The hysteresis phenomenon of the field emission from the graphene film

Jiangtao Chen (陈江涛),1 Jun Li (李军),1,2 Juan Yang (杨娟),1 Xingbin Yan (阎兴斌),1,a) Beng-Kang Tay,3 and Qunji Xue (薛群基)1
1State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China
2Graduate University of Chinese Academy of Sciences, Beijing 100080, China
3School of Electrical and Electronic Engineering, Nanyang Technological University, Nanyang Avenue, Singapore 639798, Singapore

(Received 19 August 2011; accepted 3 October 2011; published online 24 October 2011)

A cycle-testing of field emission behavior was carried out for graphene film prepared by electrophoresis deposition followed by annealing at 700 °C in argon atmosphere. The result shows that the graphene film displays a stable field emission characteristic after a period of conditioning. Also, it is interesting that the field emission hysteresis takes place when the film is measured in loops of raised and felled voltages. The possible physical mechanism of this hysteresis phenomenon may be relevant to the desorption/adsorption effect of gas molecules. © 2011 American Institute of Physics. [doi:10.1063/1.3655912]

Graphene is a single layer of sp²-hybridized carbon atoms arranged in a two-dimensional hexagonal lattice. It has unique properties such as high electrical conductivity and carrier mobility, high thermal conductivity, chemical stability, high specific surface area, and mechanical stiffness. Due to these outstanding physical and chemical properties, graphene shows considerable potential applications for biosensors, super thin lubricating films, nanocomposites, supercapacitors and so on. Furthermore, because graphene possesses atomic thickness, high electrical conductivity, high aspect ratio, and good mechanical property, it has been regarded as an ideal cold cathode material for field emission devices. Qian et al. reported that the screen-printed graphene film showed low turn-on field (1.5 V/µm for 1 µA/cm²) and stable emission. Highly wrinkled hydrogen exfoliated graphene film prepared by spin-coating method showed low turn-on field (1.18 ± 0.02 V/µm for 10 µA/cm²) and stable emission. Vertically aligned nitrogen-doped graphene film exhibited enhanced field emission properties compared with pristine graphene film. Wu et al. reported that the electrodeposited graphene film showed excellent electron field emission behaviors, which are comparable or even better than those of carbon nanotubes (CNTs) because of the rich edges and homogeneity of graphene film.

The characteristic of the cold field emission which derived from quantum tunneling effect is not only dependent on the morphology, chemical and thermal stability, mechanical property, adsorption kinetics characteristic, emission site density, electrical conductivity, and work function of the cathode materials but also the conditions (vacuum, temperature, and distance between cathode and anode) of the measurement. Therefore, understanding the inherent physical process and mechanism of the field emission for an emitter is necessary and this can open an avenue for controlling the emission property and fabricating a cold cathode.

Field emission hysteresis is a discrepancy in emission current at the same voltage but applied in the raised and fallen voltage process. This phenomenon has been observed in many cold cathode materials, including CNTs, porous diamond-like carbon (DLC), and AlN films. The reliable results of the field emission could be obtained after “a period of conditioning” (with repeatedly ramped up and down voltages) and the hysteresis is an undesirable characteristic for practical applications. However, the physical mechanism of this hysteresis phenomenon needs further investigated. In this letter, the field emission measurement was carried out for graphene film and the hysteresis from graphene film was reported. The possible physical mechanism of this hysteresis phenomenon was discussed.

The graphene powders were synthesized by chemical conversion from natural graphite by following the methodology that has been reported previously in literature. Graphene film was deposited on n-(100) Si substrate which was coated with Ti transition layer by ion beam sputtering in advance. Before the electrophoretic deposition, the powdery graphene was dispersed in isopropyl alcohol by sonication at 500 W for 30 min and decorated with Mg²⁺ ions (lending positive charges on the surfaces of the graphene sheets). The deposition was carried out at an applied DC voltage of 300 V for 3 min. After that, the film was rinsed with deionized water and dried in air. Subsequently, the graphene film was annealed in argon atmosphere at 700 °C for 2 h. The microstructure of the film was investigated by a Raman spectroscopy (Renishaw inVia, the excitation wavelength of 633 nm) and the surface morphology was investigated by a Field emission scanning electron microscope (FESEM, JSM 6701 F). The field emission characteristics of the graphene film were measured in a parallel-plate-electrode configuration and the vacuum was higher than 1.0 × 10⁻⁵ Pa. In the measurements, the interelectrode distance remained 300 µm. The current-voltage (I-V) characteristics were measured by LabVIEW programming through a Keithley 248 power source with a computer-controlled data-acquisition card. The field emission behaviors were studied by a cycle-testing for 50 loops with the raised and felled voltage between 2~8 V/µm which was showed in Figure S1. The Raman spectrum of the graphene film (Figure S2(a)) shows two prominent peaks at 1325 cm⁻¹ and
1580 cm$^{-1}$, attributing to the D (the mode of $A_{1g}$ symmetry) and G (the $E_{2g}$ mode of sp$^2$ carbon atoms) bands, respectively. Moreover, the graphene film exhibits a loose surface morphology and some exposed sheet edges are observed on the surface (Figure S2(b)).

Figure 1 shows the curve of the current density as a function of the testing time. The anode voltage was increased or decreased by 30 V/step and the current value was recorded as an average of 3 points obtained once the voltage had stabilized. Seen from Figure 1, an obvious increment in current density is observed at the beginning loops and the emission current reaches relatively stable after a period of the conditioning. The increment in current density is possibly due to the desorption of the gas molecules from the graphene surface. The as-prepared graphene film exposed in the air would adsorb oxygen and water molecules. Although the measurements were carried out in a high vacuum chamber, the adsorbed molecules can not be removed completely. If the surface of the emitter material adsorbs gaseous molecules and forms monolayer, the work function will change. More electronegativity of the adsorbate leads to higher work function, and vice versa. It is reported that O terminated at the surface (Figure S2(b)).

The as-prepared graphene film exposed in the air would adsorb oxygen and water molecules. Although the measurements were carried out in a high vacuum chamber, the adsorbed molecules can not be removed completely. If the surface of the emitter material adsorbs gaseous molecules and forms monolayer, the work function will change. More electronegativity of the adsorbate leads to higher work function, and vice versa. It is reported that O terminated at the surface (Figure S2(b)).

The as-prepared graphene film exposed in the air would adsorb oxygen and water molecules. Although the measurements were carried out in a high vacuum chamber, the adsorbed molecules can not be removed completely. If the surface of the emitter material adsorbs gaseous molecules and forms monolayer, the work function will change. More electronegativity of the adsorbate leads to higher work function, and vice versa. It is reported that O terminated at the surface (Figure S2(b)).

Although the Ti transition layer has been deposited for 30 min, the slope difference among three linear segments indicates the changes in the characteristics of the work function and field enhancement factor $\beta$. On the assumption that the morphology of the film does not change during the testing, namely the field enhancement factor $\beta$ keeps constant, based on the equation above, the work function $\phi$ decreases at high electric field.

Figure 3 shows the Fowler-Nordheim plots of the graphene film. The Fowler-Nordheim plot could be divided by three segments. The Fowler-Nordheim in each region exhibits linear characteristic, which is the signature of tunneling process. The slope K of ln(J/E$^2$) versus 1/E plots can be expressed as:

$$K = -6.83 \times 10^3 \phi_{work \ function}^{3/2} / \beta_{enhancement \ factor},$$

the slope difference among three linear segments indicates the changes in the characteristics of the work function and field enhancement factor $\beta$. On the assumption that the morphology of the film does not change during the testing, namely the field enhancement factor $\beta$ keeps constant, based on the equation above, the work function $\phi$ decreases at high electric field. The exposed surface where desorption of the molecules occurs in high electric field is more easy for the electron emission compared with the surface coated by adsorbed monolayer molecules. Furthermore, in high electric field region (I), field- and Joule-heating-induced desorption jointly reduce the work function. In intermediate region (II), the desorption effect is not remarkable as that in high electric field region. And the intrinsic adsorption occurs in low electric field region (III). However, in the field voltage process, the decrease in the current density at a given electric field may derive from the re-adsorption of the molecules. To further verify the desorption/adsorption effect on the field...
emission hysteresis, the J-E curves under different voltage sweep rates were recorded, as shown in Figure 4. The time intervals for collecting each data point were chosen at 0.6, 1, 3, 5, 10, and 30 s while keeping the vacuum level identical. It is reported that the formation of the adsorbed monolayer for water or oxygen in a vacuum of $2.4 \times 10^{-3}$ Pa needs several seconds assuming sticking coefficient of 0.5, and higher vacancy, longer time needs.\(^\text{21,27}\) Here, the vacuum is higher than $1.0 \times 10^{-3}$ Pa, therefore, the formation of the adsorbed monolayer needs a longer time. From Figure 4, it is observed that the field emission hysteresis becomes unnoticeable as the time interval increases. Therefore, we believe that the desorption effect is dominant in the rising voltage process but the adsorption effect is dominant in the falling voltage process. For long time intervals, desorption and adsorption may reach an equilibrium state, so the hysteresis becomes unnoticeable. It is to be noted here that, in long term stability and long time intervals testing, more Joule heat could be generated in the graphene film. However, due to high thermal conductivity of the graphene, the dissipation of Joule heat is quick in the graphene film, which is advantageous for good stability of the field emission.

In conclusion, the field emission hysteresis for the graphene film prepared by electrophoresis deposition is observed during the field emission measurements. The desorption or adsorption of adsorbed gaseous molecules on graphene during the rising or falling voltage process would decrease or increase the work function of the graphene, which possibly leading to the hysteresis.

This work is financially supported by the Natural Science Foundation of China (51002161) and the Top Hundred Talents Program of Chinese Academy of Sciences.

FIG. 3. (Color online) Fowler-Nordheim plots of the graphene film for different testing loops (10, 20, 30, 40, and 50). The Y-axis of curves for 20, 30, 40, and 50th loops are moved down by 1.5, 3, 4.5, and 6, respectively.

FIG. 4. (Color online) The typical J-E curves of the graphene film measured using different time intervals of 0.6, 1, 3, 5, 10, and 30 s.