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Non-crystallization and enhancement of field emission of cupric oxide nanowires induced by low-energy Ar ion bombardment

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ABSTRACT

The effect of low energy Ar ion bombardment on the structure and field emission properties of CuO nanowires was studied. The morphology and structure were characterized by scanning electron microscopy and high resolution transmission electron microscopy. Non-crystallization of the nanowire was found after bombardment, which was due to the diffusion of the defects induced by knock-on ions. The work function of nanowires decreased after bombardment which was attributed to the preferential sputtering of oxygen. Field emission measurements showed that after bombardment with different energy the turn-on field decreased first and then increased with increasing ion energy. The lowest turn-on field was obtained with the optimal ion energy of 215 eV. The typical turn-on fields of the as-grown samples and samples after Ar ion bombardment with energy of 215 eV were about 6.5 V/μm and 5.25 V/μm, respectively. The lowered field emission turn-on field was attributed to the increase of field enhancement factor and decrease of work function.

1. Introduction

Cold cathodes have the merits of low power consumption, fast response, and long lifetime. They have important applications in various vacuum electronic devices, such as X-ray source [1], mass spectrometer [2], field emission display [3] and microwave tube [4]. Recently, novel quasi one-dimensional nanomaterials, such as carbon nanotubes (CNTs) and semiconductor nanowires are extensively studied for cold cathode application due to their high aspect ratio and good crystallinity [5].

As p-type semiconductor, CuO nanowires have attracted much attention due to their good field emission performance and feasibility of preparation method. CuO nanowires can be synthesized by solution approach [6], catalysis method [7], thermal oxidation method [8], etc. Remarkably, CuO nanowires can be easily synthesized through thermal oxidation under mild temperature [9]. Therefore they can be fabricated as cold cathodes on glass substrate which is important for large area application [10]. Stable and uniform field emission has been achieved from CuO nanowires [11–14]. Application of CuO nanowire field emitter arrays in field emission display has been demonstrated [15].

Bombardment with energetic ion is a post-treatment method which is often adopted by researchers to improve the field emission properties of nanomaterial cold cathode. On the other hand, from the aspect of application, it is also very important to study the effect of ion bombardment on the field emission of nanomaterial cold cathode because cold cathode may suffer from damages induced from ion bombardment while being applied in field emission display [3], neutralizer for ion engine [16], etc. Therefore, to understand how the ion bombardment affects the field emission and find a cold cathode material that is resistant to the ion bombardment is important. Extensive researches have been carried out [17–20]. Most of these researches focus on carbon-based nanomaterials, especially on CNTs [18,21]. Most of these researches showed that after suitable ion bombardment the field emission properties of CNTs can be enhanced which was attributed to cleaner surface, larger field enhancement factor, etc. For example, Hazra et al. found that multiwalled carbon nanotubes with ultra-low energy nitrogen and hydrogen ion irradiation exhibit remarkable field emission property due to high aspect ratio of the irradiated tips and nano-defects induced by irradiation. The turn-on electric field decreased from ∼0.36 V/μm to ∼0.16 V/μm [20]. There are also some literatures which concern about the effect of plasma treatment on CuO nanowires. Zhu et al. used oxygen and argon plasma to treat CuO nanowires [22]. They found that treatment with oxygen plasma could enhance the field emission and attributed this to sharpened morphology, cleaner surface and generation of

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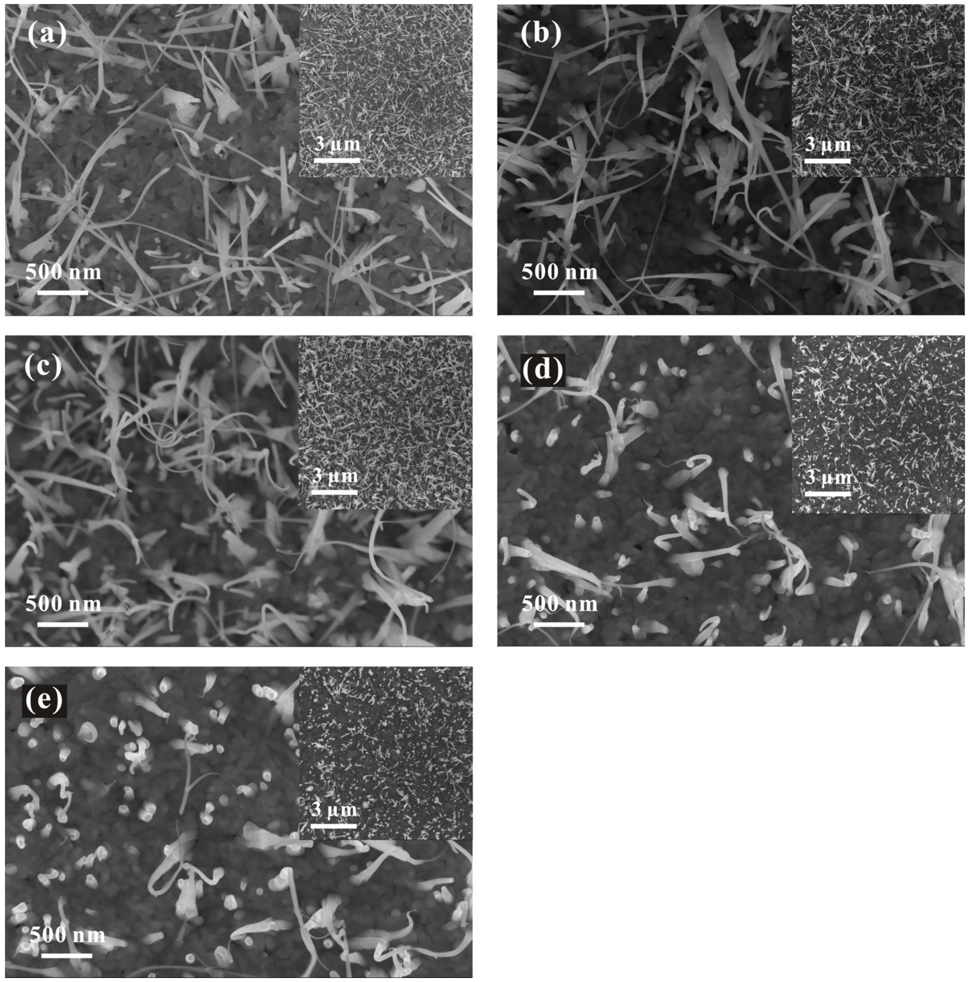

Fig. 1. SEM images of the CuO nanowires, (a) before bombardment, after ion bombardment with energy of (b) 115 eV, (c) 215 eV, (d) 315 eV, and (e) 415 eV. The insets show corresponding low magnification SEM images.

superoxides. But Ar plasma caused deterioration of field emission due to increased work function after treatment. Meanwhile, some results showed that field emission properties of nanomaterial cold cathodes deteriorate. For instance, Cui et al. investigated the effect of ion bombardment on the field emission property of tetrapod ZnO. They found that after a long time ion bombardment the field emission property of ZnO nanostructure deteriorated due to a decrease in the field enhancement factor and the increment of the work function [23]. In summary, ion bombardment has great influence on the morphology, work function, microstructure and defect state of nanomaterial. It is important to discern how these changes happened and how these changes affect the emission properties of nanomaterial cold cathodes.

In this study, the effects of Ar ion bombardment on field emission properties of CuO nanowires were studied. Enhancement in field emission was observed after ion bombardment of proper energy ion. The mechanism accounting for the observed phenomena will be discussed in details.

2. Experimental

CuO nanowire was prepared using a thermal oxidation method [9]. High purity (99.998%, Alfa Aesar) copper foil with size of 0.5 cm × 0.5 cm was used as the substrate. After being cleaned by acetone, ethanol and deionized water, the copper substrate was oxidized in a tube furnace under atmospheric environment. The furnace was heated up to 400 °C and kept at that temperature for 3 h. A layer of oxide with CuO nanowires on top was formed during this process.

Ion bombardment was carried out in a vacuum chamber equipped with a Kauffmann ion source. The base pressure was below 7.4×10^{-6} Torr during the experiment. Ar ions produced

Table 1
Density, height, turn-on field, work function and Cu^{2+} to Cu^{+} ratio of the nanowire samples before and after ion bombardment.

Ion energy (eV)	As-grown	115	215	315	415
Population density (/cm^2)	8.89×10^6	8.82×10^6	8.94×10^6	7.93×10^6	7.73×10^6
Height (μm)	2.0	2.0	2.3	2.1	1.8
Turn-on field (V/μm)	6.5	6.5	5.25	6.35	6.1
Work function (eV)	4.78	4.46	4.56	4.50	4.53
Cu^{2+}:Cu^{+}	–	2.03	0.94	5.53	3.12