Phase Transformation and Enhancing Electron Field Emission Properties in Microcrystalline Diamond Films Induced by Cu Ion Implantation and Rapid Annealing *

Yan-Yan Shen(申艳艳)**, Yi-Xin Zhang(张一新), Ting Qi(祁婷), Yu Qiao(乔瑜), Yu-Xin Jia(贾钰欣), Hong-Jun Hei(黑鸿君), Zhi-Yong He(贺志勇), Sheng-Wang Yu(于盛旺)**

Research Institute of Surface Engineering, Taiyuan University of Technology, Taiyuan 030024

(Received 2 May 2016)

Cu ion implantation and subsequent rapid annealing at 500°C in N_2 result in low surface resistivity of 1.611 ohm/sq with high mobility of 290 $cm^2 V^{-1} S^{-1}$ for microcrystalline diamond (MCD) films. Its electrical field emission behavior can be turned on at $E_0 = 2.6\,V/\mu m$, attaining a current density of 19.5 $\mu A/cm^2$ at an applied field of 3.5 $V/\mu m$. Field emission scanning electron microscopy combined with Raman and x-ray photoelectron microscopy reveal that the formation of Cu nanoparticles in MCD films can catalytically convert the less conducting disorder/a-C phases into graphitic phases and can provoke the formation of nanographite in the films, forming conduction channels for electron transportation.

PACS: 81.05.ug, 68.55.Ln, 73.25.+i DOI: 10.1088/0256-307X/33/8/088101

Diamond films have been extensively investigated for potential applications in field electron emission (FEE) due to their unique physical and chemical properties.[1,2] However, due to the high resistivity of diamond, the replenishment and transport of electrons in bulk diamond are diminished, so that it is difficult to form depletion regions required for rectification and modulation.[3] Therefore, efforts are still needed to improve the electrical properties of diamond films to be used as the emitter showing lower turn-on voltage with associated high density of emission sites for field emission.

Recently, studies have been conducted to modify sp^2-bonded carbon within diamond films that are thought of as the electron conduction channel in diamond FEE.[4–7] However, the electron conductivity of disorder/amorphous carbon (a-C) is not sufficiently high, which limits the electrical field emission (EFE) properties attainable for diamonds.[5] The incorporation of N_2 into chemical vapor deposition (CVD) process can induce the conversion of amorphous phase to high conducting graphite phase at the grain boundaries, increasing the number of conduction paths in the diamond films.[6,7] However, since N_2 is energetically preferred in the grain boundary sites, the diamond grains give slight contribution to the conductivity. Ion implantation can virtually introduce any element into diamond grains and grain boundaries without the constraint of solubility limit. Moreover, ion implantation can efficiently modify the sp^3/sp^2 ratio of the diamonds by properly selecting the fluence and implant energy.[8] Also, Cu has been utilized for synthesizing the graphene in the CVD process, which implies that Cu has some degree of solubility to carbon and catalytically induces the formation of the graphite-like phase. Therefore, it is desirable to modify the electrical properties of diamond films by Cu ion implantation.

In this work, microcrystalline diamond (MCD) films are implanted by Cu ions combined with post rapid annealing at 500℃ in N_2 for obtaining high electrical conductivity and superior EFE properties. The modifications to the microstructure of these films due to Cu ion implantation/annealing processes are investigated in detail by using several common techniques. The role played by the implanted Cu ions to enhance the EFE properties of MCD films is discussed.

In our experiment, the MCD films were grown on n-type silicon substrates by a home-made microwave plasma chemical vapor deposition apparatus in H_2(98.6%)/CH_4 (1.4%) plasma excited by 7 kW with the total gas flow rate 406 sccm at a total pressure 105 torr for 10 h. Cu ion implantation was performed at room temperature at 100 keV with a fluence of 1.0×10^{17} ions/cm^2. After implantation, the samples were cut into small pieces and subjected to rapid annealing in N_2 atmosphere at 500℃ for 1 h, which are designated as MCD_{Cu}/annealing. The pristine MCD films are designated as MCD_P.

The surface morphologies and the crystal structure were investigated by using a scanning electron microscope (SEM) and a grazing x-ray diffractometer (GXRD). The crystalline quality and the chemical bonding structures of the MCD films were characterized by the Raman spectroscopy ($\lambda = 632$ nm) and x-ray photoelectron spectroscopy (XPS). Hall measurements were carried out in a van der Pauw configura-

*Supported by the National Natural Science Foundation of China under Grant No 11405114, and the Natural Science Foundation of Shanxi Province under Grant No 2015021065.

**Corresponding author. Email: shenyanyan@tyut.edu.cn; yushengwang@tyut.edu.cn

© 2016 Chinese Physical Society and IOP Publishing Ltd

tion (Accent HL5500 Hall System) to observe the conducting behavior of these films. The EFE properties of the films were measured with a parallel plate configuration at room temperature in a vacuum ($\sim 10^4$ Pa), in which the distance of cathode (MCD films) to anode (indium tin oxide coated glass) was 300 μm.

Table 1. Comparison of conducting properties for kinds of diamond films measured by the Hall system.

Materials	Surface resistance (Ω/sq)	Hall mobility ($cm^2V^{-1}S^{-1}$)	Carrier density n (cm^{-3})	References
MCD_p	86.26	0.686	1.05×10^{15}	This study
MCD_{Cu}/annealing	1.611	290	1.3×10^{18}	This study
Ag ions implanted FSD/annealing	2.17×10^3	34.76	1.73×10^{13}	Ref. [11]
O^+-implanted UNCD films	25.19	11.4	2.17×10^{16}	Ref. [12]
N_2 doped UNCD		1–2	1×10^{20}–1×10^{21}	Ref. [13]

Hall effect parameters are important to characterize the electrical properties of semiconductor materials.[9–11] Comparison of carrier concentration and Hall mobility for kinds of diamond films are listed in Table 1. The MCD_p film shows high surface resistivity of 86.6 ohm/sq with carrier concentration of 1.05×10^{15} cm^2 and low mobility of 0.686 $cm^2V^{-1}S^{-1}$. The surface resistance of MCD_{Cu}/annealing film decreases to 1.611 ohm/sq, and its carrier concentration increases to 1.3×10^{18} cm^2. Moreover, the Hall mobility of the MCD_{Cu}/annealing film attains to 290 $cm^2V^{-1}S^{-1}$, which is much larger than that of the Ag-implanted FSD film,[12] O^+-implanted UNCD films,[13] and N-doped diamond films,[14] etc. These results indicate that Cu ion implantation/rapid annealing could efficiently improve the electrical properties of diamond films.

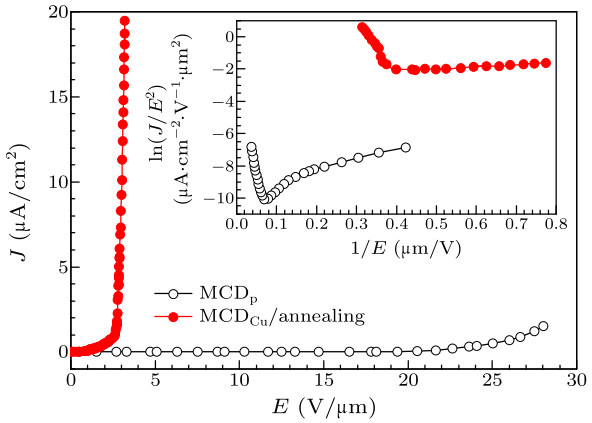

Fig. 1. EEF properties (J_e–E curves) of MCD_p and MCD_{Cu}/annealing films with the inset showing the corresponding F–N plots.

Figure 1 gives the EFE properties of the MCD films with the corresponding F–N plots shown in the inset. The turn-on field (E_0) is designated as the interception of the high- and low-field line segments of the F–N plots.[15] Owing to the higher resistivity and nonuniformity of the diamond grains, the MCD_p film exhibits a high turn-on field (E_0 = 17.1 V/μm) and low current density. The process of Cu ion implantation combined with the subsequent 500℃ annealing remarkably improves the EFE properties of the MCD films, which are evidently due to the increase of conductivity and Hall mobility of the film. The value of E_0 for the MCD_{Cu}/annealing film decreases to 2.6 V/μm, while the EFE current density increases from 1.7 μA/cm^2 at an applied field of 28.1 V/μm (MCD_p film) to 19.5 μA/cm^2 at an applied field of 3.5 V/μm.

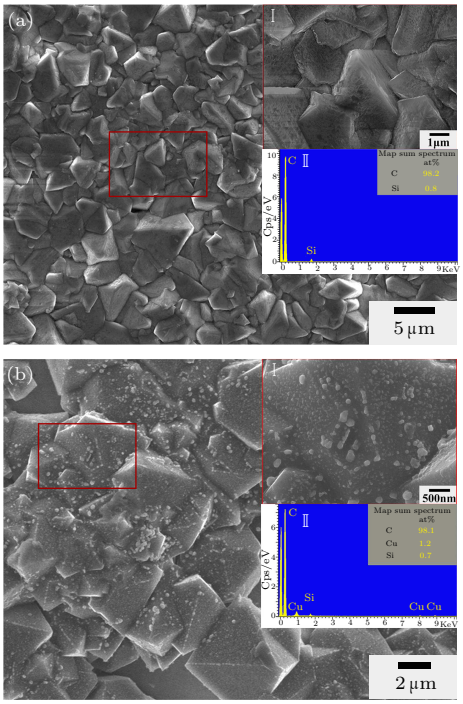

Fig. 2. Top-view SEM images of MCD surfaces with inset I showing the close views and the inset Ⅱ showing the EDX spectrum for the elemental composition of the corresponding FESEM image of (a) MCD_P and (b) MCD_{Cu}/annealing films.

The surface morphologies of the samples detected by SEM are shown in Fig. 2. The MCD_p film shows good continuity and compactness with an average grain size about 3 μm. the surface morphology of the MCD films is remarkably altered by high fluence Cu ion implantation and the subsequent 500℃ rapid annealing and its cover of nanometer scale particles reveals the formation of Cu NPs. The energy dis-

persive x-ray spectroscopy spectrum corresponding to the SEM image of MCD_{Cu}/annealing films (Fig. 2(b)) clearly shows the Cu peak, indicating the Cu presence in the films, whereas the spectrum corresponding to the MCD_p film shows the presence of C and Si only (Fig. 2(a)).

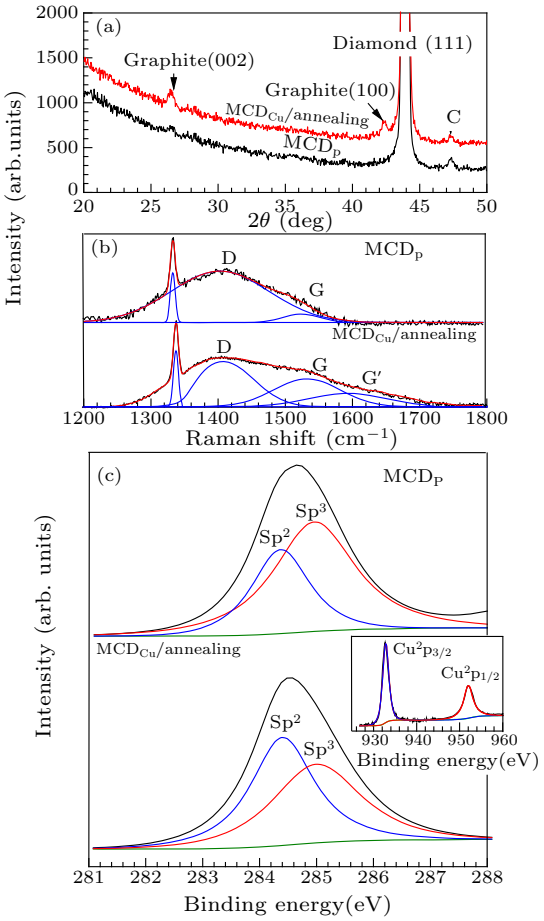

Fig. 3. (a) GXRD, (b) Raman and (c) XPS spectra, patterns of MCD_p and MCD_{Cu}/annealing films.

GXRD patterns (Fig. 3(a)) present a sharp diffraction peak at $2\theta = 43.92°$ for MCD diamond, which can be assigned to plane (111) of the diamond.[12] The appearance of the weak graphite (111) peak ($2\theta = 26.3°$) and graphite (100) peak ($2\theta = 42.2°$) reveals the existence of graphitic content in the MCD_{Cu}/annealing film.[11] Although it is difficult to identify directly the existence of Cu NPs for the Cu (111) peak has almost the same peak position ($2\theta = 43.3°$) with the diamond (111) peak, the significant Cu $2p_{3/2}$ and Cu $2p_{1/2}$ peaks from the $UNCD_{Cu}$/annealing film (the inset in Fig. 3(c)) indicate the formation of Cu NPs. The effect of Cu ion implantation/rapid annealing on altering the bonding characteristics of MCD films are investigated by using the Raman spectroscopy (Fig. 3(b)). Both the Raman spectra show the well-defined diamond peak (sp^3-bonded carbon) at approximately 1332 cm^{-1}. The broad band in the region of 1350–1600 cm^{-1} indicates the existence of non-diamond phase. By using the multi-peak Lorentzian fitting method, this broad band can be deconvoluted into two subpeaks, that is, the D-band (1399 cm^{-1}) and the G-band (1530 cm^{-1}) which assign to the disorder/a-C phases and graphites, respectively.[16] Moreover, a peak near 1600 cm^{-1} (G'-band) appears in the MCD_{Cu}/annealing film, and shows the formation of nanocrystalline graphite in the films.[17] Actually, the increase of the IG/ID values (from 0.161 to 0.603) and the appearance of G'-band imply that part of disorder/a-C phases are converted into graphitic phases due to the Cu ion implantation and rapid annealing processes. The C 1s photoemission spectra of the MCD films investigated by XPS microscopy are shown in Fig. 3(c). The data are fitted with the Lorentzian peaks with binding energies at 284.4 eV and 285.0 eV, corresponding to sp^2 C=C and sp^3 C–C bonds, respectively. In MCD_P films, sp^3 C–C bonding is predominant with the peak intensity of 55.3% accompanied by sp^2 C=C intensity of 36.7%, whereas sp^2 C=C peak is predominant with the peak intensity of 71.5% in the MCD_{Cu}/annealing films. This increase in sp^2 content further confirms that more sp^2-bonds have been introduced in the near surface region of the MCD film after Cu ion implantation and rapid annealing in 500℃.

Based on the above results from SEM, GXRD, Raman and XPS measurements, the conduction mechanism for the improved conductivity could be discussed as follows: (1) The Cu ion implantation and rapid annealing result in the formation of electron-rich Cu NPs on the MCD films, which could act as conductive paths, permitting charges to pass through them easily. (2) During the annealing, these Cu NPs catalytically convert the less conducting disorder/a-C phases into graphitic phases and provoke the formation of high-electron-mobility nanographitic phases in the films. Consequently, the electrons are transported easily through the graphitic phases and Cu NPs as well as through the conduction channels of the diamond grains to the emitting surface, then they emit to vacuum without any difficulty as the diamond surfaces are negative electron affinity in nature. Hence, we deduce that the formation of Cu NPs and the increase of graphitic phases are the actual factors for the enhanced EFE properties of the MCD_{Cu}/annealing films.

In summary, a possible way of fabricating high-field emitting MCD films due to Cu ion implantation is demonstrated. The MCD_p film shows comparatively inferior EFE properties that are ascribed to the a-C phases formed in the boundaries of the diamond grains, which hinders the transportation of electrons. As for the MCD_{Cu}/annealing films, the formation of Cu NPs and the introduction of nanographitic phases

in the diamond grains advance the conducting nature of the films, which result in the enhancement of EFE properties. The present study shows the possibility of using high fluence Cu ion implantation and rapid annealing processes to improve the EFE of diamond.

References

[1] Yamaguchi H, Masuzawa T, Nozue S, Kudo Y, Saito I, Koe J, Kudo M, Yamada T, Takakuwa Y and Okano K 2009 *Phys. Rev.* B **80** 165321
[2] Lv F X 2003 *Physics* **32** 383
[3] Beloborodov I S, Zapol P, Gruen D M and Curtiss L A 2006 *Phys. Rev.* B **74** 235434
[4] Gruen D M 1999 *Annu. Rev. Mater. Sci.* **29** 211
[5] Sankaran K J, Chen H C, Lee C Y, Tai N H and Lin I N 2012 *Appl. Phys. Lett.* **101** 241604
[6] Birrell J, Gerbi J E, Auciello O, Gibson J M, Gruen D M and Carlisle J A 2003 *J. Appl. Phys.* **93** 5606
[7] Arenal R, Bruno P, Miller D J, Bleuel M, Lal J and Gruen D M 2007 *Phys. Rev.* B **75** 195431
[8] Talapatra S, Cheng J Y, Chakrapani N, Trasobares S, Cao A, Vajtai R, Huang M B and Ajayan P M 2006 *Nanotechnology* **17** 305
[9] Zhu L L 2015 *Chin. Phys.* B **24** 016201
[10] Zhang H, Yang S Y, Liu G P, Wang J X, Jin D D, Li H J, Liu X L, Zhu Q S and Wang Z G 2014 *Chin. Phys.* B **23** 017305
[11] Zeng L, Xin Z, Chen S W, Du G, Kang J F and Liu X Y 2014 *Chin. Phys. Lett.* **31** 027301
[12] Shen Y Y, QiaoY, He Z Y and Yu S W 2015 *Mater. Lett.* **139** 322
[13] Hu X J, Ye J S, Liu H J, Shen Y G, Chen X H and Hu H 2011 *J. Appl. Phys.* **109** 053524
[14] Achatz P, Williams O A, Bruno P, Gruen D M, Garrido J A and Stutzmann M 2006 *Phys. Rev.* B **74** 155429
[15] Wang R Z, Wang B and Yan H 2002 *Physics* **31** 84
[16] Swiatowska J, Lair V, Pereira-Nabais C, Cote G, Marcus P and Chagnes A 2011 *Appl. Surf. Sci.* **257** 9110
[17] Ferrari A C and Robertson J 2000 *Phys. Rev.* B **61** 14095