Residual gas properties in a field emission device with ZnO emitters*

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In this paper, a vacuum system is employed to compare the emission stabilities of the same ZnO cathode in a sealed field emission (FE) device and under ultrahigh vacuum (UHV) conditions. It is observed that the emission current is more stable under the UHV level than in the device. When all conditions except the ambient gases are kept unchanged, the emission current degradation is mainly caused by the residual gases in the sealed device. The quadrupole mass spectrometer (QMS) equipped on the vacuum system is used to investigate the residual gas components. Based on the obtained QMS data, the following conclusions can be drawn: the residual gases in ZnO-FE devices are H_2, CH_4, CO, Ar, and CO_2. These residual gases can change the work function at the surface through adsorption or ion bombardment, thereby degrading the emission current of the cathode.

Keywords: residual gas, ZnO, field emission, degradation, vacuum

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1. Introduction

Nanostructured materials have been widely used as efficient emitters for field emission (FE) devices and relevant vacuum microelectronic devices. The reduced size in the nanomaterials achieves a high local electric field and large emission current.[1] During the last few years, zinc oxide (ZnO) has been synthesized and used as the cathode material for field emission.[2–4] For example, well-aligned ZnO arrays grown on substrates have good FE properties.[5] The screen printing method was proposed to fabricate FE cathodes at low cost and in a large area. This method has promoted the future application of ZnO in FE-based flat-panel displays.[6]

For better application of ZnO in commercial FE devices, long-term current stability is one of the most important aspects that needs to be ensured. Although ZnO is considered as a most promising candidate for FE, its emission current degradation or failure has been reported in the literature.[7] One possible cause of this deterioration is the high residual gas pressure inside. The gas adsorption on a ZnO surface can influence the emission properties by changing the work-function at the surface.[8] The FE properties of ZnO nanorods exhibited in different gas conditions were reported.[9] It was found that O_2 can reduce the emission current of ZnO, while H_2 can enhance the current.[10]

However, few reports have focused on the practical working condition of ZnO cathodes in sealed devices. So in this paper, an experimental system will be set up to measure the emission current stabilities of the same cathode, respectively, in sealed FE devices and in an ultrahigh vacuum (UHV) system. Meanwhile, the ambient gas condition, in the sealed ZnO-FE device, will be analyzed.

2. Experimental details

2.1. Samples

The FE devices used in the experiments were of diode type and provided with evaporated Ba-getters. To start with, a metal layer on glass was employed as an anode substrate. The screen-printing method was adopted to deposit the ZnO paste on a cathode substrate. The ZnO paste was a mixture of organic binder material, organic solvent, and tetrapod ZnO. To remove the organic binders and solvent, the cathode substrate was baked at 420 °C for 6 h. Figure 1 shows the scanning electron microscope (SEM) image of the ZnO emitters. Then, the anode and cathode glass plates were sealed using a conventional glass frit at a temperature of 430 °C in air. Later, the diode device was placed in an oven at a temperature of 340 °C and pumped though the exhaust tube at 3×10^{-4} Pa for about 2 h, and sealed just after the pumping process had ended. The vacuum condition in this device was maintained by the

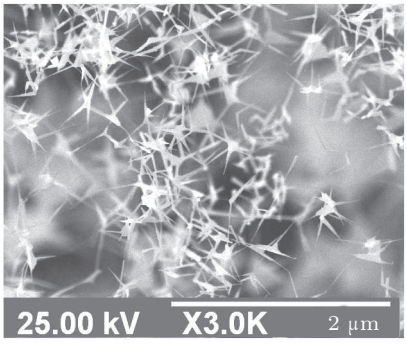


Fig. 1. SEM image of the nano-scaled ZnO.

Ba-getters. Finally, the device was mounted on the vacuum system through an opening set consisting of a metal tube with

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a glass breaking tool, and sealed on the anode plate.

2.2. Experimental system

In order to study whether the ambient gases affect the emission current stability of the ZnO cathodes, the cathodes should be the same. In addition, the working condition, except the ambient gas inside, should be retained as much as possible to avoid other possible effects which may also lead to the emission current degradation of the cathodes. Thus, attention was focused on the influence of the residual gases. Based on the above considerations, an experimental system was set up as shown in Fig. 2, and was composed of a vacuum system equipped with a quadrupole mass spectrometer (QMS) and the FE device together with testing parts. This vacuum system was composed of a stainless steel vacuum chamber of 1.5 liter in volume, a sputter ion pump, a UHV ionization gauge (B-A gauge), two UHV valves, and connection tubes. It could be baked to 400 °C, higher than the temperature used in these experiments. A mechanical pump and a turbo molecular pump were used for the initial pumping down into the high-vacuum range in the chamber. Then the total pressure in the chamber was measured with a conventional UHV ionization gauge (B-A gauge). The pressure measured with the B-A gauge is indicated in N_2 equivalent pressure.

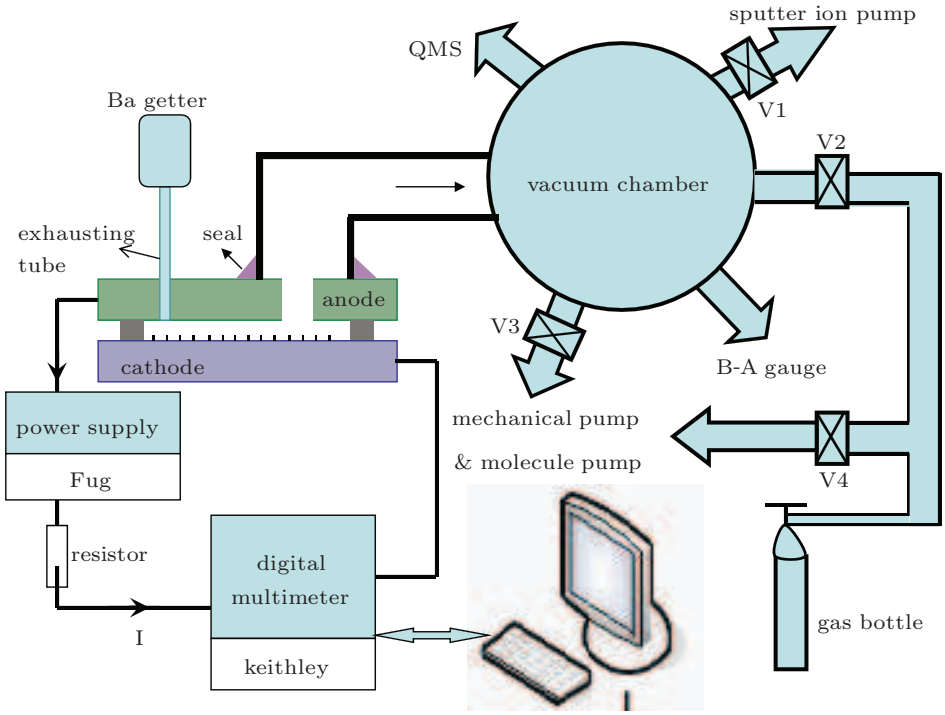


Fig. 2. (color online) Schematic diagram of the experimental system.

2.3. Experimental process

Firstly, an aging process was carried out to obtain a better emission stability and uniformity of the cathode. Then, the FE device to be analyzed was 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 had been measured in terms of the *I*–*V* characteristic and current stability of the device working at the preset anode voltage. Next, the vacuum chamber and the opening sets were pumped by the mechanical pump and the turbo molecular pump, and meanwhile, the vacuum chamber and the opening set were baked at about 250 °C for 24 h to reach a good vacuum level. When the baking temperature was reduced down to room temperature, valve V_2 was shut off, and the system was pumped by the ion sputter pump. The final gas pressure in the system was 2×10^{-6} Pa. The residual gas spectra were recorded by QMS mounted on the vacuum chamber. Then, the device was broken by the opening set and the residual gases in the device diffused into the vacuum system. From the QMS mass spectra obtained before and after the device was broken, the residual gases can be confirmed. After being broken, the FE device became a part of the vacuum system that can be pumped by the ion sputter pump. Finally, the outgassing components of the device under operation can then be recognized by the QMS.

After the ultrahigh vacuum was obtained, the FE properties and the emission current stability were measured and compared with those gained in the practical device with much

higher gas pressure.

3. Results and discussion

To investigate the residual gases in sealed ZnO-FE devices, the gases should be introduced into the vacuum chamber, where they can be distinguished by the QMS. The usual way to accomplish this task is to make a hole in the glass plate and thus the gases can enter into the chamber. The residual gas components can be found by comparing the gas spectra in the vacuum chamber before and after the device has been opened to the system.

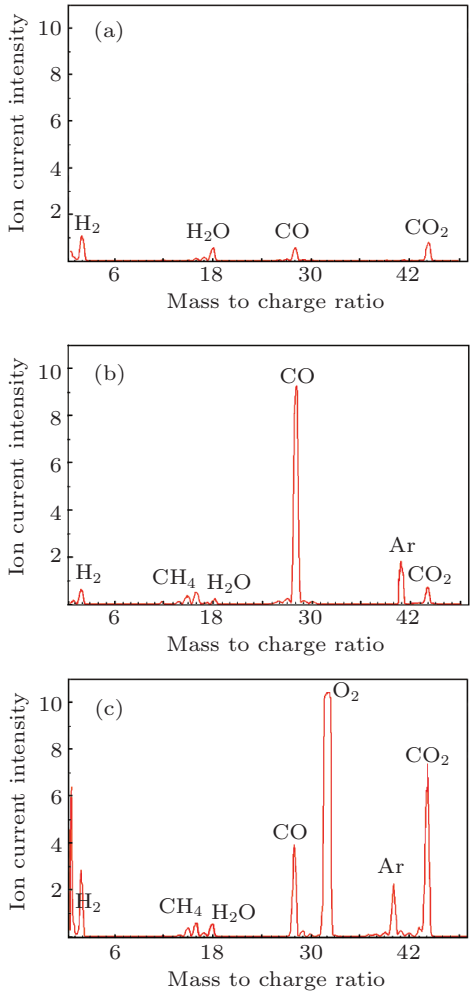


Fig. 3. (color online) The mass spectra in the vacuum chamber before the device is opened (a), after the device is opened (b), and when the device is working (c).

Figure 3 shows the mass spectra in the vacuum chamber before the ZnO-FE device was opened, after the device was opened, and when the device was working at 5.2 V/μm after being opened, respectively. From the mass spectra in the vacuum chamber at different stages, it can be concluded that the residual gases in the sealed ZnO-FE device are H_2, CH_4, CO, Ar, and CO_2, and the outgassing components are composed of H_2, CH_4, CO, O_2, Ar, and CO_2. From the mass spectra shown in Fig. 3(c), the increase in O_2 can be observed during the operation of the ZnO-FE device. In the sealed ZnO device, the active outgassing component of O_2 can be easily pumped away by the getter. Thus, O_2 was not observed in the residual gases.

Figure 4 shows the energy-dispersive X-ray (EDX) spectra of the ZnO paste and organic paste without ZnO after baking. From this figure, it can be observed that most of the organic components in the paste are removed after the baking process. However, the organic binder is not removed absolutely. So, the remaining component will also become the contributor of O_2. In addition, there is another method to produce O_2 from the decomposition of ZnO under ion bombardment.[11]

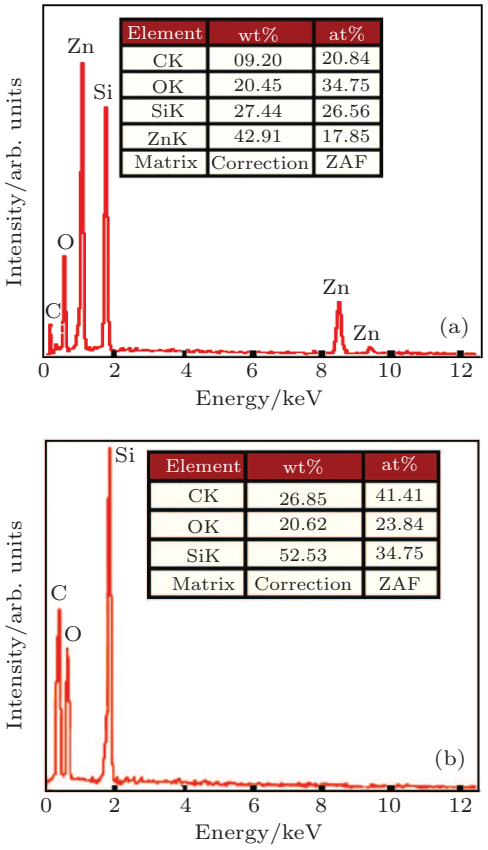


Fig. 4. (color online) The EDX spectra of (a) ZnO paste after baking, and (b) organic paste without ZnO.

According to the above analysis, it is clear that the residual gases and outgassing components are partially different between the FE devices using MWCNT emitters[12] and the tetrapod ZnO emitters. This difference is mainly due to the interaction between different cathode materials and the ambient gases in the fabrication or operation process of the device.

In the CNT-FE device, where carbon is abundant due to the disassociation or evaporation of CNT during electron emission,[13] the chemical reaction between C and CO_2 or O_2 will lead to the increase of CO in the device using the CNT cathode. This will result in the absence of CO_2 in CNT-FE

devices. While during the fabrication or operation of the ZnO-FE device, unstable ZnO will be decomposed by heat or ion bombardment. Then, the oxygen ion recombines with carbon monoxide and creates a new molecule of CO_2 (see Eq. (1)). The chemical reaction between CO and ZnO will also result in the decrease of CO and increase of CO_2, as shown in Eq. (1). These kinds of interactions between ambient gases and cathode materials directly result in different residual gases in FE devices using different cathode materials.

$$\begin{aligned} &\mathrm{ZnO} \overset{\text{decompose}}{\longrightarrow} \mathrm{Zn^{2+}} + \mathrm{O^{2-}}, \\ &\mathrm{CO} + \mathrm{O^{2-}} \longrightarrow \mathrm{CO_2} + 2\mathrm{e}; \qquad (1) \\ &\mathrm{ZnO} + \mathrm{CO} \longrightarrow \mathrm{Zn} + \mathrm{CO_2}. \qquad (2) \end{aligned}$$

Residual gas goes into the vacuum chamber and is pumped away by the sputter ion pump. After a stable gas pressure was obtained under the operation of the sputter ion pump, the emission current of the same cathode that was measured previously was recorded again. Figure 5 shows the emission current stability of ZnO tested in the device and the UHV chamber. From this figure, it can be observed that the currents degraded continuously. In the device, the emission currents reduced from 50 μA to 26.5 μA after 5 hours of continuous operation under an electrical field of 5.9 V/μm. In the UHV chamber, the emission currents reduced from 48 μA to about 41.9 μA for the same period at an electric field of 4.5 V/μm. This is due to the fact that the emission current degradation became slower than that in the sealed FE panels. The improvement in the emission current stability is mainly ascribed to the change in gas condition, because all the working conditions remain unchanged except for the gas environment.

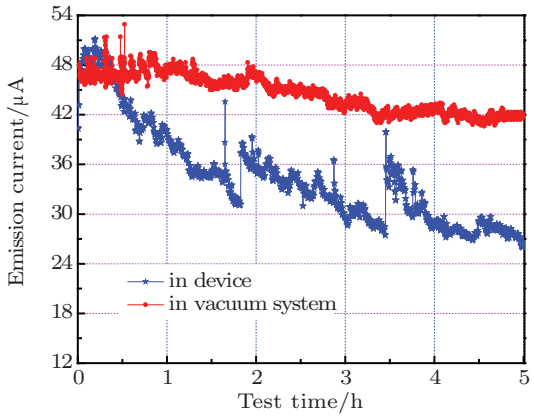


Fig. 5. (color online) Anode current stabilities of the same cathodes tested in different gas conditions.

Figure 6 shows the FE properties of the ZnO cathode before and after the device is opened to the UHV system, and the inset shows the F–N curve. The turn-on electric field is 2.65 V/μm (at a current density of 0.5 μA/cm^2), measured in the sealed device, and decreases to 2.1 V/μm when working in the UHV condition. This indicates that residual gases do influence the field emission properties of the ZnO cathode in another way. Residual gases are absorbed on the surface of the cathode, and change its work function, which can also be seen from the curve slopes in the inset.

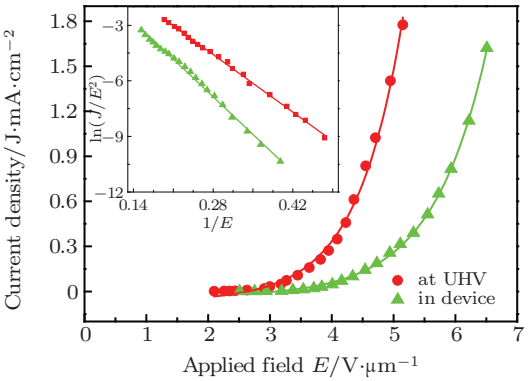


Fig. 6. (color online) The field emission properties of ZnO before and after the device is opened to the UHV system.

So the conclusion can be drawn that the residual gases within the device do influence the emission current stability and the lifetime of the cathode. The residual gases in the device affect the emission properties in several ways. Firstly, adsorption of the residual gas molecule on the surface of the emitter increases the work function of the cathode,[14] thereby influencing the emission current of the cathode. Secondly, ambient gas molecules can be ionized through collision with electrons during electron emission and motion. The ionized positive charge may bombard the cathode under the low applied electric field and cause ion sputter and injection at the surface of the cathode, which changes the work function and geometrical structure at the cathode surface as well.[15] Finally, a chemical reaction occurs between the cathode material and the residual gases,[16] which results in permanent emission current degradation of the cathode. Therefore, a more stable current can be gained by reducing the residual gas pressure in the device. In addition, a more reliable device can be achieved by enhancing the stability of the cathode material and avoiding the interaction between the cathode materials and the ambient gases, which will affect the field emission characteristics of the cathodes.

4. Summary and conclusions

By measuring the emission current degradation of the same cathode in different vacuum conditions, it is proposed that residual gases are responsible for the emission current degradation of ZnO cathodes in sealed FE devices. The residual gases inside a sealed ZnO-FE device are H_2, CH_4, CO, Ar, and CO_2. These residual gases can change the work function at the surface of the cathode through adsorption or ion bombardment, thereby degrading the emission current of the

cathode. A more reliable device can therefore be achieved by enhancing the stability of the cathode material and avoiding the interaction between the cathode materials and the ambient gases that will affect the field emission characteristics of the cathodes.

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