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Electron emission from diamond thin films deposited by microwave plasma-chemical vapor deposition method

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Abstract

Diamond films with different crystal structures, morphologies and surface characteristics were synthesized under various deposition parameters and annealing conditions by the microwave plasma chemical vapor deposition (MWPCVD) method using gas mixtures of CH_4, CO and H_2. The effects of CH_4 concentrations, grain sizes, grain orientations, film thicknesses and annealing technologies in various ambient gases on planar electron emission of diamond films were studied. The results show that small-grained and (011)-oriented diamond films deposited under the condition of high CH_4 concentration present the properties of high emission current and low threshold voltage; the emission current increases with decreasing the film thickness. There are largest current density and lowest threshold voltage at the film thickness of 1.5 μm. The annealing in H_2 after deposition appears to be more beneficial in lowering the threshold voltage, increasing emission current and improving stability for electron emission of films than annealing in N_2 or Ar. These results indicate that diamond thin films with high emission current, low threshold voltage and high stability can be obtained by selecting suitable deposition parameters of diamond films.

Keywords: Diamond films; Field emission; Microwave plasma-chemical vapor deposition; Annealing; Grain boundary

1. Introduction

Many materials and configurations have been used for cathodes over the years. While hot cathodes are suitable for many applications, the developments of cold cathodes could lead to improved performance in many existing applications. More importantly, with the advancement of vacuum microelectronics, cold cathode development has changed the scope. Some advancements have been made such as field emission arrays, wedge emitters and thin film cold cathodes [1]. Many scientists have researched the development of reliable and efficient cold cathode materials for electron field emitters. It has been found that thin metal films of Mo, Cs, or Co, etc., on semiconductors (such as Si or GaAs) with nanometer-sized sharp tips result in an electron emission. However, high emission voltages and complicated fabrication processes were needed for these classical field emission tips because of the high work function for these materials [2].

One of the largest potential applications for chemical vapor deposition (CVD) diamond is in electron field emitting devices due to its low work function, negative electron affinities (NEA), high thermal conductivity, as well as chemical and physical robustness. These properties resulted in the development of planar cold cathodes that were to become revolutionary next-generation electron emission devices replacing conventional field emission tips. It was postulated that flat structures could be manufactured cheaply and that an efficient electron source could be produced by a process

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not requiring submicrometer scale techniques, a drawback of sharply pointed field emission.

Recently, there have been many articles about electron field emission from diamond films and discussions about the emission mechanism [3,4]. Although a considerable research effort has been made in the past few years, the influences of deposition parameters for diamond film on emission properties are not yet completely understood. Meanwhile, some results and discussions are also generally ambiguous [5], these apparent contradictions may be due to differing unclear emission mechanisms. Further theory and experimental studies are necessary to develop a stable and efficient diamond planar display device.

In this paper, we report the characteristics of electron emission from diamond films with different crystal structures synthesized under various deposition parameters and annealing conditions by the microwave plasma chemical vapor deposition (MWPCVD) method. The effects of CH_4 concentrations, grain sizes, orientations, film thicknesses and annealing processes in various ambient gases on planar electron emission of diamond films were studied.

2. Experiments

Mirror-polished *n*-type Si(001) wafers with a resistivity of 6–9 $\Omega \cdot$cm, an area of 0.2 cm^2 and a thickness of 300 μm were used as substrates. Before the deposition of diamond films, the substrates were polished by diamond powders with various grain sizes and durations in an ultrasonic bath to acquire high nucleation density and various grain sizes in completed films. The films were prepared by the MWPCVD method using gas mixtures of CH_4, CO and H_2, the experimental conditions are given in Table 1. The growth velocity for diamond film was approximately 0.3–1.2 $\mu m\ h^{-1}$. The substrate temperature was measured by an optical pyrometer. Field emission experiments were performed at a pressure of 10^{-8} torr. Sputtered indium tin oxide (ITO) glass was used as the anode. The anode–cathode spacing was approximately 120 μm. Diamond films with different impurity concentrations, grain sizes, orientations, film thicknesses and surfaces treated by annealing processes can be synthesized by changing the parameters listed in Table 1.

Table 1
Experimental parameters of the MWPCVD method for the deposition of diamond films

Microwave power (W)	400–500
H_2 flow rate (sccm)	100
CH_4 flow rate (sccm)	1–5
CO flow rate (sccm)	0–5
Pressure (mbar)	45
Substrate temperature (°C)	750–950
Film thickness (μm)	0.5–5
Grain Size (μm)	0.3–3
Annealing temperature (°C)	900

The morphologies, crystallographic orientations and structures of the films were evaluated by scanning electron microscopy (SEM) and X-ray diffraction (XRD); micro-Raman spectroscopy was used to obtain phase purity information in films.

3. Results and discussion

Diamond films of 2 μm thickness were synthesized on Si substrates polished with 50-μm diamond powders for 10 min at CH_4/H_2 with CH_4 concentration ranging from 1 to 5%. Fig. 1 shows the typical current-voltage (I–V) curve from the emissions of diamond films deposited at various CH_4 concentrations. For film deposited at 1% CH_4, the emission increased rapidly at an applied voltage of approximately 1700 V and reached 30 μA at 2500 V. For the samples deposited at high CH_4 concentration (3.5%), the emission characteristics shifted in the low voltage region, the current increased clearly at 700 V and reached 30 μA at 1200 V (Current density: $J = 150\ \mu A\ cm^{-2}$). Calculations of the threshold field at 1% CH_4 and 3.5% CH_4 based on curve fitting of the Fowler–Nordheim equation gave the value of 14.2 V μm^{-1} and 5.8 V μm^{-1}. However, at higher CH_4 concentration (5%), the form of the I–V plot remained the same as at lower CH_4 concentration (1%). The result shows that suitable high CH_4 concentration is advantageous to obtaining a high emission current and low emission threshold. That is because that a suitable ratio of diamond, impurities, graphite and nanocrystal carbon can provide more efficient emission sites and electron sources. The phase purifies of the films have been verified by micro-Raman spectroscopy. There is a clear broad feature at approximately 1580 cm^{-1} of amorphous carbon for the film deposited at 3–5% CH_4 concentration. However, the film quality at high CH_4 is poor and the growth velocity at low CH_4 is slow, 2–4% CH_4 concentration was accepted in our experiments considering the suitable growth velocity and film quality for acquiring high and stable emission current.

In order to study the effects of grain boundary density in films on field emission, 2-μm-thick diamond films with various grain sizes were synthesized at 2% CH_4. To acquire different scratching densities on substrate surfaces, the substrates were polished with various grain sizes of diamond powders from 0.1 to 50 μm and various durations from 10 min to 1 h before the depositions. SEM was used to measure the grain size. The results present that the substrates polished with small diamond powders and long durations are advan-

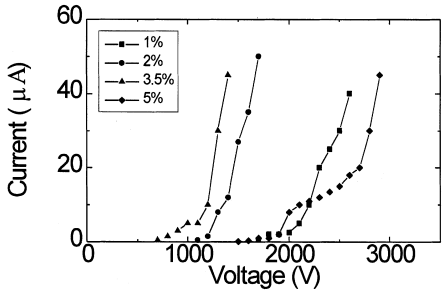

Fig. 1. I–V emission curve from diamond films measured as a function of the CH_4 concentrations.

tageous to grow small-grained diamond films, and small-grained films have a high emission current. That is due to the increasing of the density of grain boundary and forming high-density defects, more emission sites were supplied in small-grained films. Fig. 2 shows the changes in emission current as a function of grain sizes in films. The emission current of films with grain size of 0.3 μm is 10 μA at a voltage of 1200 V, and that of film with grain size of 2 μm is 5 μA at 2000 V. Here we observed a dramatic change in Raman spectroscopy of small-grained films (average grain size is 0.3 μm) which has a high emission current, there is a clear broad peak at approximately 1140 cm^{-1} (Fig. 3). This feature has been suggested to arise from either small grain size or disorder in the tetrahedrally bonded carbon network [6]. The Raman peak at approximately 1140 cm^{-1} seems to be a way to predict the emission properties of diamond films.

We also investigated the effects of grain orientation on the field emission of diamond films. (001), (011) and (111)-textured films with 2 μm thickness can be deposited by changing the concentrations and ratios of CH_4 and CO or the substrate temperatures listed in Table 1. XRD has verified the orientation characteristics and degrees, the experimental details have been

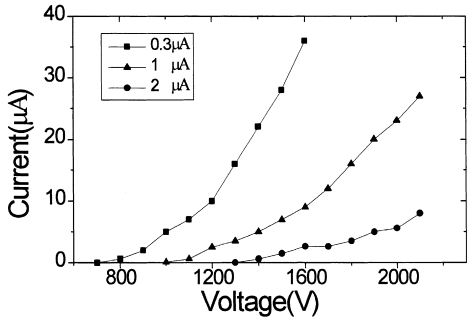

Fig. 2. I–V emission curve from diamond films measured as a function of the grain sizes.

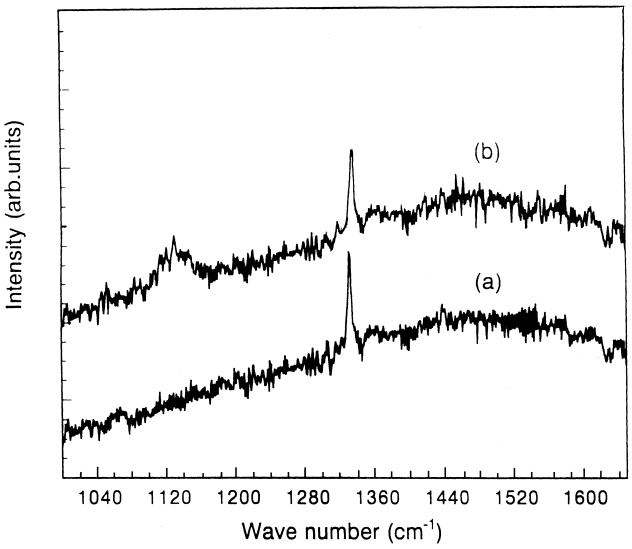

Fig. 3. The Raman spectra obtained from different grain sizes of (a) 2 μm and (b) 0.3 μm.

described by Gu et al. [7]. The results show that the crystal structures in films clearly affect its emission properties (Fig. 4). (011)-textured film enhances the emission current more than those of (111)- and (001)-textured films because of the high grain boundary density of (011)-textured film, which is more suitable for emission of large current. In addition, the surface of (011)-textured film is more rough than those of (001) and (111) textured films, it can supply more efficient emitting microprotrusions. The surface of diamond films is usually rough, according to the microprotrusions model, electron emission from rough surface films can be explained in terms of classical field emission with local field enhancement due to microprotrusion at the emitting surface [8]. To (001)-textured film, it has a low boundary density and the smoothest surface than those of (011) and (111)-textured films. In our experiments, the surface average roughnesses of (001), (111) and (011) textured films are 5.2 nm, 7.8 nm and 22.5 nm measured by Dektak[3] (the average roughness of mirror-polished silicon wafer is 0.8 nm). Specifically, in Table 2 we listed the changes of emission currents from (011)-textured films with various surface average roughnesses and the same thicknesses at 1600 V.

For further studies on the effects of grain boundaries, the changes in emission current with the thicknesses of (001)-textured films were given in Fig. 5. By controlling the deposition conditions, the surface roughnesses of (001)-textured films have an approximate value so that we can neglect the effects of rough-

Table 2
The emission currents from (011)-textured films with various surface average roughnesses at 1600 V

Surface average roughnesses (nm)	10.7	15.5	22.5	30.2	41.7
Emission currents (μA)	2	8	16	27	42

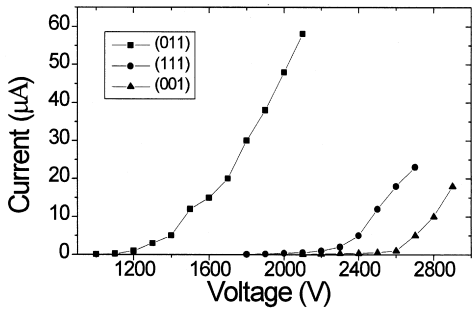

Fig. 4. I–V emission curve from diamond films measured as a function of the grain orientations.

ness on emission. The results show that suitable thinner films lead to higher emission current. An emission current of 35 μA ($J = 175$ μA cm^{-2}) at 1000 V is obtained when the thickness is 1.5 μm (the threshold field is 4.2 V μm^{-1}). However, for very thin films, the closed films have not been formed, they can not provide more efficient emission sites than those of closed thin films and result in lower emission current. The cross-section analysis of a thick film (4.5 μm) by SEM shows a growth property of pillar and low boundary density, which does not favor to the emission of elections.

The annealing processes in H_2, N_2 and Ar to as-grown films were performed at 900°C and 500 sccm for 30 min for changing the surface states of diamond films. The changes of emission properties after annealing were studied. After annealing the resistivities of films have clearly changed from 10^{10} Ω·cm for as-grown films to 10^{15} Ω·cm for annealing in N_2 and Ar, and 10^7 Ω·cm for annealing in H_2. The emission current of the film annealed in H_2 clearly increased, and the threshold voltage decreased dramatically (Fig. 6). Here, the enriched H on the surface of the film results in a H-termination diamond surface, which will affect the surface energy distribution and decrease the work function. It is more advantageous to emit electrons at low voltage. However, the H-termination diamond surface can be removed under the condition of annealing in N_2 and Ar and results in higher resistivity and emission

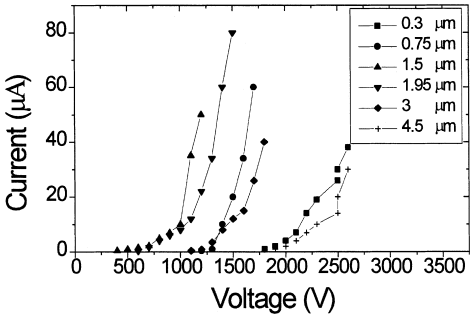

Fig. 5. I–V emission curve from diamond films measured as a function of the film thicknesses.

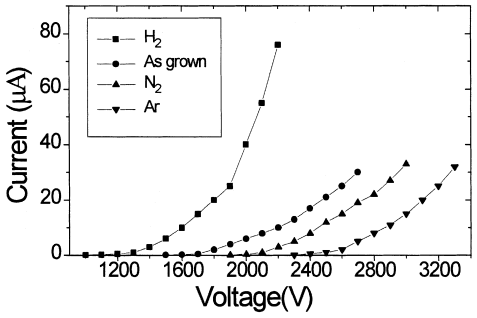

Fig. 6. I–V emission curves from diamond films measured as a function of annealing gases.

voltages [9,10]. Finally, we have also conducted lifetime tests for H_2-annealing films, the results show continuous emission for over 2 h, with small variation in the emission current (less than 5%).

4. Conclusion

We have deposited diamond thin films on Si(001) substrates by the MWPCVD method using gas mixtures of CH_4, CO and H_2. The electron emission properties of diamond films with various structures and morphologies synthesized by controlling the growth parameters were reported. The results show small-grained and (011)-textured diamond films deposited at high CH_4 concentration present the properties of higher emission current and lower threshold voltage. The emission current increases with decreasing film thickness, the largest current density and lowest threshold field occurred at the thickness of 1.5 μm. The films annealed in H_2 after deposition appear to be beneficial in lowering the threshold voltage, increasing emission current and improving stability for electron emission than annealing in N_2 and Ar. All above results indicated that diamond thin films with high emission current, low threshold voltage and high stability could be obtained by selecting suitable deposition parameters.

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