Field emission characteristics of carbon nanotubes under residual gases

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Abstract

The field degradation of carbon nanotube field emitters in diode emission at constant current was demonstrated to be highly dependent upon the presence of residual gases at partial pressures. Upon exposure to a higher pressure of oxygen containing gases, for example, O_2 and CO increased the voltage. Those gases give rise to chemical etching to CNTs emitters. On the contrary, CH_4 affected the emission properties in the opposite direction as decreasing the voltage which was probably attributed to the introduction of adsorbate tunneling states. The mixed gas may cause a combined effect of both adsorbate tunneling states and CNT etching.

1. Objectives and Background

Carbon nanotubes (CNTs) are one of the most promising field emitter materials due to their excellent electrical conductivity and superior chemical and mechanical stability as well as their high aspect ratios.[1,2] Although much effort has been made to commercialize CNT field emitter devices, several obstacles, in particular, emitter lifetime, still remain to be overcome. Even though there are many factors affecting the lifetime of emitters working in a vacuum, residual gases inside a panel would be unarguably one of the most crucial causes. Especially when the CNT emitters and phosphor anode are usually made of pastes, some organic binders can be left even after firing, possibly acting as a source to release gases inside a vacuum panel. Furthermore, nano- or submicrometer-sized particulates frequently involved in the pastes inherently bear a large surface area and then likely have a considerable amount of adsorbed gases released under a vacuum. Thus, the issue of residual gases would be very important to the lifetime of the emission devices prepared from the paste. The residual gases can cause a catastrophic damage to the vacuum microelectronic devices by electrical arcing or ion bombardment onto the cathode or the anode plates. In addition to such a physical damage, some gases can also give rise to chemical etching to CNTs emitters. In particular, oxidative gases are strongly detrimental to the CNT emitters. Composition as well as pressure of the residual gases should be considered in addressing their effect on the emitter lifetime. Since the residual gases are a mixture of several gases of different kinds, effects of individual gases on the field emission characteristics of CNT emitters have to be separately investigated according to their kinds to solve the complex problems related to them. Individual gas species would affect the emission properties of CNTs in different ways, by adsorption or chemical reaction.
This study first analyzed the composition of residual gases inside the vacuum-sealed panel which was composed of a CNT emitter cathode plate, a phosphor anode, and glass spacers, all kept in a vacuum. The residual gas analysis (RGA) data were obtained from the panel electrically operated for 3 days. H_2, CO, CO_2, N_2, CH_4, H_2O, C_2H_6, and Ar were detected, but C_2H_6 and Ar were negligible. The CNT emitter cathode was prepared in a diode structure by screen printing and photolithography of the photosensitive CNT paste.

2. Results

The field emission measurement scheme is shown in Fig. 1. The sample was electrically conditioned in an oxidative ambient to secure uniform emission over a large area by level the height of the protruding CNTs which would first participate in the electron emission. This oxidative electrical trimming would rapidly diminish the electron-emitting CNTs due to Joule heating and burning out under the oxidative ambient, increasing the number of working emitters even though the operation voltage is elevated.[3,4] It is expected that such a electrical oxidative conditioning enhances their emission stability and lifetime. The electrical conditioning was carried out by applying the pulse voltages with the duty ratio of 3.3%, which varied to keeping the constant emission current of 28 μA.

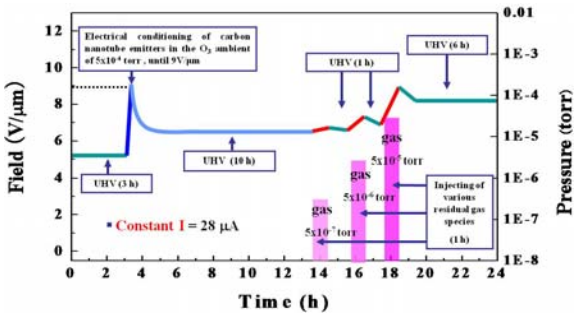

Fig. 1. Experimental scheme to investigate the effect of individual residual gas species on the emission properties of CNTs at three different pressures.

The conditioning was continued until the electric field reached 9 V/μm under the oxidative gas ambient of $5x10^{-4}$ torr. The chamber was then evacuated and maintained at a high vacuum of $\sim10^{-8}$ torr for 10 h while field emission of still 28 μA, which would level off an emission current. Thereafter, each gas species were introduced to a vacuum chamber up to three different pressures ($5x10^{-7}$, $5x10^{-6}$, and $5x10^{-5}$ torr) each for 1 h while electron emission where three different pressure regions were separated by keeping a high vacuum of $\sim10^{-8}$ torr for a 1 h. Here we attempted to study the effect of individual gas species and their pressures on the emission properties at the same time. The emission was terminated 6 h after the third gas exposure was completed.

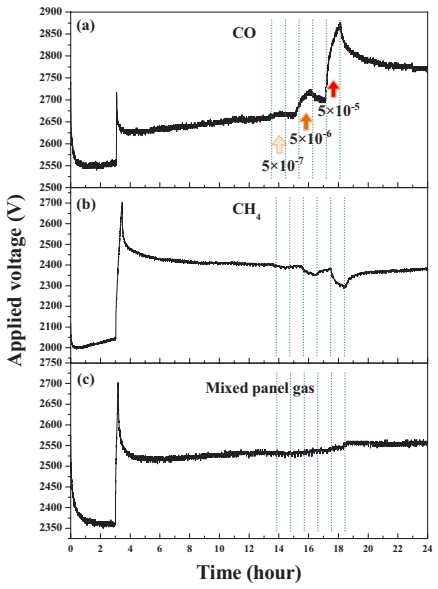

Fig. 2. Variations of voltages applied to keep the constant emission current of 28 μA from CNTs at three different pressures of (a) CO, (b) CH_4, and (c) mixed gas.

Fig. 2 showed the variations of applied voltages to keep the constant current of 28 μA from the CNT emitters in the ambient of CO, CH_4, and mixed gas(CH_4 89.5%, Ar 5.1%, H_2 4%, and CO_2 1.4%). We also performed the same experiment for H_2, N_2, H_2O, O_2, and Ar, but not shown here due to a limited space. Upon exposure to a higher pressure of CO, voltage increased more greatly but dropped more when returning to a high vacuum. It seems that CO adsorbed on the CNT surface does not only increase the work function but also damages CNTs by oxidation. On the contrary, CH_4 affected the emission properties in the opposite direction. Exposure to a higher pressure of CH_4 lowered the voltage more, which is probably attributed to introduction of adsorbate tunneling states.[5] The mixed gas causes a combined effect of both introduction of adsorbate tunneling states and CNT etching. Effects of other gases will be discussed as well.

3. Impact

We analyzed the composition of residual gases inside the vacuum-sealed panel by RGA, investigating the effects of individual gases of different kinds at partial pressures on the field emission characteristics of CNT emitters. This study can provide some meaningful insight into the ways of improving the emission stability and lifetime of emission vacuum device panels.

4. Acknowledgements

5. References

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