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COMMUNICATIONS

DIAMOND COATED TUNGSTEN WIRE FIELD EMITTERS: DIAMOND THICKNESS EFFECT

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Graphitic tungsten wires were coated with diamond in a double bias-assisted hot filament CVD reactor. A comparison of the field emission characteristics before and after coating showed significant shifts of the emission current depending on the thickness of the coatings. A model of emission through the diamond layer is proposed. The influence of different growth conditions on the film quality has been investigated by micro-Raman measurements and optical microscopy.

K e y w o r d s: field emission of diamond films; micro-Raman spectra; field cold cathodes; double bias-assisted hot filament CVD method

1 INTRODUCTION

Diamond possesses a high carrier mobility, a high breakdown field, extreme hardness and chemical stability. These extreme properties make it an excellent material for fabrication of electronic devices [1-3]. In addition, it has a wide band gap (5.47 eV), and a small, or even negative electron affinity. The latter is particularly important for the electron emitting behaviour of field emission devices as cold cathodes and flat panel displays. The search for an efficient cold field electron emitter has been in the focus centre of vacuum microelectronics research for many years. Diamond cold field electron emitters should be prepared as electron sources over thermionic emitters because no heating current is required and these emitters provide a high current density and lower electron energy spread than thermionic emitters. Most of the emitting diamond films are deposited on either metallic or semiconductor substrates. In this work we have deposited diamond films on graphitic tungsten wires to investigate field electron properties because emission characteristics of un-doped diamond thin films are significantly improved by increasing sp^2 content of diamond [4]. Diamond thin films have prepared by an advanced deposition process to achieve high density diamond nucleation via double bias-assisted hot filament CVD [5]. Emission properties before and after diamond coatings with different thicknesses are compared. A possible emission mechanism is discussed.

2 EXPERIMENTAL DETAILS

Diamond nucleation and growth were conducted in a double bias-assisted (HFCVD) system (Fig.1). With this arrangement, stable plasma can be generated between the grid and the hot filaments. Ions in the plasma are then driven to the substrate by a negative substrate bias voltage. With the controlled ion bombardment, a high nucleation density of diamond can be achieved routinely.

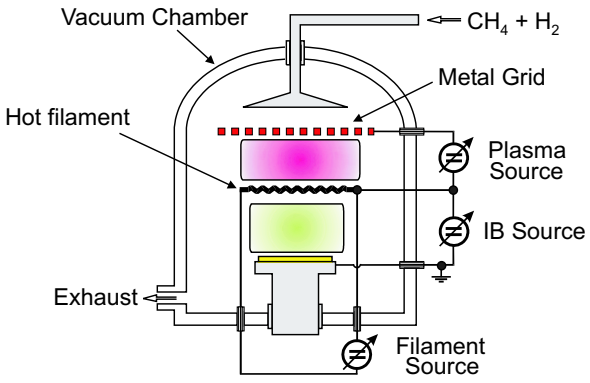

Fig. 1. Schematic diagram of double bias-assisted HFCVD apparatus.

A tungsten wire substrate was held on a copper holder, and other three tungsten hot filaments were hung above the substrate. The substrate holder is heated by an independent source with a special control unit. The experimental parameters of the deposition process were as follows: the gas flow H_2/CH_4 was 300/3 sccm (standard cubic centimetre per minute), the total pressure was 3×10^3 Pa; filament was heated to $\approx 2000\,^{\circ}\mathrm{C}$; the substrate temperature was approximatelly $670\,^{\circ}\mathrm{C}$, and the distance between the three wires and the substrate was $\approx 4-5$ mm. Prior to deposition of diamond films the filaments were heated in a methane-hydrogen atmosphere to enhance the formation of the tungsten carbides layer covering the filament surface in order to reduce the tungsten evaporation during the deposition process. The deposition process consisted of two stages: nucleation period

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and growth period. Nucleation was performed at a negative substrate bias of - 170 V (nucleation time was 2 hours). The growth was performed at a positive substrate bias of +100 V. A linear growth rate of roughly 0.6 μm was achieved under conditions quoted above.

Micro-Raman spectra were measured by means of a Dilor system (Jobin Yvon /Spex /Dilor, Horiba Group) working with a He-Ne laser, which was focused on the sample to a spot size of 1 μm in diameter at the sample surface in the backscattering geometry. ISA Labram equipment was used for Raman measurements. Excitation was carried out with a He-Ne laser with a wavelength of 632.817 nm. All measurements were made by focusing a laser beam through a 100× lens on the surface of the sample. For all measurements, a confocal hole diameter of 200 μm, a spectrograph entrance slit of 150 μm, and a 1800 grooves/mm diffraction grating were employed.

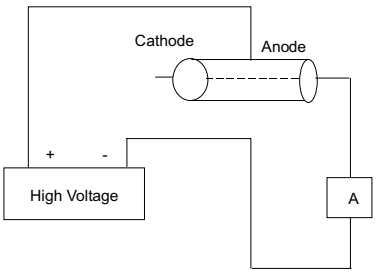

Fig. 2. Electrical scheme of the set-up for measuring of the electron emission properties.

The performance of the electron emitter was examined in a high vacuum chamber (6×10^{-6} Pa) by means of an electrical circuit schematically shown in Fig.2. The electron field emission properties were analysed using the Fowler-Nordheim (FN) model [6]. In this model, the equation for the magnitude I of the emission current may be written as

$$I = Aa\Phi^{-1}F^2e^{(}-b\Phi^{3/2}/F) \equiv R^{el}F^2e^{(}S^{el}/F)$$

where a and b are universal constants ($a = 1.541434 \times 10^{-6}\mathrm{AeVV}^{-2}$, $b = 6.830888 \times 10^9\ eV^{-2/3}\mathrm{Vm}^{-1}$), Φ is the effective work-function of the emitting surface, F is the external electrical field (taken as a positive quantity), and A is the area of emission. R^{el} and S^{el} are parameters defined as follows $R^{el} \equiv Aa\Phi^{-1}$, $S^{el} \equiv -B^{3/2}$. The tungsten wires had a diameter of 0.1 mm with a length of 51 mm. Electrons emitted from the wire emitter to vacuum were collected by anode. The distance between the wire and the anode was 10 mm.

3 RESULTS AND DISCUSSION

Two wires with different diamond thickness $\approx 1.2\,\mu$m (2 hour growth time), $\approx 0.6\,\mu$m (1 hour growth time), and one uncoated graphitic wire were used in the tests. The quality of diamond and its sp^2 content were characterised by micro-Raman spectroscopy and optical microscopy. Raman spectra taken from the wires are shown in Fig. 3. Figure 3 shows the Raman spectrum of the sample prior to the deposition process (graphitic wire). The Raman spectrum of the sample deposited for one hour consists of diamond band centred at 1330cm^{-1}. This spectrum is broadened, which can be attributed to a low quality of diamond present in small grains. A band visible at around 1600 cm^{-1} represents the non-diamond sp^2 phase component within the film. There exists also a Raman spectrum of the diamond film deposited on the wire where the growth time was 2 hours. The expected diamond band at 1331 cm^{-1} can be attributed to diamond grown on the layer pre-coated tungsten wires. A band visible at around 1590 cm^{-1} is due to a graphitic component within the film. It can be seen that the thinner film exhibits higher a background and more non-diamond phases than the thicker film, indicating that the film quality improves with the diamond growth.

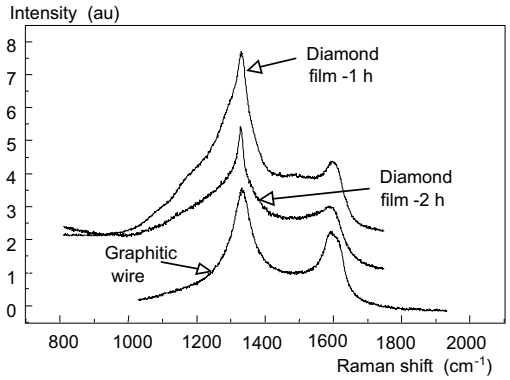

Fig. 3. Raman spectra of tungsten wires

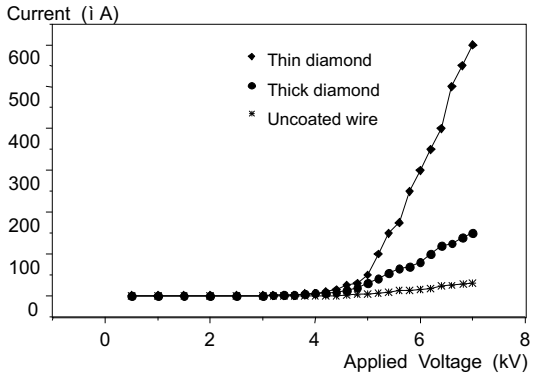

Fig. 4. Electron field emission behaviour of the films.

Figure 4 shows $I-V$ characteristics measured in an experiment. The effective work function (Φ), which is the ratio of the work function and field enhancement factor (β), was calculated from the slope of the Fowler-Nordheim plots. The Φ estimated by Fowler-Nordheim plots of the $I-V$ characteristics were $\Phi = 0.053$ eV and $\Phi = 0.058$ eV for 2 hours growth time and 1 hour, respectively. The one hour grown thin diamond film shows

a relatively large emission current in comparison with thet graphitic wire surface and the thicker diamond film. The current density was $J_e = 2000\mu\mathrm{A/cm}^2$ under applied field 24 V/μm (the turn-on voltage for diamond films was about 12 V/μm). The emission current density decreased from $J_e = 2000\mu\mathrm{A/cm}^2$ to $J_e = 660\mu\mathrm{A/cm}^2$ under 24 V/μm when the growth increased from one to two hours. It can be seen that field emission with high sp^2 content and lower quality of diamond is enhanced compared with the field emission when the quality of diamond film is higher (see Fig.4). Let us compare these results with those published by Yung-Hsin Chen at el. [7]. For the diamond thin films ($\approx 0.6\,\mu$m) grown on a Si wafer using microwave reactor the application of a positive bias voltage (+50 V) during the growth period gave an effective work function $\Phi = 0.0792$ eV. Our results lead to $\Phi = 0.058$ eV and higher current density than that achieved in [7]. These results are probably related to different substrates.

To explain the above results we believe that electrons are not emitted directly from the valence band of diamond into vacuum. The origin of electrons should be the Fermi-level of the metal back contact. However, the exact nature of the mechanisms occurring in the field emission processes is not well understood yet [8, 9]. The voltage drop across diamond under a high applied electrical field is sufficient to bend down the conduction band of diamond. This allows electrons to tunnel into the conduction band of diamond. However, electrical field in diamond is small compared to vacuum field (the dielectric constant for diamond is relatively large). As a result, the electron tunneling distance into the conduction band of diamond, W, is very wide. This leads to a very small electron tunneling probability and low electron emission current. The present of sp^2 phase reduces W - the electrical field in diamond with the sp^2 content increases and it also increases the probability for electrons tunneling from metal into conduction band of diamond. It enhances the emission current of diamond thin film. The expected low electron affinity at the diamond-vacuum interface promotes the emission of the electrons from conduction band into vacuum. This could explain the difference between the results shown in Fig 4.

4 CONCLUSION

The emission properties of diamond films prepared by double bias-assisted HFCVD method satisfy the requirement for applying as electron emitters. With the present double bias design, high nucleation density can be achieved for diamond thin films. It can be seen that field emission properties of tungsten wire emitters depend on the growth time of diamond coatings. The quality of grown diamond films increases with the growth time - the sp^2 phase is more etched during a longer deposition than diamond one. It changes the structure of the film. However, the high quality of the deposited diamond leads to a low field electron emission. It is important to deposit undoped diamond films with a small thickness and lower quality.

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