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Full Length Article

Electron emission enhancement of long hybrid emitters prepared using ZnO nanowires decorated with Zn nanoflakes

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ABSTRACT

Hybrid emitters consisting of ZnO nanowires decorated with Zn nanoflakes were prepared for electron emission applications. The ZnO nuclei, having a pyramidal shape, were deposited on the ZnO:Al buffer layer, which offered surface protrusions for vertical nanowire growth. The Zn hexagonal nanoflakes, having thicknesses of 15–20 nm, were decorated to increase the conductivity and number of emission sites of the ZnO nanowires. The field enhancement factor increased from 8623 to 18108 and the work function was reduced from 5.3 to 3.35 eV after decorating the nanowires with Zn nanoflakes. A low turn-on field of 0.65 MV/m and high current density of 1.46 mA/cm^2 were obtained. The current density variation measured at 350 V was less than 23% over a measurement time of 180 min.

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1. Introduction

The growth of ZnO nanowires has attracted considerable attention in recent years owing to their wide applicability in the fields of conductors [1], sensors [2], electrochromic devices [3], and electron emitters [4]. Of particular importance are high-aspect-ratio nanowires, which are essential for applications in electron emission [5,6].

The electron field emission capability of nanowires can be enhanced by using a low-work function material, and by improving the crystallinity and morphology of the nanowires. Moreover, increasing the number of electron emission sites and improving the electrical conductivity of the nanowires are also effective methods for enhancing electron field emission. Field emission related research has become increasingly popular and Ding et al. previously reported that the growth of ZnO nanowires on the surface of 3-D graphene foam (GF) can increase the number of emission points as well as the electron tunneling probability of ZnO-GF hybrid emitters [7]. Liu et al. showed that the doping of ZnO nanorods with Ti metal widened the energy gap, decreased the work function, lowered the turn-on field, and improved the electron emission of the nanorods. [8]. Furthermore, a higher field-emission current was obtained from the dendritic ZnO nanowires because of their higher aspect-ratio and greater number of tips [9]. Chen et al. reported that the preparation of an amorphous MgO buffer layer between the ZnO seed layer and Si substrate enhanced electron transport in the seed layer, resulting in increased electron emission from the ZnO nanowires [10].

To enhance field emission, the approaches of lowering the work function, increasing the aspect-ratio, and improving the conductivity have been extensively utilized as summarized above. Other methods, such as nanowire surface decoration also show considerable potential. Singh et al. reported that decorating ZnO nanotapers with corrugated Au islands induced mid-gap states formed at the ZnO–Au interface. These interface states reduced the effective work function of the nanotapers and achieved a significant enhancement of field emission [11]. The Ag/ZnO hybrid cathode exhibited improved electrical conductivity and significantly enhanced field emission owing to the coating of Ag nanowires on tetrapod-like ZnO nanostructures [12]. The decoration of CuO nanoribbons with Ag nanoparticles also led to enhanced field emission [13]. Ding et al. also reported that an ultrathin Pt coating not only modified the linear defects on the surface of the ZnO nanorods, but also created electron emission centers. This resulted in highly conductive paths, which facilitated directed electron emission from the nanorods toward the vacuum [14].

Zn has a lower work function (3.36–4.90 eV) [15] than other metals such as Ag (4.26–4.74 eV) [16], Au (5.10–5.47 eV) [17], and Pt (5.12–5.93 eV) [18], making it suitable for electron emission applications. Furthermore, its low electrical resistivity and low melting point (419.5 °C), make it suitable for thermal deposition [19]. Accordingly, in this study, we investigate decorating the surfaces of ZnO nanowires with Zn nanoflakes. The crystallization and

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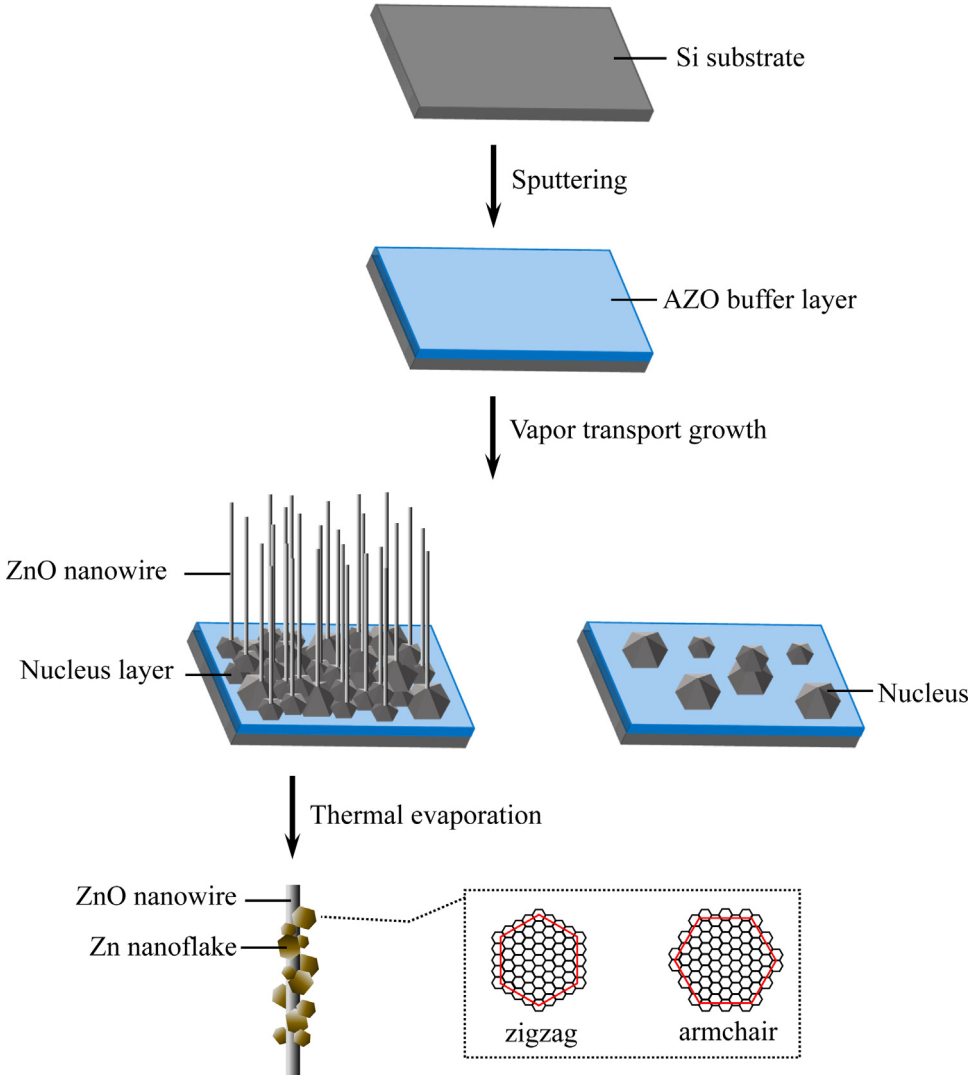

Fig. 1. Flow chart for the growth of Zn nanoflake-decorated ZnO nanowires.

field emission properties of the Zn/ZnO hybrid emitters are investigated and the electron emission mechanism is also discussed.

2. Experimental process

The source materials used in this study were ZnO (Alfa Aesar, 99.99%), Zn (Alfa Aesar, 99.9%), and graphite (CiCa, 99.995%) powders. A $2 \times 2\,cm^2$ (100) p-type Si wafer with a resistivity of 10 Ω−cm was used as the substrate.

To prepare the ZnO nanowires, a 40-nm-thick ZnO:Al (AZO) buffer layer was deposited on a Si substrate by RF magnetron sputtering at 2×10^{-2} Torr in an Ar atmosphere. Subsequently, ZnO nanowires were synthesized by the vapor phase transport method. The ZnO and graphite source powders were mixed at a weight ratio of 1:1. This mixture, along with the AZO/Si substrate, was placed in a quartz tube (diameter = 3 cm) which was sealed at one end and placed in a tube furnace. The AZO/Si substrate was positioned 2 cm downstream of the ZnO/graphite powder mixture. The nanowires were grown at a pressure of 10 Torr in an Ar/O_2 atmosphere at a flow rate ratio of 10. The synthesis parameters of the furnace heating rate, growth temperature, and time were varied in range of 20–40 °C/min, 950–1050 °C, and 20–40 min, respectively. Measurements indicated that the optimal crystallinity and field emission characteristics of nanowires were obtained when the heating rate was set at 30 °C/min.

The deposition of Zn nanoparticles on the nanowires was performed by thermal evaporation at a pressure of 5×10^{-5} Torr. The evaporation source of Zn powder was placed on a tungsten boat, positioned 3–6 cm from the ZnO nanowires and heated using a constant current of 20 A. The nanowires were not heated during the evaporation process and the deposition time was 1–5 min.

The crystallinities and morphologies of the nanowires were analyzed using X-ray diffraction (XRD, SIEMENS D5000, employing Cu-K_α radiation) and high resolution scanning electron microscopy (HR-SEM, JEOL-6330), respectively. Elemental compositions were determined using an energy dispersive X-ray spectroscope (EDS) which was attached to the SEM system. In addition, a real space image of the distribution of atoms was obtained by transmission electron microscopy (TEM, JEOL-3010) with a high-coherence LaB_6 electron gun operated at 300 kV.

The field-emission characteristics of the nanowires were investigated with a diode structure at room temperature in a vacuum chamber at a pressure of 6×10^{-6} Torr. A 130-μm-thick mica spacer was used to isolate the cathode (ZnO nanowires) from the anode (indium-tin oxide (ITO)/glass). Current-voltage characteristics were measured simultaneously using a Keithley 2410 SourceMeter.

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