the field emission properties after such a processing was not observed, but the H_2 plasma etching sometimes reduced the emission

Fig. 3. Lowest emission field E_{off} vs diamond film thickness; three sample series correspond to various growth substrate temperature and methane content.

fields as well as the hysteresis of I-E plots. The emission data presented in Fig. 2 corresponds to the 12 μm film etched in O_2 plasma.

A positive effect on the field emission was found for diamond films coated with ultrathin (transparent for emission) metallic and metal oxide films. Two types of ultrathin films were used: a 4 nm Ni and 5 nm InSnO conductive coatings. For both the original diamond films (1 μm thick) the emission was observed at fields above 100 $\text{V}/\mu\text{m}$, but the coated diamond film emitted electrons at fields above 20 $\text{V}/\mu\text{m}$ (Fig.4a). The data implied a reduction of the (FN) work function from 0.5 eV to 0.06 eV (Fig.4b). A possible mechanisms of the emission enhancement could be the additional negative surface band bending due to local Schottky barrier formation, or the creation of surface electronic levels close to the diamond conduction band supplying electrons to the negative (or low) electron affinity surfaces of diamond crystallites.

Fig. 4. Field emission from diamond films coated with ultrathin metallic layers: a) I-E plots, b) FN-plots

Also an improvement of the field emission from the diamond films was achieved by laser-induced surface graphitization of the diamond films during laser ablation. After the treatment the surface conductivity of the thick (about 20-30 μm) diamond films became high (like graphite). The electron emission was observed at fields as low as 15-20 $\text{V}/\mu\text{m}$. The I-E behaviour was characterized by a current jump at initial turn-on emission process and then the hysteresis between the increased and decreased I-E curves was vanished. The observed reduction in the emission fields appears to be due to the modification in the valence band structure of the laser-ablated diamond [16].

Using charge-based deep level transient spectroscopy (Q-DLTS) [17,18] and photoelectrical characterization it was found that for low field emission films the integral density of electronic states is higher than for the poorly emitting films. Besides, the surface band bending for the first ones is often negative (in contrast to the positive band bending for the second ones) that reduces the surface tunneling barrier for emitted electrons. A possible explanation of these facts could be the presence of non-diamond conductive inclusions at the diamond grain boundaries, or the presence of a high concentration of defect states at the surface of the well emitting diamond films.

A specially designed, high vacuum scanning tunneling-field emission microscope [19] was employed for simultaneous mapping of the topography, work function and local field electron emission intensity (being reversely proportional to field at fixed emission current) to study the electronic and structural properties of field emission centers (energy barrier for electrons, geometric field enhancement factor). The microscope uses both tunneling and field electron emission regimes at a both current polarities and a wide range of the applied voltage (0-100 V) to study semiinsulating and semiconducting diamond films. The surface profiles of the field electron emission, work function and topography made at the same surface site of 1 μm thick diamond film are shown in Fig. 5. The peaks of the field electron emission intensity (emission centers numbered from 1 to 4 in Fig. 5) do not correlate with the tips of diamond crystallites. The emission maxima are associated with

minima of the work function which coincide often (not always) with topography pits. That results in a suggestion that the field emission is likely to occur from grain boundaries.

Fig. 5. Surface profiles of the field electron emission intensity, work function and topography for 1 μm thick CVD diamond film.

4. CONCLUSION

Field electron emission properties of diamond films grown by dc plasma CVD were studied in dependence on CVD condition and post-growth surface treatments. Stable and homogeneous field electron emission current at fields of 15-20 V/ μm were observed for the best of the samples. The typical fields needed to obtain electron emission from diamond films were about 30-60 V/ μm . Very low values of the effective work function of 0.1-0.5 eV were formally derived from Fowler-Nordheim fit to the I-E data. These values are probably explained by a strong field enhancement on nanometric features of the film structure.

Direct correlations between field emission properties and diamond film growth conditions and thickness were not observed. The best emission properties were found for the diamond films of 200-400 nm thick. That fact is perhaps connected with the presence of a small quantity of graphitic or diamond-like inclusions in the diamond grain boundaries of submicron films as it may be conclude from the Raman spectra analysis [10]. A dependence of field emission properties on the electrical conductivity of films studied was not detected.

For most of the films studied, emission I-E curves showed a hysteresis with an uncontrollable current jump. That jump leads to the shift of I-E curves to lower field values so a weaker hysteresis develops for all the samples, and in many cases the hysteresis almost vanishes. Such a behaviour of the electron emission is likely a consequence of the field/current-induced modification of the diamond film properties, which may be accompanied by submicron damaged surface areas. In contrast to submicron films thick (2-12 μm) diamond films often exhibited a smooth I-E behaviour without hysteresis and an emission-induced surface modification appears unlikely for these films.

A large positive effect of ultrathin metallic coatings and laser-induced surface graphitization on the field emission from the diamond films was found. These post-growth surface modifications may decrease the effective work function derived from FN plot fitting almost by an order of magnitude, hardly connecting with a geometric field enhancement.

Employing a specially designed scanning tunneling-field emission microscope it was found, that the electron field emission from the diamond films is not correlated with surface protrusions. The field emission centers are often associated with minima of the work function located in topography pits. The current originates probably from grain boundaries.

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