Field emission characteristics of nano-diamond cathode surface by graphitization pretreatment*

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Cathode samples of nano-diamond by graphitization pretreatment with different temperatures were fabricated by electrophoresis, then the structures and morphologies of the cathode samples were characterized by scanning electron microscope (SEM) and X-ray diffraction (XRD), and the field emission tests were conducted. The effects of graphitization pretreatment on the field emission characteristics of nano-diamond cathode surface on titanium substrate are studied. The results indicate that the surface morphologies of nano-diamond cathode samples after graphitization pretreatment change a lot, and the field emission characteristics in low-voltage area are improved obviously. However, in high-voltage area, the curve distortion happens, and it doesn't conform the mechanism of field emission characteristics.

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Because diamond has many advantages, such as good chemical stability, high hardness and high conductivity[1], especially the negative electron affinity, it has become a good field emission cathode material[2-4]. In recent years, diamond composites have better field emission characteristics than diamond, as doping, mixing, cladding and modification can modify the field enhancement factor of material surface and introduce conductive grain boundary into film materials, which are helpful to improve the conductivity of thin films, thus enhancing the electron transport capacity and field emission characteristics[5]. Cathode materials with low threshold filed and high emission current have become a hot research topic of field emission cathode[6]. However, compared with other field emission materials, the field emission current of nano-diamond is relatively low and the impressed voltage is relatively high[7]. Recently, field emission characteristics of nano-diamond have been investigated theoretically and experimentally. Chang et al[8] indicated that coating diamond films on top of carbon nanotubes (CNTs) could increase markedly the robustness of CNTs. Harniman et al[9] successfully synthesized diamond by chemical vapor deposition (CVD). Long et al[10] deposited nanocrystalline diamond (NCD) films through a novel technique with periodic magnetic field and studied the influence of magnetic field on the nano-diamond growth. Han et al[11] studied the surface nanostructure of nitrogen-doped NCD films via nickel nanodots-protected reactive plasma etching process. Meanwhile, the microelectronic integrated devices and circuits have been studied intensively for the nano-diamond field emission[12]. But there are still problems to be solved for field emission characteristics of nano-diamond. In this paper, the nano-diamond cathode surface was pretreated by different temperature graphitization treatments, and the field emission characteristics of the nano-diamond cathode surface after graphitization pretreatment on Ti substrate are studied.

Before electrophoretic deposition, Ti substrates must be grinded and polished, and they also needed to be cleaned by detergent and ultrasonic and rinsed with deionized water, then they were reserved to be used after ethanol dehydration reaction[7,13]. The nano-diamond purified powder (the purity is 97%) produced by Beijing GRISH company was placed in the hot filament chemical vapor deposition (HFCVD) to carry out graphitization pretreatment. The system vacuum pressure is 3×10^{-3} Pa, treatment time is 20 min, and treatment temperatures are 1 000 °C, 1 100 °C, 1 200 °C and 1 300 °C, separately.

Then 20 mg diamond powders with and without graphitization pretreatment were weighted separately to

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prepare electrophoresis liquid. The experimental conditions are as follows. The mixed solutions with the same composition of 5 mg iodine, 1 mL acetone, 40 mL isobutanol, 2 mL deionized water and the nano-diamond powder treated by different temperatures were placed into five beakers separately. After the solutions were stirred uniformly, they were placed into the ultrasonic machine to conduct ultrasonic dispersion for 60 min separately, and the ultrasonic temperature is 50 °C. Electrophoresis began separately after ultrasonic dispersion was finished, where the space between the cathode and anode is 1 cm, electrophoresis voltage is 60 V, and time is 1 min. Then five deposited samples were placed into HFCVD to carry out heat treatment separately, where the heat treatment temperature is 800 °C, and time is 10 min. Finally, the field emission characteristics tests were conducted. The five samples were marked as sample 1, sample 2, sample 3, sample 4 and sample 5, separately. Sample 1 is the diamond cathode that was not pretreated by high-temperature graphitization, while others are diamond samples that were pretreated at 1 000 °C, 1 100 °C, 1 200 °C and 1 300 °C, separately.

Fig.1 shows metallomicroscope images of samples fabricated by electrophoretic deposition. It can be seen that the coating thickness from sample 1 to sample 5 increases gradually, the coating color becomes darker and darker, and surface particles distribution is more and more uniform and dense. The reason may be that the degree of diamond graphitization increases with the rising of pretreatment temperature, so graphite phase of electrophoresis liquid also increases, which will reduce the permittivity of electrolytic solution, increase electrophoresis current and accelerate the electrophoretic deposition. Consequently, more particles that were not reunited in the diffusion liquid were deposited on the substrate, the coating thickness increases, and more uniform and dense coating is formed.

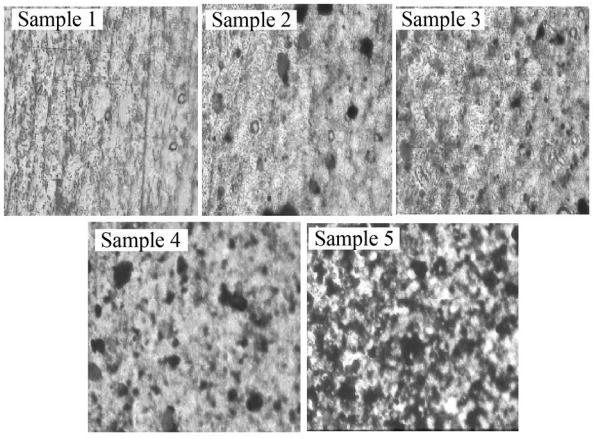


Fig.1 Metallomicroscope images of nano-diamond coating samples 1—5 fabricated by electrophoretic deposition after graphitization pretreatment

The scanning electron microscope (SEM) images of samples 2—5 after heat treatment are shown in Fig.2. It can be found that cracking phenomenon happens to the deposited samples 2 and 3 after 800 °C heat treatment, which may be due to their coatings are relatively thin. However, the bonding reaction is stronger when heat treatment is carried out at 800 °C, so the cracking phenomenon occurs under thermal stress. However, for sample 4 and sample 5, 800 °C heat treatment temperature is moderate, cracking phenomenon does not happen, both surfaces have some larger aggregates, and denser particles distribution can be seen on the coating surface.

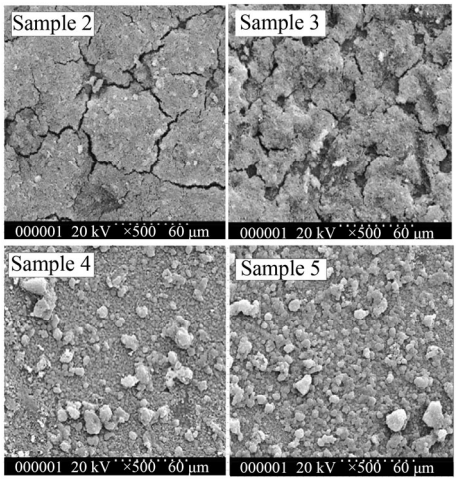
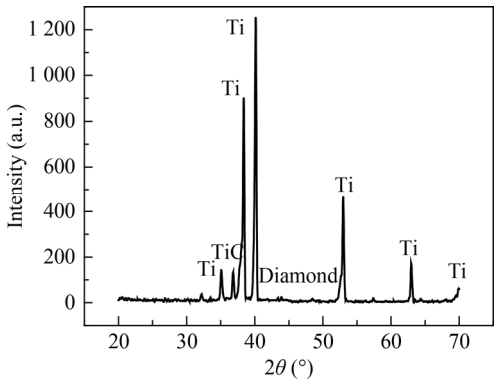


Fig.2 SEM images of nano-diamond coating samples 2—5 fabricated by electrophoretic deposition after graphitization pretreatment

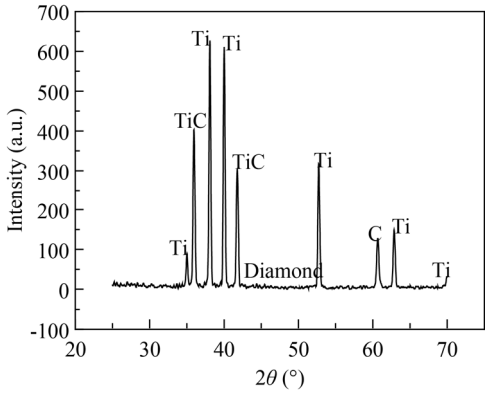
Fig.3 gives X-ray diffraction (XRD) patterns of sample 1 and sample 4 after heat treatment. Obviously, it can be known that the diffraction peaks of TiC, Ti and diamond appear in the XRD patterns of two samples, but the diffraction peaks of diamond are very weak, and they can't be seen nearly. The appearance of TiC diffraction peaks indicates that the bonding reaction indeed occurs between diamond and Ti substrate, thus realizing good bonding[14,15], and ohmic contact is formed[7,16]. Meanwhile, because Ti is substrate material, diffraction peaks of Ti also appear. Moreover, diffraction peak intensity of Ti for sample 1 is very high, while that of TiC is low, as the coating is relatively thin. However, for sample 4, the intensity of diffraction peaks of Ti decreases, while that of TiC increases, which indicates the coating is relatively thick. What's more, the diffraction peak of graphite occurs in the XRD pattern of sample 4, which may be caused by diamond surface graphitization of high-temperature heat treatment.

Field emission characteristic curves of samples are given in Fig.4, where (a) shows current-voltage (*I-V*) characteristics and (b) shows $\ln(I/V^2)$ versus $1/V$ (*F-N*) characteristics. It can be seen that *I-V* characteristic curves of five samples are nearly identical. The turn-on voltage of sample 5 is the lowest, while the current density is the largest in the same impressed field, which in-

dicates that as the graphitization degree of diamond increases, the field emission current of cathode becomes larger. The *F-N* curves of samples present large differences, where the slope of sample 5 is the minimum. Meanwhile, after graphitization pretreatment, in low-voltage area, field emission characteristics of diamond on Ti substrate are improved a lot, while in high-voltage area, the curve distortion happens and it does not conform the field emission mechanism any more[17,18].



(a) Sample 1

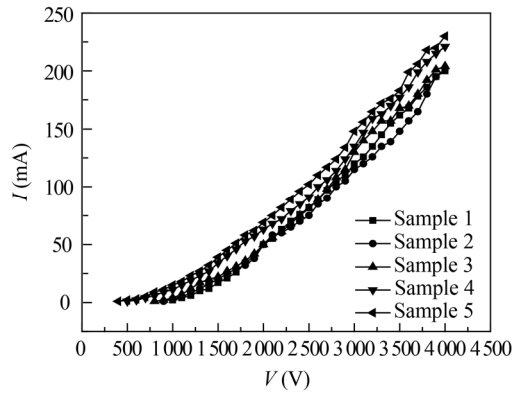


(b) Sample 4

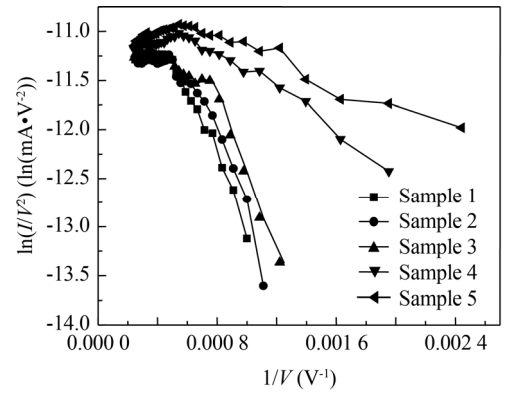
Fig.3 XRD patterns of samples 1 and 4 after heat treatment

As the degree of graphitization pretreatment increases, the content of TiC in the coating increases, which will improve the electron transportation capacity of coating. Moreover, the conductivity capacity of diamond is worse after graphitization pretreatment, and conductive graphite sp^2 bonds are coated on the surface of diamond particles, which makes the conductive capacity of cathode coating improved, and then the field emission characteristics of low-voltage area are improved. The results are consistent with those of Xu et al[19] and W. Zhu et al[20].

However, in high-voltage area, because the current is high, the temperature of cathode tip rises, which will bring two kinds of effects on field emission[21]. The increase of temperature means that the internal electrons motion of semiconductor is accelerated, and energy gets larger, so electrons are easy to escape from surface constraint, making field electron emission easier and the slope of *F-N* curve decreased. On the other hand, the increase of temperature can generate thermal electron emission. When the temperature is much higher, the thermal electron emission is more intense. Consequently, the *F-N* curve will not follow field emission mechanism. At this time, both field emission current and a certain degree of diamond thermal electron emission will appear. Moreover, considering that the graphite is produced by surface graphitization pretreatment, and the substrate material Ti of cathode samples and TiC have similar metallic property in the transition layer, in high-voltage area, not only diamond participates in the electron emission, but also the substances such as substrate Ti, TiC and graphite[22,23] may participate. In the above experiments with various temperatures of field emission, *F-N* curves of purified Ti sheet were tested as shown in Fig.5. Results show that the field emission characteristics of substrate Ti have a certain sensitivity to temperature and voltage[21]. Therefore, after surface graphitization pretreatment, in the coating cathode of nano-diamond based on Ti substrate, Ti substrate and other substances may also participate in electron emission. As a result, the field emission characteristics of nano-diamond after surface graphitization pretreatment in high-voltage area still need to be researched.



(a) *I-V* characteristic curves



(b) *F-N* characteristic curves

Fig.4 Field emission characteristic curves of samples 1—5

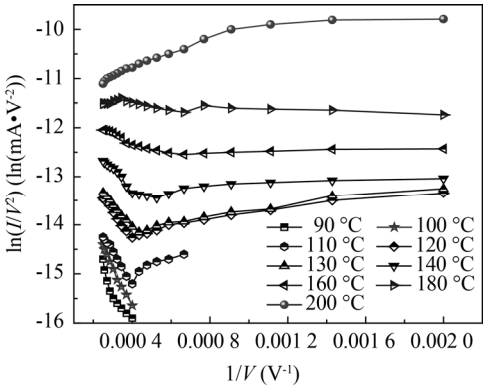


Fig.5 *F-N* curves of the purified Ti sheet after varied-temperature tests

Nano-diamond cathode samples after surface graphitization pretreatment were fabricated by electrophoresis, the structures and morphologies were characterized, and the field emission tests were conducted. Results indicate that the morphologies of nano-diamond cathode samples after graphitization pretreatment change a lot, which is related to pretreatment temperature. Moreover, by means of surface graphitization pretreatment, low-voltage field emission characteristics of nano-diamond cathode are improved a lot; but in high-voltage area, the curve distortion occurs and the mechanism of field emission is not confirmed any more, so it should be further researched.

References

[1] Qian Li-rong, Dai Wei, Li Cui-ping, XU Sheng and YANG Bao-he, Journal of Optoelectronics · Laser **26**, 700 (2015). (in Chinese)

[2] Guang R G and ITO Toshimichi, Applied Surface Science **257**, 2455 (2011).

[3] Wang Tao, Li Rui-shan, Pan Xiao-jun, Zhang Zeng-pei, Zhou Ming, Song Xi and Xie Er-qing, Chinese Physics Letters **26**, 066801 (2009).

[4] Zhang Yan-yang, ZHANG Zhi-yong, ZHAI Chun-xue and YANG Wan-chang, Piezoelectrics & Acoustooptics **32**, 119 (2010).

[5] YANG Xia-xi, ZHANG Xiao-bing, YANG Yang, LEI Wei, LI Jing, QU Ke, ZHANG Peng, LI Chi and DING Mei-bin, Chinese Journal of Luminescence **29**, 551 (2008).

[6] Ye Yun, Cai Shou-jin, Yan Min, CHEN Tian-yuan, LIU Yu-hui, GUO Tai-liang and LIN Zhi-xian, Journal of Optoelectronics · Laser **25**, 101 (2014). (in Chinese)

[7] YANG Yan-ning, ZHANG Zhi-yong, YAN Jun-feng, LI Wei-xia, ZHANG Fu-chun, LIU Qiao-ping and CUI Hong-wei, Acta Photonica Sinica **44**, 0216001 (2015). (in Chinese)

[8] Ting-Hsun Chang, Ping-Yen Hsieh, Srinivasu Kunuku, Shiu-Cheng Lou, Divinah Manoharan, Keh-Chyang Leou, I-Nan Lin and Nyan-Hwa Tai, Applied Materials & Interfaces **7**, 27526 (2015).

[9] Robert L. Harniman, Oliver J.L. Fox, Wiebke Janssen, Sien Drijkoningen, Ken Haenen and Paul W. May, Carbon **94**, 386 (2015).

[10] Hangyu Long, Shasha Li, Hao Luo, Yijia Wang, Qiuping Wei and Z.M. Yu, Applied Surface Science **353**, 548 (2015).

[11] Wenhong Han, Ying Xiong, Bing Wang, Xiangkun Li and Li Xu, Applied Surface Science **346**, 484 (2015).

[12] W. P. Kang, S. H. Hsu, S. Raina and M. Howell, Implementation of Nanodiamond Field Emission Microelectronic Integrated Devices and Circuits, International Vacuum Nanoelectronics Conference, 2015.

[13] DENG Zhou-hu, WANG Xue-wen, ZHAI Chun-xue, ZHAO Wu, YAN Jun-feng and ZHANG Zhi-yong, Journal of Northwest University (Natural Science Edition) **36**, 209 (2006). (in Chinese)

[14] LI Zheng-lin, Deng Shao-zhi, Xu Ning-sheng, Fei Liu and Chen Jun, Chinese Physics Letters **27**, 068504 (2010).

[15] Li Wei-xia, Yang Yan-ning, Liu Qiao-ping, Ruan Xing-xiang, Zhang Fu-chun and Jiang Shuo, Advanced Materials Research **1015**, 453 (2014).

[16] YUAN Guang, GUO Da-bo, GU Chang-zhi, Dou Yan and Song Hang, Acta Physica Sinica **56**, 143 (2007). (in Chinese)

[17] Chang T H, Panda K, Panigrahi B K, Lou S C and Chen C, The Journal of Physical Chemistry C **116**, 19867 (2012).

[18] Yan J K and Chang L, Thin Solid Films **498**, 230 (2006).

[19] Xu N S, Latham R V and Tzeng Y, Electronics Letter **29**, 1596 (1993).

[20] Zhu W, Kochanski GP, Jin SM and Seibles L, Journal of Vacuum Science & Technology B **14**, 2011 (1996).

[21] Yang Yan-ning, Zhang Zhi-yong, Zhang Fu-chun, Zhang Wei-Hu, Yan Jun-Feng and Zhai Chun-Xue, Acta Physica Sinica **59**, 2666 (2010). (in Chinese)

[22] Yang Yan-ning, Zhang Zhi-tong, Zhang Fu-chun, DONG Jun-Tang, ZHAO Wu, ZHAI Chun-Xue and ZHANG Wei-Hu, Chinese Physics Letters **29**, 018103 (2012).

[23] Qiao L, Wang C C, Qu C Q, Zeng Y, Yu S S and Hu X Y, Diamond & Related Materials **18**, 657 (2009).