Residual Gas Components and Their Effect on Field Emission Devices with Nanoscale Emitters

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The emission currents of zinc oxide (ZnO) and carbon nanotube (CNT) cold cathodes show continuous degradation in sealed field emission (FE) devices when the anode voltages are maintained at a constant value; more stable currents are observed when the same cathodes are operated under ultra-high vacuum (UHV) conditions. This shows that ambient gases in the devices play an important role in degrading the emission currents of ZnO and CNT cathodes. To investigate the gas conditions in sealed FE devices, a vacuum system with a quadrupole mass spectrometer (QMS) was employed here. QMS data obtained before and after the gases in the FE devices were removed showed that the residual gases in the CNT-FE panels were H₂, CH₄, CO, and Ar, while in the ZnO-FE panels the residual gases were H₂, CH₄, CO, Ar, and CO₂. It was clear that the residual gases in the two kinds of FE devices were slightly different; this was mainly due to the different cathode materials used in the FE devices. The residual gases affected the emission current of the CNT and ZnO FE devices by changing the work function at the cathode surface; this was confirmed by the F-N curves measured when the same cathodes were tested in the devices and in the UHV chamber.

1. Introduction

Nanostructured materials are considered efficient field emitters for field emission devices (FEDs) and related vacuum microelectronic devices. The reduced dimensions of the nanomaterials result in high local electric fields, and large emission currents can be achieved¹⁾. In the last few years, carbon nanotubes and zinc oxide have been applied as cathode materials for field emission applications^{2,3)}. The simplicity of the methods required for the synthesis of CNT and ZnO mean that these materials have been widely applied in field emission devices. Much attention has been paid to the FE properties of CNT and ZnO, motivated especially by the fact that screen printing methods have been proposed for the low-cost fabrication of large-area FE cathodes.

The field emission from CNTs and ZnO can be described by the Fowler-Nordheim (F-N) equation⁴⁾

$$\ln\left(\frac{I}{V^2}\right) = \ln\left(A\alpha\frac{\beta^2}{\Phi}\right) - B\left(\frac{\Phi^{3/2}}{\beta}\right)\left(\frac{1}{V}\right), \quad (1)$$

where I is the emission current, A and B are constants, α is the emission area, Φ is the work function, V is the applied voltage, and β is the geometric field enhancement factor. This equation shows that the emission current of the emitters depends strongly on the work function and geometry of the cathode surface.

For the application of CNTs and ZnO in commercial FEDs to be feasible, long-term current stability must be ensured. Although CNTs and ZnO have been reported as the most likely candidate for FE devices, some investigations⁵⁻⁹⁾ have reported emission current degradation or failure in these materials. One of the causes for this deterioration is an excessive residual gas pressure inside the sealed FEDs; FEDs require a high vacuum for

their operation¹⁰⁻¹²⁾. The presence of these residual gases in these devices can be due to a number of factors, including the outgassing of emitters and other device materials, residues from the fabrication process, electron-stimulated desorption from surfaces that are bombarded by electrons or positive ions, phenomena associated with extremely high electric fields, dissociation and ion sputtering, and the electron-impact ionization of gases between cathode and anode¹³⁾. These residual gases can influence the field emission current of the FE cathode¹⁴⁾ via adsorption, chemical reactions, or ion bombardment, therefore affecting the emission stability of the cathode. It is therefore important to analyze whether the residual gases do in fact affect the emission current stability of the cathodes and the residual gas components inside sealed FEDs. However, few reports have focused on the real working conditions for CNT and ZnO cathodes.

In this work, an experimental system was set up to measure the emission current stability of the same cathode in a sealed FE device and in a high vacuum (UHV) system, and the ambient gas conditions in sealed CNT-FE and ZnO-FE devices were analyzed.

2. Experimental

The FE-devices used in the experiments were of the diode type, and they were provided with evaporated Ba-getters. A metal-on-glass layer was employed as the anode substrate. The screen-printing method was adopted to deposit the CNT or ZnO paste on the cathode substrate. The ZnO or CNT paste was a mixture of organic binder material, organic solvent, and multi-wall CNTs or tetrapod ZnO. A scanning electron microscope (SEM) was used to characterize the surface morphology of the printed film. **Figure 1** shows the surface morphologies of an as-prepared CNT-cathode and a ZnO-cathode. The anode and cathode glass plates were then sealed using a

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Fig. 1 Surface morphology of an as-prepared CNT-cathode (a), and a ZnO-cathode (b).

conventional glass frit, at a temperature of 430°C, in air. After this, the diode device was pumped at a pressure of 3×10^{-4} Pa for approximately 2 hours at a temperature of 340°C, and was sealed after the pumping process. The device was then installed on the vacuum system using an opening set (consisting of a metal tube with a glass breaking tool) that was mounted on the anode plate.

3. Results and Discussion

To study whether the ambient gases affected the emission current stability of the CNT and ZnO cathodes, it was necessary to use the same cathode in different experiments. In addition, the other working conditions were kept constant while the gas conditions inside the device were varied, so that other factors that might also have led to the emission current degradation of the cathode could be avoided. Thus, only the influence of the residual gases was observed. Following these considerations, an experimental system was set up as shown in **Fig. 2**. It consisted of a vacuum system with a quadrupole mass spectrometer (QMS), the FE device, and the testing apparatus. The vacuum system was composed of a 1.5 l stainless steel vacuum chamber, a sputter ion pump, a UHV ionization gauge (B-A gauge), two UHV valves, and connection tubes. The experiments could be carried out at 400°C, but typically, lower temperatures were used. A mechanical pump and a turbo molecular pump were used for the initial pumping down to the high-vacuum range in the chamber. The total pressure in the chamber was measured using a conventional UHV ionization gauge (B-A gauge). The pressures measured with the B-A gauge are given here as N_2 equivalent pressures.

An aging process was first carried out to obtain better emission stability and uniformity in the device. The FED to be analyzed was then connected to the main vacuum chamber through an opening set. Before the glass wall between the FE device and the vacuum system was broken, the FE properties of the device were measured in terms of the I-V characteristics and the current stability working at a constant anode voltage. The vacuum chamber and the opening sets were then pumped using the mechanical pump and the turbo molecular pump, and meanwhile, the vacuum chamber and the opening set were baked at approximately 250°C for 24 hours, to obtain a good vacuum level. When the baking temperature was reduced to room temperature, valve V_2 was shut off,

Fig. 2 Schematic diagram of the experimental system.

and the system was pumped down using the ion sputter pump. The final gas pressure in the system was 2×10^{-6} Pa. The residual gas spectra were recorded using the QMS mounted on the vacuum chamber. The device was then broken by the opening set, and the residual gases in the device diffused into the vacuum system. The residual gases were measured from the QMS mass spectra obtained before and after the breaking of the device. After being broken, the FE device became a part of the vacuum system that could be pumped on using the ion sputter pump. Thus, the outgassing components of the device under operation could be recognized using the QMS.

After an ultra high vacuum was obtained in the whole system, the FE properties and the emission current stability were measured and compared with those measured in the real device, where the gas pressure was much higher.

Figure 3 shows the emission current stabilities of the CNT and ZnO cathodes, as measured in the sealed FE device, and after the device was opened to the UHV chamber. After continuous operation at a constant anode voltage of 1150 V in the devices for 4 hours, the emission currents reduced from 47 μA to approximately 19.7 μA for CNT cathode, and from 50 μA to 15.3 μA for the ZnO cathode also at an anode voltage of 1150 V. After the device was opened to the UHV system, the anode voltage was applied at 1100 V for CNT cathode and 1030 V for ZnO cathode, so that the initial emission current was close to the value tested in the device. This means lower anode voltage was needed to obtain the same emission current. And experimental data showed

Fig. 3 Current stability of CNT (a), and ZnO (b) FEs in the device, and under UHV conditions.

that lower current degradation was achieved for the same cathode tested in the UHV system. The emission currents reduced from $42.5 \mu\text{A}$ to approximately $41.4 \mu\text{A}$ for the CNT cathode, and from $48 \mu\text{A}$ to approximately $42.5 \mu\text{A}$ for the ZnO cathode, over a period of 4 hours. It was therefore clear that the emission current degradation was much more significant in the sealed FE device than under UHV conditions. The fact that all of the working conditions were kept constant except the gas environment meant that the improvement in the emission current stability was mainly due to the changes in the ambient gases of the cathode. We therefore concluded that the residual gases within the device did in fact impact the emission current stability and the lifetime of the cathodes. Because the gas pressure is higher in real sealed devices than in the UHV system, the presence of more residual gases lead to the degradation of the emission current. The residual gases in the device affect the emission properties in the several ways: First, the adsorption of residual gas molecules on the surface of the emitter increases the work function of the cathode¹⁵⁾, and influences the emission current of the cathode. Second, ambient gas molecules can be ionized through collisions with electrons as they (the electrons) are emitted and move to the anode. The ionized positive charges bombard the cathode under the low applied electric field, and cause ion sputtering and injection at the surface of the cathode, which also changes the work function and geometrical structure at the cathode surface¹⁶⁾. Finally, chemical reactions occur between the cathode material and the residual gases¹⁷⁾, which results in permanent emission current degradation of the cathode. Therefore, more stable currents can be obtained by lowering the residual gas pressure in the device, and more reliable devices can be achieved by enhancing the stability of the cathode material and avoiding the interactions between the cathode materials and ambient gases that can affect the field emission character of the cathodes.

To investigate the residual gases in sealed ZnO-FE and CNT-FE devices, the gases must be introduced into the vacuum chamber, where they can be distinguished by the QMS. Typically, this task is accomplished by making a hole in the glass plate, and permitting the gases to enter the chamber. The residual gas components can then be determined by comparing the gas spectra in the vacuum

Fig. 4 Mass spectra in the vacuum chamber before the CNT-FE device was opened (a), after the device was opened (b), and when the device was working (c).

chamber before and after the device was opened to the system.

Figure 4 shows the mass spectra in the vacuum chamber before the CNT-FE device was opened, after the device was opened, and when the device was working after being opened. From the mass spectra in the vacuum

chamber at these different stages, it was concluded that the residual gases in the sealed CNT-FE device were H₂, CH₄, CO, Ar, and CO₂; some C was also observed in the outgassing components of the CNT-FE device. As shown in the mass spectra in Fig. 4(c), an increase in the C contents was observed during the operation of the CNT-FE device. This indicated the decomposition of the CNTs or organic components during electron emission, or under ion bombardment.

For the sealed ZnO-FE device, the residual gases were H₂, CH₄, CO, Ar, and CO₂, and the outgassing components were composed of H₂, CH₄, CO, O₂, Ar, and CO₂, as shown in Fig. 5. From the mass spectra shown in Fig. 5(c), large amounts of O₂ were observed during the operation of the ZnO-FE device. This component can be produced by the decomposition of ZnO—or the decomposition of organic components in the ZnO paste—under ion bombardment¹⁸. Outgassing O₂ components were not observed among the residual gases for the ZnO-FE device. The outgassing mass spectra were measured using QMS. The active component of O₂ was finally pumped away using the getter in the device, and thus O₂ was not observed in the residual gases.

Fig. 5 Mass spectra in the vacuum chamber before the ZnO-FE device was opened (a), after the device was opened (b), and when the device was working (c).

According to the analysis above, it is clear that the residual gases and outgassing components were different for the FE devices using MWCNT emitters and those using tetrapod ZnO emitters. These differences were mainly due to the interaction between the different cathode materials and the ambient gases during the fabrication or operation processes of the device. In the CNT-FE device, where carbon was abundant—due to the disassociation of the CNTs or non-graphitic carbon in the CNT paste, or the evaporation of the CNTs during electron emission¹⁹—chemical reactions between C and CO₂ or O₂ would have led to increases in the amount of CO in the device using a CNT cathode. This would have resulted in an absence of CO₂ in the CNT-FE devices. During the fabrication or operation of the ZnO-FE device, unstable ZnO would have decomposed under heat or ion bombardment. The oxygen ions would then have recombined with carbon monoxide to create new CO₂ molecules, as shown in equation (1). Chemical reactions between CO and ZnO would also have resulted in decreases in the amount of CO, and increases in the amount of CO₂, as shown in equation (2). These kinds of interactions between the ambient gases and cathode materials were directly responsible for the different residual gases measured in the FE devices when different cathode materials were used.

Figure 6 shows the field emission properties of the CNTs and ZnO before and after the device was opened to the UHV system. For the CNT cathode, the turn-on voltage measured in the sealed device was 700 V (at a current of 0.5 μA), and this decreased to 530 V under UHV conditions. The same results were found for the ZnO cathode; the turn-on voltage reduced from 800 V in the sealed device to 700 V under UHV conditions. This result showed that the residual gases in sealed FE devices influence the field emission properties of the CNT and ZnO cathodes in another aspect.

From equation (1), it is clear that $\ln(I/V^2)$ is linearly related to $1/V$. The slope and intercept of the FN proximity curve based on the data plots is decided by the work function (Φ) at the surface of the cathode and field enhancement factor (β). Their relationships can be described as following functions,

$$\begin{cases} \text{intercept} = \ln \left(A a \frac{\beta^2}{\Phi} \right) \\ \text{slop} = -B \left(\frac{\Phi^{3/2}}{\beta} \right) \end{cases} \quad (4)$$

The intercept and slop of the FN plot in Fig. 6(b) and (d) are shown in table 1. Put these data into equation (4), the change of work function and geometrical factor can be obtained which was also shown in **Table 1**. This result shows that geometrical factor reduced for both kinds of cathode after being exposed to UHV condition. The

Fig. 6 IV (a), and FN (b) curves for the CNT cathode, and IV (c), and FN (d) curves for the ZnO cathode, in the sealed device and in the UHV chamber.

Table 1 Relationship between FN characteristics and work function or geometrical factor.

	CNT		ZnO	
	Device	UHV	Device	UHV
Intercept	-5.5	-7.0	-1.04	-1.75
Slope	-5570	-3060	-10509	-8583
Work function	$\Phi_{CNT-device} \approx 3.8\Phi_{CNT-UHV}$		$\Phi_{ZnO-device} \approx 2.4\Phi_{ZnO-UHV}$	
Geometrical factor	$\beta_{CNT-device} \approx 7.5\beta_{CNT-UHV}$		$\beta_{ZnO-device} \approx 1.8\beta_{ZnO-UHV}$	

reduction of geometrical factor will lead to lower emission current. But opposite experimental result has been displayed in Fig. 3. This is mainly attributed to the reduction of work function, which will make it easier to emit electrons.

According to the above discussions, the residual gases in sealed FE devices had obvious effects on the reliability and lifetime of both kinds of cathode materials. Residual gases absorbed on the surface of the cathode and raised its work function. Even the increase of geometrical factor can not balance this degradation. The ambient gas conditions were achieved by making a hole in the device to let gas into the UHV chamber. That is not to say that each kind of residual gas degraded the emission current for the CNTs and ZnO; the degradation of the emission current in the sealed FE devices resulted from the combined effects of all of the ambient gases around the cathode.

4. Summary and Conclusions

The emission current degradation of the same cathode was measured under different vacuum conditions, and it was proposed that the residual gases were responsible for the emission current degradation of the CNT and ZnO

cathodes in sealed FE devices. The residual gases inside the sealed CNT FE device were H_2 , CH_4 , CO , and Ar , while in the ZnO FE device they were H_2 , CH_4 , CO , Ar , and CO_2 . The different cathode materials were directly responsible for the different gas components in the devices. These residual gases changed the work function at the surface of the cathodes through adsorption or ion bombardment, and thus degraded the emission current of the cathodes. Therefore, more reliable devices could be achieved by enhancing the stability of cathode material, and avoiding the interactions between the cathode materials and ambient gases that can affect the field emission character of the cathodes.

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