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# Formation of carbon cluster on the surface of diamond films for improving electron field emission properties

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**Abstract**

The electron field emission properties of the diamond films were significantly improved via the formation of nano-sized carbon clusters on their surface. The microstructures and Raman spectroscopy are markedly altered when the diamond films were coated with a thin layer of Fe/Co films (<10 nm) and then post-annealed at high enough temperature (>800°C). The turn-on field was decreased from 14.8 to 7.6 V/μm and the electron field emission current density was increased more than 2 order of magnitude, from 20 to 2400 μA/cm$^2$, due to post-annealing process. 

*Keywords:* Carbon nanotubes; Diamond films; Electron field emission

## 1. Introduction

Diamond films possess negative electron affinity (NEA) characteristics [1] and are considered to be highly promising for applications in electron field emission devices, such that the related emission properties have been widely investigated [1–3]. However, the electron field emission properties of boron- and nitrogen-doped diamond films [4–9] are still much inferior to that of carbon nano-tubes. In this paper, a novel process was adopted to form nano-tube like carbon clusters on the surface of diamond films, so as to improve their electron field emission properties.

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## 2. Experimental

Diamond films (~1 μm) were grown by a microwave plasma enhanced chemical vapor deposition process. The $CH_4/H_2$ gases with flow rate of 18 sccm/300 sccm (~70 Torr) were excited by 2500 W microwave power. In addition, 1 sccm $B(OCH_3)_3$ and 3 sccm $(NH_3)_2CO$ were incorporated to grow boron/nitrogen co-doped diamond films on silicon substrates. To modify the surface characteristics of the diamond films, a thin layer of $Fe_{0.8}Co_{0.2}$ alloy (<10 nm) was deposited on diamond films using a DC sputtering process, followed by post-annealing in a reducing atmosphere ($N_2$/3% $H_2$) at 500–950°C for 1 h.

The morphology and structure of the diamond films were examined using SEM and Raman spectroscopy (Renishaw), respectively.

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The electron field emission properties of these diamond films were measured using a parallel setup, using 100 μm glass beads as spacer. The current–voltage ($I$–$V$) characteristics of the diamond films were measured by Keithley 237 electrometers. The current–voltage ($I$–$V$) properties of the diamond films were analyzed using Fowler–Nordheim model [10].

## 3. Results and discussion

The as-deposited diamond films contain faceted diamond grains about 0.5–0.8 μm in size (Fig. 1a), possessing unsatisfactory electron field emission properties. It requires $(E_0) = 14.8\,\mathrm{V/\mu m}$ to turn on the electron field emission, achieving only $(J_e) = 20\,\mu\mathrm{A/cm^2}$ at $21.6\,\mathrm{V/\mu m}$ applied field (Fig. 2a). Raman spectrum of these films, as shown in Fig. 3a, is predominated by D-band resonance ($1335\,\mathrm{cm^{-1}}$) and G-band resonance ($1680\,\mathrm{cm^{-1}}$) peaks, the characteristics of the strained diamond grains.

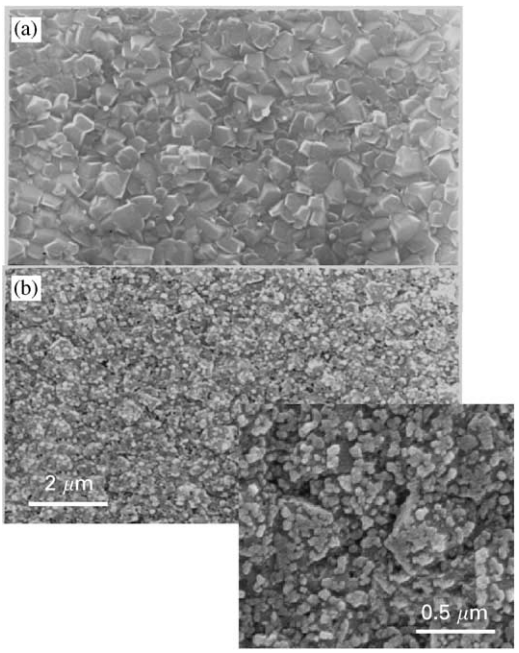


Fig. 1. SEM micrograph of (a) as-deposited diamond films, and (b) Fe/Co-coated and 800°C post-annealed diamond films.

The surface morphology changes markedly when the Fe/Co-coated (~10 nm) diamond films were post-annealed in reducing atmosphere at a temperature higher than 500°C. The tiny clusters (<100 nm) presence on the diamond grains for 500°C post-annealed films, indicating that interaction has occurred between the Fe/Co thin layer and the diamonds. Fig. 2b shows that the turn-on field has been lowered to $(E_0)_{500} = 10.8\,\mathrm{V/\mu m}$ and the electron field emission current density has been increased to $(J_e)_{500} = 100\,\mu\mathrm{A/cm^2}$ at $21.6\,\mathrm{V/\mu m}$ applied field. Raman spectroscopy in Fig. 3b cannot resolve the nature of the reacted layer.

The interaction between the Fe/Co layer and diamonds increases with post-annealing temperature. So do the electron field emission properties of the films. Fig. 2c indicates that post-annealing at 800°C results in the most significant improvement on the materials' electron field emission properties. The turn-on field is further lowered to $(E_0)_{800} = 7.6\,\mathrm{V/\mu m}$ and the electron field emission capacity has been increased more than 2 order of magnitude, i.e., $(J_e)_{800} = 2400\,\mu\mathrm{A/cm^2}$ at $21.6\,\mathrm{V/\mu m}$ applied field, for the 800°C post-annealed diamond films. SEM micrograph in Fig. 1b and the inset reveals the presence of nano-sized carbon clusters on these samples. Raman spectrum shown in Fig. 2c indicates clearly the presence of $G_1' = 1586\,\mathrm{cm^{-1}}$ resonance peak, and the higher order resonance peaks at around $G_2' = 2708\,\mathrm{cm^{-1}}$, the characteristics of graphitic materials, which supports the assumption that interacted layer is nano-sized carbon clusters. Similar interaction occurs when the Fe/Co-coated diamond films were post-annealed at 950°C, but the Fe/Co-to-diamond interaction was much more rigorous such that the carbon soots were resulted and the electron field emission properties of the films are degraded markedly (Fig. 2d).

It should be noted that the presence of Fe/Co layer on diamond surface is of prime importance to induce the formation of nano-sized carbon clusters. The mechanism for the formation of these carbon clusters due to post-annealing process is not clear yet. The most probable process is the dissolution and re-precipitation of carbon species in diamonds into the Fe/Co layer during annealing.

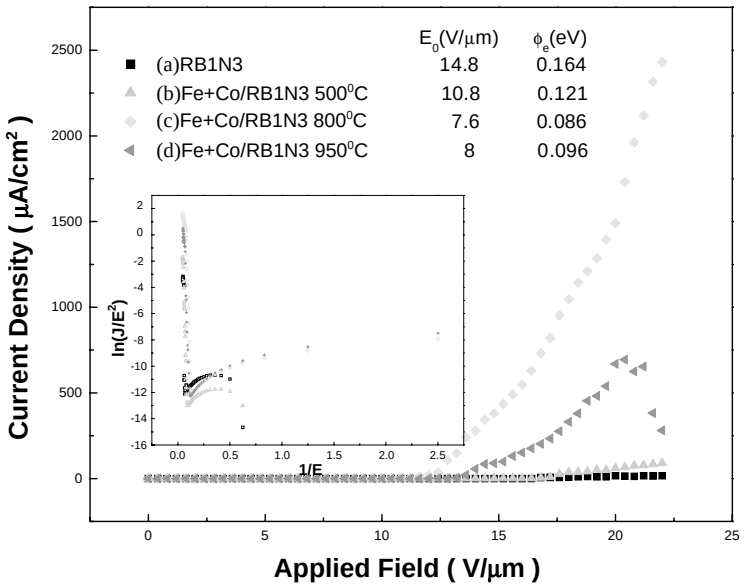


Fig. 2. Electron field emission properties and the corresponding Fowler–Nordheim plot of (a) as-deposited diamond films, and those of Fe/Co-coated and post-annealed diamond films: the post-annealing temperatures are (b) 500°C, (c) 800°C and (d) 950°C.

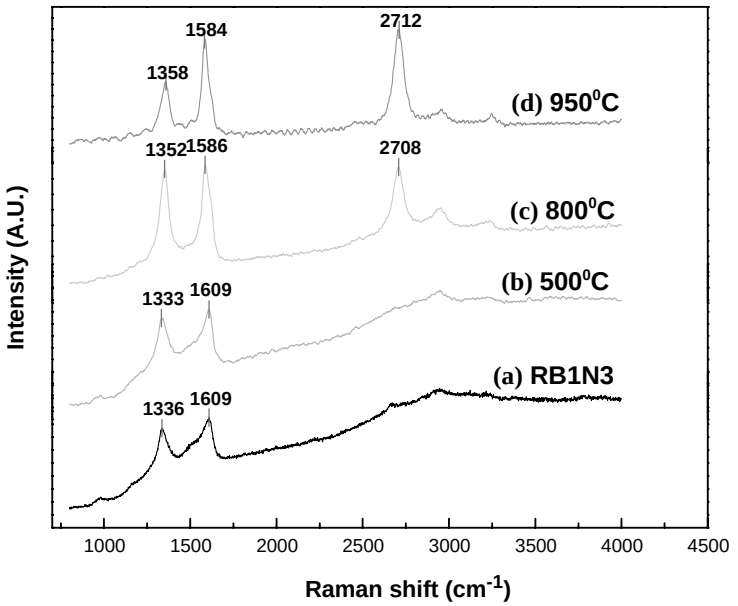


Fig. 3. Raman spectra of (a) as-deposited diamond films, and those of Fe/Co-coated and post-annealed diamond films: the post-annealing temperatures are (b) 500°C, (c) 800°C and (d) 950°C.

## 4. Conclusion

Electron field emission properties of the diamond films were markedly improved, when they were coated with ultra-thin Fe/Co alloy (< 10 nm) and post-annealed at high enough temperature (> 800°C). Such a phenomenon is ascribed to the formation of nano-sized carbon clusters on their

surface. The electron emission current density for the diamond films increased more than 2 order of magnitude, achieving $J_e = 2.4\,mA/cm^2$.

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## References

[1] C.A. Spindt, I. Brodie, L. Humphrey, E.R. Westerberg, J. Appl. Phys. 47 (1976) 5248.
[2] G.G.P. Van Gorkom, A.M.E. Hoeberechts, J. Vac. Sci. Technol. B 4 (1986) 108.
[3] F.J. Himpsel, J.A. Knapp, J.A. Van Vechten, Phys. Rev. 20 (1979) 624.
[4] W. Zhu, G.P. Kochanski, A.E. White, Appl. Phys. Lett. 68 (1995) 1157.
[5] T.K. Ku, S.H. Chen, H.C. Cheng, IEEE Elec. Device Lett. 17 (1996) 208.
[6] J.W. Glesener, A.A. Morrish, Appl. Phys. Lett. 69 (1996) 785.
[7] K. Okano, S. Koizumi, S.R.P. Silva, G. Amaratunga, Nature 381 (1996) 140.
[8] K. Okano, K.K. Gleason, Electron. Lett. 31 (1) (1995) 74.
[9] M.W. Geis, J.C. Twichell, T.M. Lyszczarz, Appl. Phys. Lett. 68 (1996) 2294.
[10] A. Vander Ziel, Solid State Physical Electronics, Prentice-Hall, Englewood Cliffs, NJ, 1968, p. 144.