Field emission performances of diamond complex ceramic thin film

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ABSTRACT

Diamond maybe is an ideal electron emission material for field emission display because of its low work function and better chemistry stability. In this research, complex diamond conduct ceramic thin film is fabricated by using Ag-Bi-Pb-B-O base in organic conduct paste and diamond grains. The research aim is to find a method for making large area diamond-base electron emission material. Field emission performances of complex diamond ceramic are studied, too. The turn-on voltage and maximum stable emission current of material are 300V and 760 μ A , respectively. The material also shows better emission stability at low vacuum pressure. The emitting center view is employed to explain the electron emission from diamond ceramic thin film.

Keywords: Field emission, Complex diamond ceramic

1, INTRODUCTION

Field emission display (FED) is evolving as one of the promising techniques for the future generation of flat panel display. In making a successful FED, one of the critical issues is the fabrication of the cold cathode, which not only generates a high emitting current at relatively low operating voltages but also is stable and reliable to the operating conditions. The key of cold cathode fabrication is selection of electron emission material. Diamond material may be ideal electron emission material for vacuum microelectron devices and field emission display because of its low emission work function, high hardness, high thermal conductivity and better chemistry stability. These desirable properties come from the sp^3 structure of carbon atoms in diamond. The field emission characteristics of chemical vapour deposition (CVD) diamond thin film have been universally studied by lots of authors[1,2,3]. Many theories have been employed to explain the electron emitting mechanism because of its complex structure and component. Most of authors considered that the sp^2-bonded carbon (in graphite or amorphous forms) as well as many structures' defects plays the important rules in electron emission. Especially the sp^2-bonded carbon (in graphite or amorphous forms) has an important action in transferring electrons. Synthetic high-pressure diamond has also been studied by some authors[4,5], and shown the better electron emission performances. The result shows that the good electric contact between diamond grains and substrate is necessary for better electron emission.

In this research, complex diamond conduct ceramics are fabricated, and its field emission performances are studied, too. The purpose of research is to find a better method solving the diamond grains' application in FED. This kind of complex diamond ceramics may be used in fabrication of large area micro-emitter.

2, EXPERIMENT

Complex diamond ceramics thin films are made from diamond grains powder synthesized and inorganic paste. Synthetic high-pressure diamond powder grains size is about 0.7 μ m on average. Diamond grains are treated with Cs-salt and annealed in H_2 firstly and then mixed with Ag-Bi-Pb-B-O base inorganic conduct paste. The Mixture of diamond and inorganic conduct paste are coated onto silicon substrate. The mixture become the complex ceramics after heated over 300 ℃. The ceramic's resistivity is about 0.03 Ω • cm. Because the diamond grains' surface is covered by paste in mix process, the ceramic on diamond grains' surface must be removed by using acid treatment and let diamond surface expose. Complex

diamond conduct ceramic (diamond ceramic) is formed after treatment. Exposure diamond grains' surface must be cleaned carefully and treated again with Cs-salt. As a comparable, some samples are made from diamond grins in Cs-salt solution by using electrolyte deposition. The diamond surface was checked by Raman spectrum. Field emission performances are measured in high vacuum chamber at pressure of 10^{-5}Pa. Indium-tin-oxide coated glass is as anode. The distance between anode and cathode are about100 μ m. The circuit of field emission performance measurement is shown in Fig. 1. Applied voltage on anode is 0-5KV.

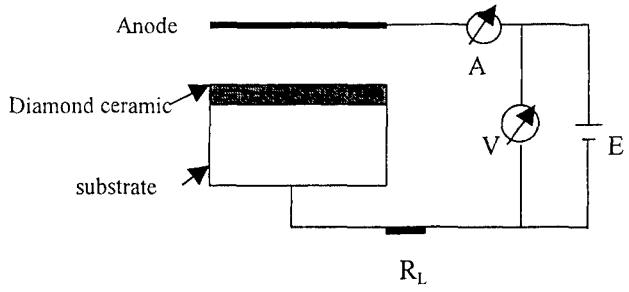


Fig. 1 The circuit diagram of field emission performances measurement

3, RESULTS AND DISCUSSION

3.1, Surface Morphology Photographs of Complex Diamond Conduct Ceramic

The seep electron microscope (SEM) photograph of the surface morphology of complex ceramic, as shown in fig.2(a). From the photograph, it could be known that the surface of diamond grains in complex ceramic is covered by ceramic. Fig. 2(b) shows the surface morphology of complex ceramic thin film after treated with acid solution for 3min. Diamond grains is exposure after treatment. The Raman spectrums confirm that the diamond grains' surface is exposure. As shown in fig.3(b). Fig.2(c) shows the surface morphology of diamond grains film deposited onto silicon substrate by electrolyte in Cs-salt solution. Diamond grains and the vacancy could be seen clearly in fig.2(c).

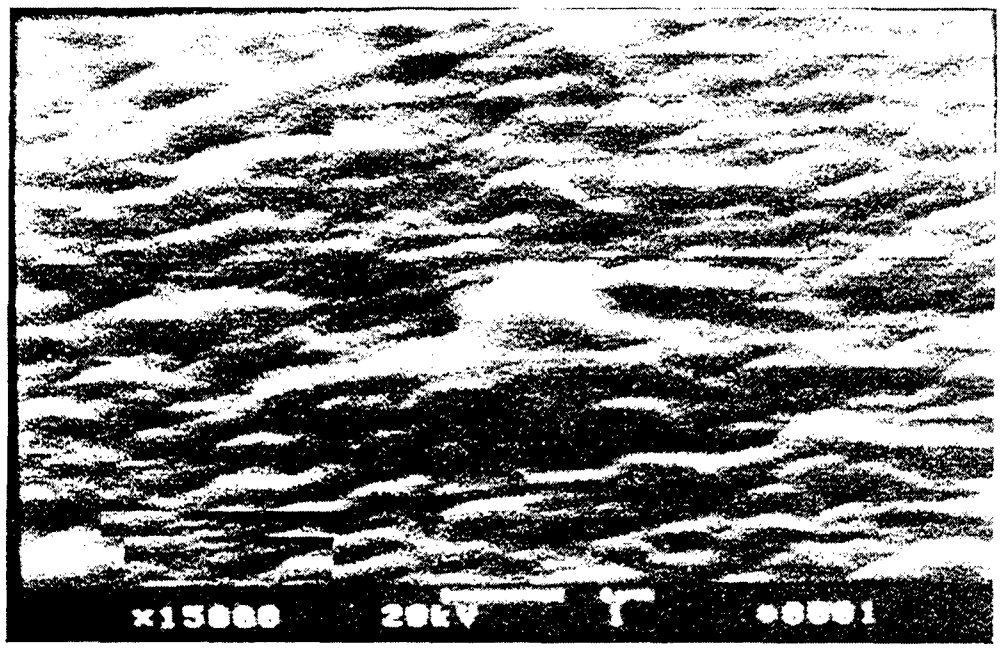


Fig.2(a) SEM photograph of complex ceramic thin film with no surface treatment.

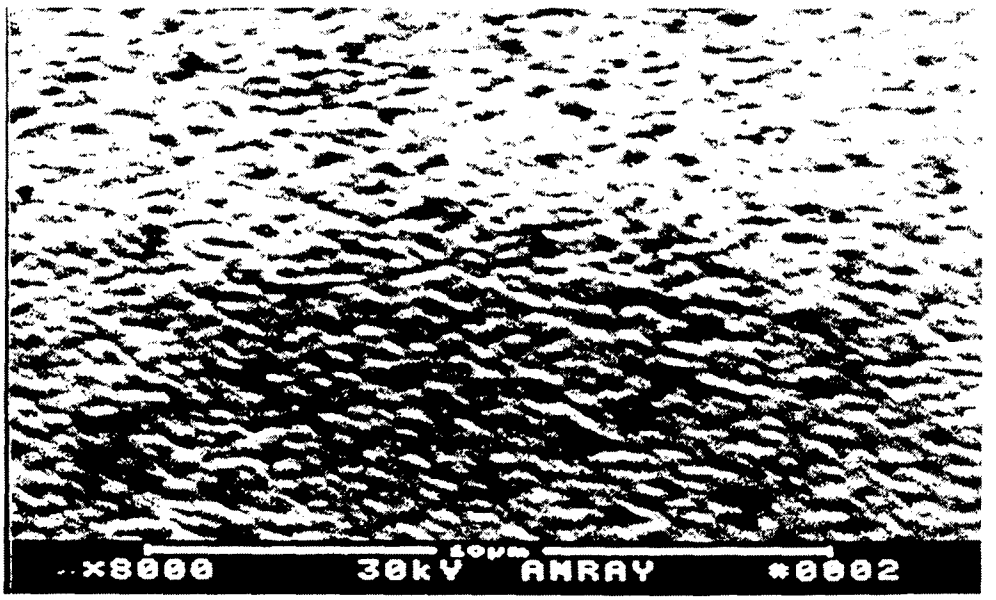


Fig.2(b) The surface morphology photograph of diamond ceramic after treated by acid solution. The diamond grains' surface is exposure, and vacancies are filled with ceramic.

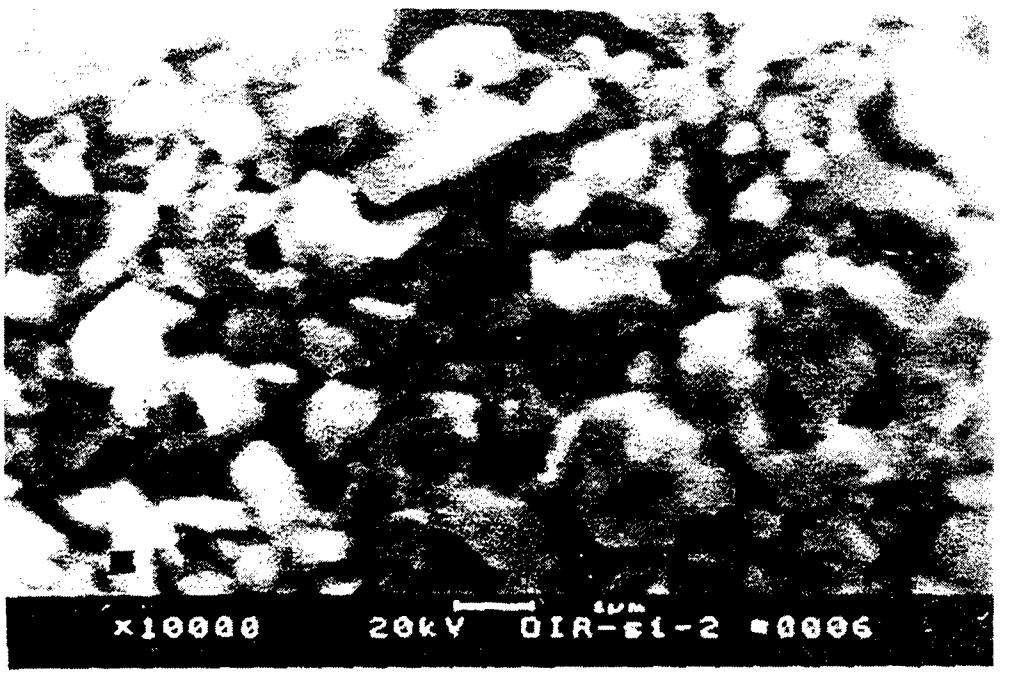
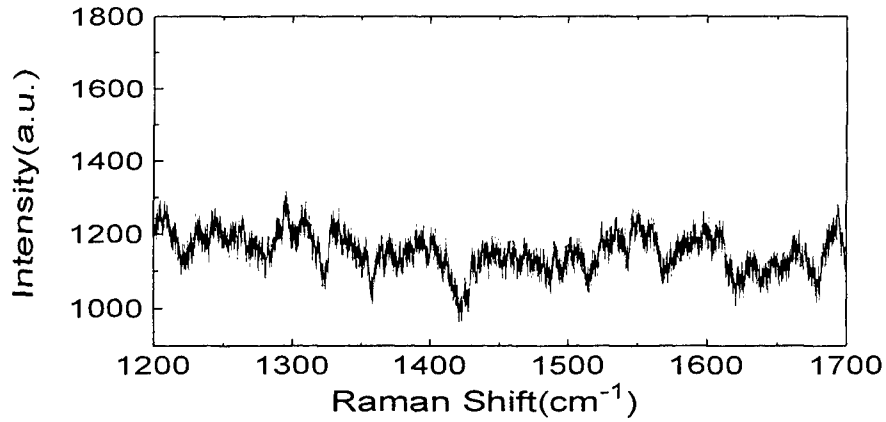


Fig.2(c) The surface morphology photograph of diamond grains deposited by electrolyte in Cs-solution.

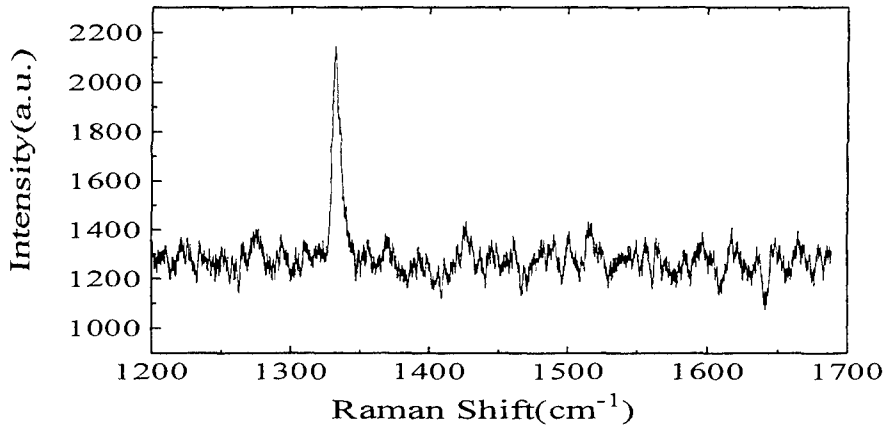
3.2, Raman Spectrum of Diamond Grains

Diamond grains is checked by Raman spectrum. The Raman peak of diamond grains is at 1332.6cm^{-1}. Fig.3(a) shows the Raman spectrum of complex diamond conduct ceramic thin film with no treatment. Due to covered of ceramic, no

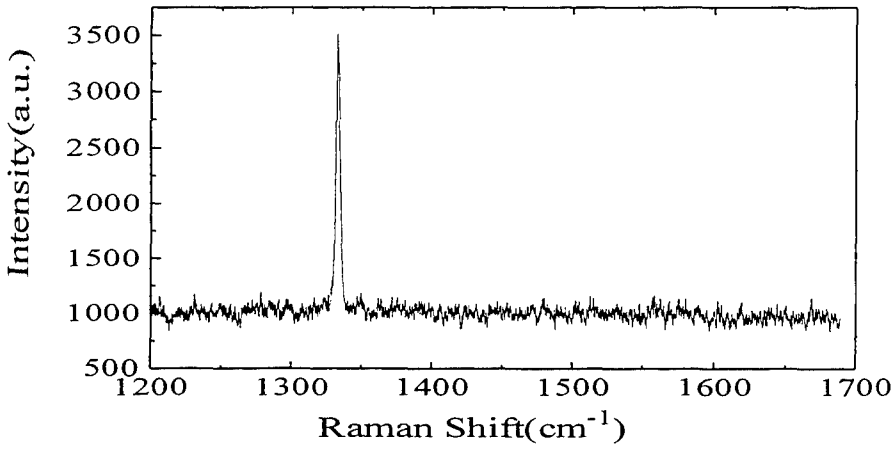
Raman peak of diamond grains is observed in spectrum. Fig.3 (b) shows Raman spectrum of diamond grains in complex diamond conduct ceramic film after treated with acid solution for 3min.. The sharp Raman peak at 1332.6cm^{-1} shows that diamond grains' surface is exposure. Fig.3(c) shows the Raman spectrum of diamond grains film. From these Raman spectra, acid treatment affect the half-peak -width ($\Delta\ \lambda$) of diamond grains Raman peak.



(a)



(b) $\Delta\ \lambda$ =9.01cm^{-1}



© $\Delta\ \lambda$ =7.8cm^{-1}

Fig.3 Raman spectra of different samples

3.3, Field Emission Performances

The field emission of diamond maybe described by Fowler-Nordheim equation, as follow:

$$I = aV^2 \exp\left[-\frac{b}{V}\right] \quad \text{.....(1)}$$

$$a = (A \times 1.5 \times 10^{-6} \beta^2 / 1.1\phi^2) \exp(\frac{10.4}{\sqrt{\phi}}) \quad \text{.....(2)}$$

$$b = -1.6 \times 10^7 \frac{\sqrt{\phi^3}}{\beta} \quad \text{.....(3)}$$

Parameter A is emitting area. β is the field enhancement factor at sharp geometry. Φ is effective work function of material.

Parameter a and b could be used to describe electrons emitting feature. In the experiment, a and b is got from experiment data, which determine the work function.

3.3.1 Field emission performances of samples

Fig.4(a) shows the field emission performance of complex ceramic (ceramic). Because diamond grains' surface is covered by Ag-Bi-Pb-B-O conduct ceramic, as shown in fig.2(a), the most of electron emission come from ceramic. The turn-on voltage Vcer is about 850V. Φ cer =0.006 eV (calculated according to equation (3)) for β =1.

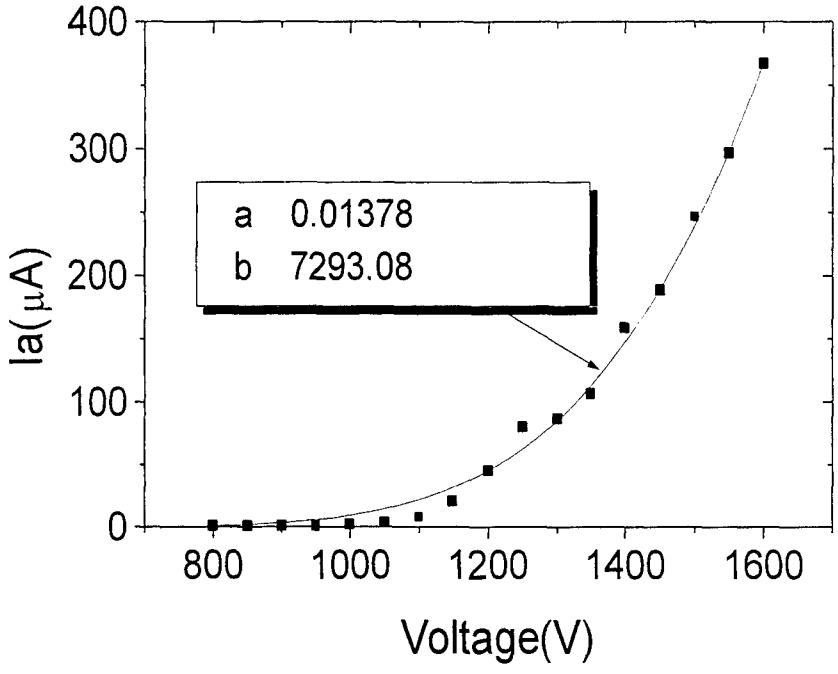


Fig.4(a) Field emission performance of diamond complex conduct ceramic thin film with no acid treatment
The solid line in figure is fitting curve by using Folower-Nordheim equation.

Fig.4 (b) shows field emission performance of diamond ceramic thin film. Diamond grains' surface is exposure after with acid treatment, as shown in fig.2(b). The turn-on voltage Vdia-cer is about 300V. According to equation (3), Effective work function Φdia-cer is calculated , and equal to 0.0025eV for β =1, The turn-on voltage is lower than Vcer. The reasons will be discussed later.

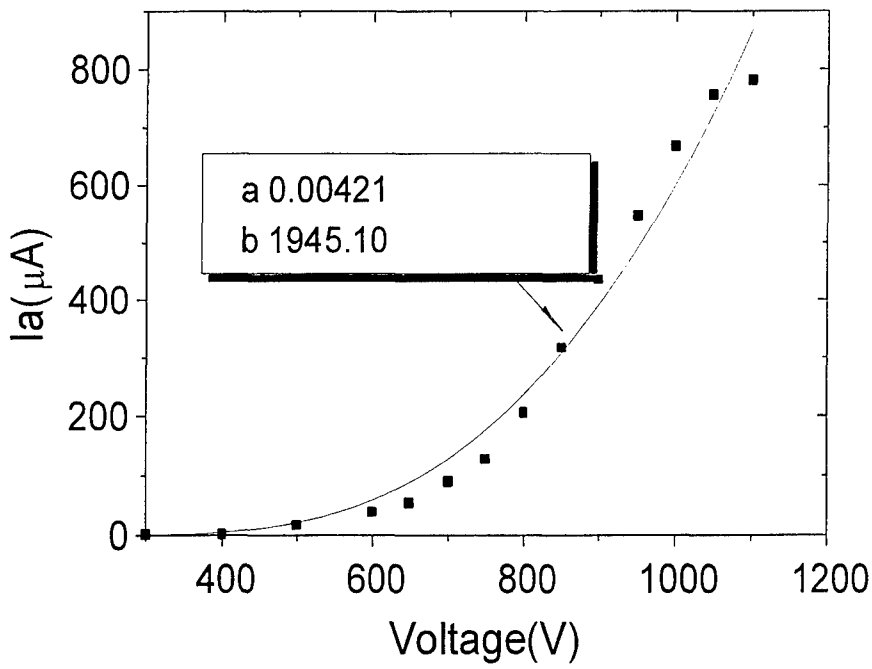


Fig.4(b) field emission performance of complex diamond conduct ceramic thin film after acid treatment
The solid line in figure is fitting curve by using Folower-Nordheim equation.

Fig.4(c) shows field emission performance of diamond grains deposited on silicon by using electrolyte. The turn-on voltage is about 300V. emitting current is about 120 μ A at maximum. Φdia is 0.002eV for β=1.

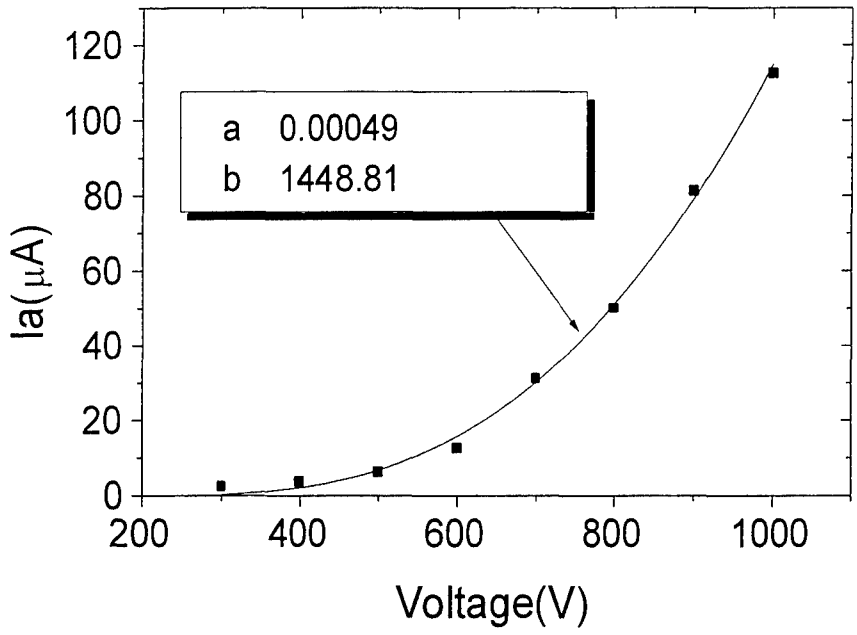


Fig.4© Field emission performance of diamond grains deposited on silicon by electrolyte
According to experiment data, effective work function ratio of ceramic and diamond grains Φcer/ Φdia is equal to 3.

It shows that diamond grains have lower effective work function than ceramic, and means that electron emission of diamond ceramic mainly comes from diamond grains. But the effective work function ratio Φ dia of diamond grains film deposited by electrolyte onto silicon is equal to 0.002eV, Φ dia-cer/ Φ dia is equal to 1.25, only small difference. Emission current of diamond ceramic is higher than that of diamond grains film, although its effective work function is almost equal to diamond grains. The result shows that good electric contact is important to transfer electrons.

3.3.2 Field emission stability

The stability of electron emitting is important for material application in FED. so the emission stability with time and pressure is researched in experiment.

Fig.5(a) shows the emission stability of diamond ceramic at 900V and 650V, emission current is about 400 μ A, and 50 μ A. Fluctuation of emission current is recorded. Emission current is unstable at high emission level, but it is stable at low emission level.

Fig.5(b) shows emission stability with pressure at 650V and 800V. The emission current is unstable at high emission level and stable at low emission level.

Fig.6 (a) shows the emission stability of ceramic film with time. The emission stability is worse.

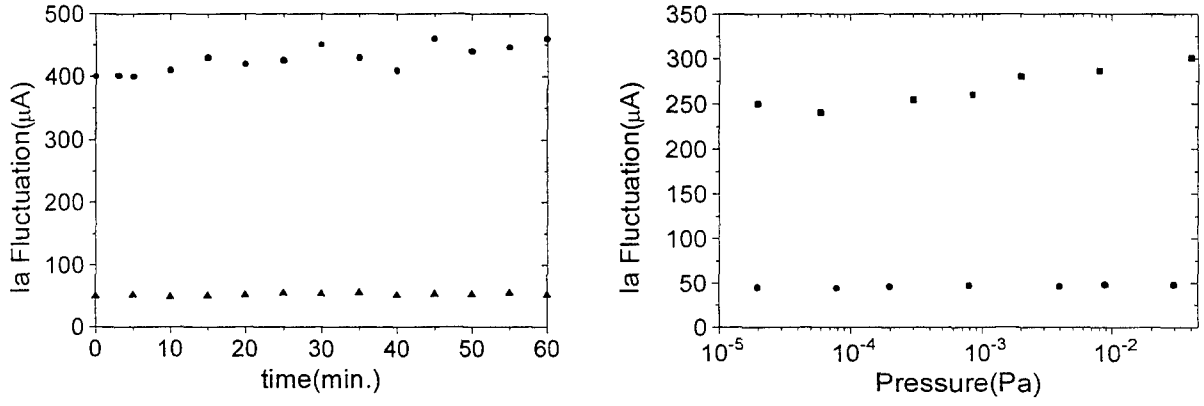


Fig.5 Field emission stability of diamond ceramic with (a) time, (b) pressure

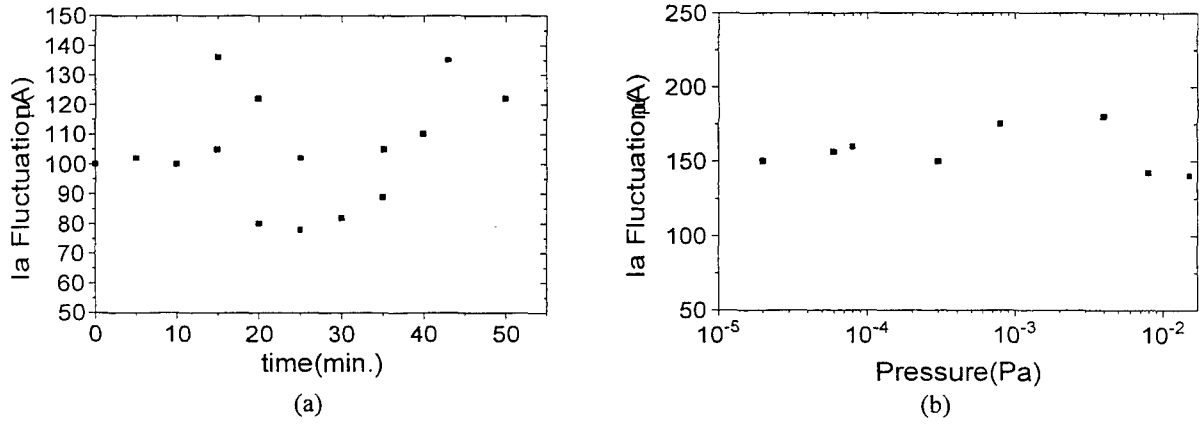
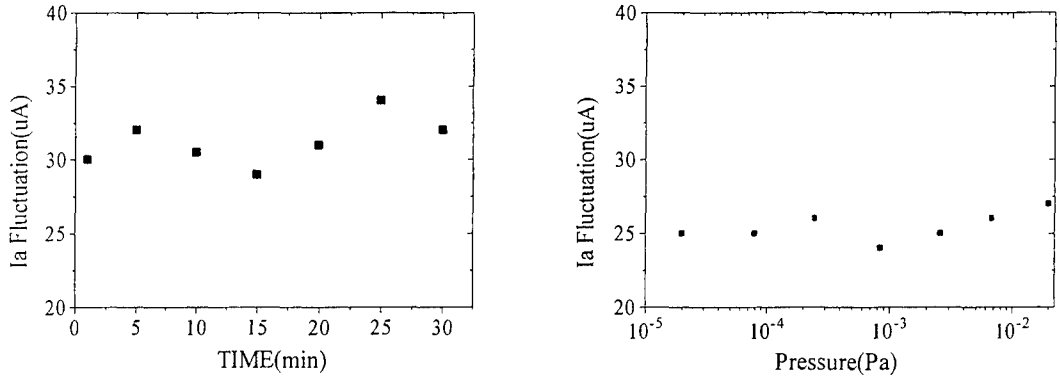


Fig.6 emission current fluctuation of ceramic with (a) time and (b) pressure

Fig.6(b) shows that emission current fluctuation of ceramic change with vacuum pressure. The current fluctuation is unstable at a high level. Fig.7(a) and (b) shows that the emission current of diamond grains film at constant applied voltage change with time and vacuum pressure, respectively. Emission stability of diamond grains film is not very well, too.



(a) (b)

Fig.7 emission current fluctuation of diamond grains film with (a) time and (b) pressure

3.4, Electrons Emitting Mechanism

Although diamond is a wide band-gap material, it is an insulator, the free carrier concentration electrons density is very low in perfect diamond due to the high energy band-gap. Diamond has been shown to have a negative electron affinity and a low work function. Fig .8 shows the band diagram for diamond. Note in this diagram that the band-gap is about 5.5eV and conduct band (Ec) is above the vacuum level Evac. Generally, the emitting current predicted by this band diagram is not very high because the free carrier concentration in diamond is very low. the primary source of free carrier in CVD diamond comes from non-diamond phase such as graphitic phase, so the emission current of perfect diamond grains is not high. If want to get high emission current, it must has a better electrons transfer passage to maintain the electron source for constant electron emission. Generally, it is not easy to form the good Ohmic contact between diamond and substrate. In our research, hard ceramic has better conductivity. It can form good contact between diamond and substrate, and plays an important role in carrier transfer.

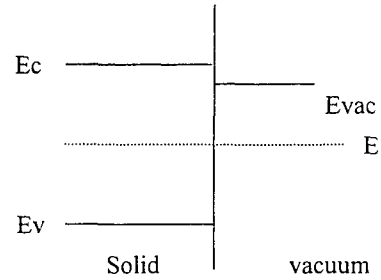


Fig.8 Band diagram of diamond at vacuum interface

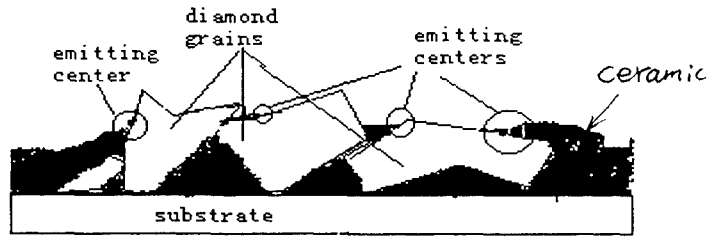


Fig.9 The sketch diagram of electron emission centers on diamond ceramic's surface.

From above experiment results, the effective work function of diamond ceramic $\Phi_{dia-cer}$ is lower than that of ceramic

Φ_{cer}, and almost equal to Φ_{dia}, also the turn-on voltage is same with that of diamond grains film, but is lower than that of ceramic. In principle, electrons emit more easily from diamond surface than from ceramic surface due to their work function difference. In fact, it is confirmed by experiment results. According to these experiment results, we consider that emitting centers are formed on surface of diamond ceramic. These emitting centers locate at the contact micro-area between diamond surface and conduct ceramic. The Electron emission comes from these emitting centers. The diagrammatic sketch of emitting center is shown in fig. 9. Electrons transfer from conduct ceramic to diamond surface near tightly ceramic, and then emit into vacuum from diamond surface because of its low effective work function. High emission current of diamond ceramic than that of diamond grains film is due to good electric contact between diamond and substrate. Current fluctuation at high emission level maybe is relation with hot carrier transfer and unstable surface. This view is used to explain the result of low turn-on voltage and high emission level of diamond ceramic than that of pure diamond grains film.

4, CONCLUSION

Diamond complex conduct ceramic field emitter is fabricated from diamond grains and Ag-Bi-Pb-B-O base conduct paste. This material is easily fabricated, and has better field emission performances. It suits to use in large area plate display. It needs to improve the emission stability of diamond ceramic at high emission level in further research work.

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