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Role of work function in field emission enhancement of Au island decorated vertically aligned ZnO nanotapers

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ABSTRACT

In this report, we demonstrate significantly enhanced field emission properties of ZnO nanotapers achieved via a corrugated decoration of Au. Field emission experiments on these Au-decorated ZnO nanotapers showed emission current densities comparable to the best results in the literature. Au decoration of 5 nm also reduced the effective turn-on field to ~0.54 V/μm, compared to the as grown ZnO nanotapers, which showed a turn-on field of ~1.1 V/μm. Tunneling atomic force microscopy measurements revealed a very uniform spatial emission profile in the 5 nm Au decorated nanotapers, which is a basic requirement for any large scale application. We believe that metal induced mid-gap states formed at the ZnO–Au interface are responsible for the observed low turn-on field because such interface states are known to reduce the effective work function. A direct measurement of effective work function using Kelvin probe force microscopy indeed showed more than 1.1 eV drop in the case of 5 nm Au decorated ZnO nanotapers compared to the pristine nanotapers, supporting the above argument.

1. Introduction

The field emission (FE) study from one dimensional (1D) nanostructures is emerging as a promising technology, which can considerably contribute to develop the next generation devices such as electron microscopes, X-ray sources, flat panel displays [1–6] etc. High mechanical stability and large field emission current density at low turn on potential enable 1D nanostructures suitable for the field-emitters [7–9] and in fact, their high aspect ratio enables them as a point electron source. In recent years, several studies on the field emitting properties of various 1D nanostructures like carbon nanotubes [8], ZnO nanowires (NWs) [10], Silicon NWs [11], diamond field emitters [12], ZnO NWs grown on carbon cloths [13] have been taken under consideration. ZnO nanostructures with direct wide band gap (3.37 eV), large exciton binding energy (60 meV), low electron affinity [14] and high thermal stability are promising semiconducting materials for applications in electronic and optoelectronic devices like field emitters [6], diodes [15], lasers [15], phonon-tunnel devices [16], nano-thermometry [17], optical switches [18]. Despite showing potential applications for nanoscale field emitters, still, there are several challenges for developing ZnO based nanoscale field emitting devices, such as the growth of 1D ZnO nanostructures, achieving high emission current density with low turn-on field, high emission efficiency. Recently, the field emission properties of ZnO nanostructures like nanowires [19], nanoneedles, nanocavities, bottle shaped [20], branched nanowires [21], nanowires on carbon cloth [22] are widely studied. Literature suggests that the FE properties of ZnO nanostructures depends on their work function, geometry and surface defects [20,21,23].

Since, the modifications in surface electronic states lead to change the effective work function φ_{eff} (Tunnelling barrier height) of ZnO nanostructures (NS), and are achievable by various techniques like annealing in different ambient [24], Hydrogen plasma treatment [25], coating with different metallic nanoparticles [26,27]. A recent report by Ghosh et al. [28] showed that lowering the work function of ZnO nanostructures grown by chemical vapour deposition (CVD) can lead to a better field emission behaviour at lower threshold fields. For CVD growth technique high-temperature, precise control over the vapors of precursors, a sophisticated and high cost equipment are required. The high temperature requirement, restricts the growth of NS on different

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substrates which have low melting point. Except that, most of the time the CVD grown nanostructures are randomly oriented, while for nanoscale device fabrication well aligned, mechanically stable and efficient nanostructures are required. Hydrothermal technique is widely used for the growth of ZnO NS, which requires very low growth temperature (<100 °C) compare to CVD. The required low temperature allows the growth over variety of substrates which is essentially desired for fabricating various devices for different applications. In hydrothermal technique, the pre growth deposited seed layer favors the growth of vertically aligned ZnO nanostructures. In addition, the low-temperature growth induces more surface defects (V_{Zn}, V_O, Zn_i), which can improve the field emission of ZnO nanostructures [23]. In this work, we studied the effect of work function on field emission characteristics of ZnO nanotapers by mapping contact potential difference of as-grown nanotapers (Sample A) and nanotapers coated with Au films of two different thicknesses of 3 nm and 5 nm (Samples B and C) by using Kelvin probe microscopy (KPFM). We also compared the local conductance of as grown nanotapers with 5 nm thick Au coated nanotapers by performing tunneling atomic force microscopy (TUNA) measurements.

2. Experimental details

Vertically aligned ZnO nanotapers used in this study were synthesized by hydrothermal process [29]. The nanotapers were grown by placing the seeded substrate in aqueous solution of precursors (zinc nitrate and Hexamethylenetetramine) of 0.01 M molar concentration each. After subsequent immersion of substrates, the solution was allowed to react at 90 °C for 3 h. The Si (100, P-type) substrate used in this study contained a seed layer of ZnO thin film (30 nm) deposited by pulsed DC magnetron sputtering system. The seed layer provides nucleation points for vertical growth of nanotapers and efficiently lowers the interfacial energy between the ZnO nucleation, the substrate and the nucleation barrier, thus facilitating the growth of smaller diameter nanotapers [30]. After the subsequent growth of nanotapers, samples were rinsed in deionized water to remove the residuals from the surface. Later on, at a base pressure 2×10^{-7} mbar, Au layers of two different thickness ~3 and 5 nm were deposited on vertically aligned nanotapers by using electron beam evaporation technique. Due to the uneven surface and rotation of the substrate (20 rpm) during deposition, Au formed islands on all faces of the nanotapers.

Structural analysis of nanotapers was performed using Field Emission Scanning electron microscope (FESEM) and X-ray diffraction using synchrotron radiation of wavelength 0.8293 Å. The presence of Au on nanotapers was confirmed by performing elemental analysis using energy dispersive X-ray spectroscopy (EDX) attached with FESEM system. The field emission measurements were recorded at room temperature in a standard vacuum chamber evacuated to 4×10^{-7} mbar. The Copper cathodes of area ~0.05 cm^2 were used to collect electrons. For the field emission measurements, samples were attached to the bottom cathode with a copper tape and emission *I–V* curves were recorded at a fixed spacing (100 μm) between sample and cathode. Both the KPFM and tunneling atomic force microscopy experiments were carried out at a user defined lift height of 40 nm by using Pt coated Si tip (radius ~ 30 nm) attached to an atomic force microscope (MFP-3D, Asylum Research).

3. Results and discussion

Fig. 1(a) shows FESEM image of as grown nanotapers. The cross sectional FESEM image of Au-decorated (5 nm) nanotapers shown in Fig. 1(b) shows that all nanotapers are vertically aligned. In addition, the bright spots on nanotapers observed in Fig. 1(b) are from Au islands, as confirmed by EDX analysis shown in Fig. 2(a). Fig. 2(b) shows grazing angle XRD patterns of samples A and C using synchrotron radiation source. In both XRD patterns, we observe that (0 0 *l*) Bragg diffracted peak dominates over (1 0 1) peak. The (0 0 *l*) diffracted peak indicates that (0 0 1) planes of nanotapers are parallel to basal plane of Si substrate. The formation of preferentially oriented nanotapers suggests that at growth stage, the value of surface free energy is minimum for the ZnO (0 0 2) plane [31]. Additionally, in X-ray diffraction pattern of sample C, an extra Bragg diffracted peak of Au (1 1 1) appears, which is a clear indication of the presence of Au on nanotapers. The inset of Fig. 2(b) shows that (0 0 2) planes of 5 nm Au decorated nanotapers exhibit a shift towards higher 2θ value, which is an indication of the evolution of compressive strain along *z* axis of Au decorated nanotapers, and is calculated ~(−0.003547) by using following relation:

$$\varepsilon_z = \frac{d_1 - d_0}{d_0}$$

where ε_z, d_1 and d_0 are the strain along *z* direction, interplanar spacing of Au decorated and pristine nanotapers, respectively. Additionally, a similar Bragg diffracted Au (1 1 1) peak was also observed for 3 nm Au decoration and in addition we didn't observe any significant shift in its (0 0 2) peak (Not shown here).

Fig. 3 summarizes the field emission results obtained from samples A, B and C. Fig. 3(a) shows the systematic observation of field emission current density versus applied electric field (*J–E*) of samples A, B, and C. To ensure stable emission from all samples, we applied 10 bias cycles for recording each data set. In Fig. 3(a), we observed that Au decoration enhanced the field emitting properties of ZnO nanotapers. From *J–E* plots it's shown that at $J \sim 100$ μA/cm^2, the turn on field decreases with increasing the thickness of Au film, and are found ~1.1 V/μm, ~0.97 V/μm and ~0.54 V/μm for samples A, B and C respectively. From *J–E* plots, the observed threshold field (*E* required to achieve $J \sim 0.2$ mA/cm^2) for samples A (~1.24 V/μm), B (1.12 V/μm) and C (~0.7 V/μm) are lower than previous reported values [32,44]. To further analyze the field emission properties of nanotapers, we applied Fowler–Nordheim (FN) theory [31], which describes the relation between the emission current density *J* and local field E_{local} near by the emitting surface [20].

$$E_{local} = \beta E_{app} = \frac{\beta V}{d} \quad (1)$$

where *V* is applied potential, *d* is inter-electrode separation and β is field enhancement factor. The relation between *J* and E_{app} is described by the FN equation as follows [31]:

$$J = A\left(\frac{\beta^2 E_{app}^2}{\phi}\right)\exp\left(\frac{-B\phi^{3/2}}{\beta E_{app}}\right) \quad (2)$$

where *J* is the emission current density (mA/cm^2), E_{app} is applied electric field between the electrodes (V/μm), $A = 1.56 \times 10^{-10}$ AeV V^{-2}, $B = 6.83 \times 10^3$ $VeV^{-3/2}$/μm, φ (eV) is the barrier height of emitting surface [33]. The β is large for tip geometries and 1 for flat surfaces. Fig. 4(b) and (c) shows the F–N plots ($1/E_{app}$ vs $\ln J/E^2_{app}$) for pure and Au decorated (3, 5 nm) nanotapers respectively. The FN plots were fitted by a straight line, which indicates the applicability of F–N mechanism and from there β is calculated by using following relation:

$$S_{FN} = \frac{-B\phi^{3/2}}{\beta} \quad (3)$$

where S_{FN} is the slope of F–N plot, $B = 6830$ V/(e$V^{3/2}$ μm) and φ (eV) is the barrier height of emitting surface. Within the above intervals of *J*, the calculated S_{FN} values for as-grown and Au decorated nanotapers (3, 5 nm) are −7.561, −4.04261 and −2.097684, respectively. For calculating β values of samples A, B and C, we used