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Novel pulsed electron deposition route to ZnO nanowire arrays

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ABSTRACT

Well aligned ZnO nanowire arrays with uniform size are grown on Au-coated indium tin oxide substrates via a novel pulsed electron deposition (PED) technique. These nanowires have single-crystal hexagonal wurtzite structure and are grown along [0 0 0 1]. Au nanoparticles are found at the tip of the nanowires, indicating the growth process follows a typical vapor–liquid–solid mechanism. It is also found that the aligned ZnO nanowire arrays can be grown on Au-coated 6H-SiC and Si substrates, revealing that the PED technique is applicable for growth of ZnO nanowires on some common substrates. All the photoluminescence spectra of the ZnO nanowires reveal strong ultraviolet emission bands, indicating that the high-quality ZnO nanowires can be fabricated via the novel PED technique.

1. Introduction

Zinc oxide (ZnO), a direct wide band gap (3.37 eV) semiconductor with large exciton binding energy (60 meV), is considered as one of the most important semiconductors for its wide applications in optoelectronics, sensors and actuators [1–5]. In recent years, one-dimensional (1D) nanowires have attracted a great research attention due to their wide usage as nanopiezotronics nanosensors, nanogenerators, nanoelectronics and nanolasers [6–14]. Moreover, the aligned ZnO nanowires are a promising candidate for field emission and light emitting [15,16]. Up to now, numerous synthesis methods, mainly divided into two routes: solution-based syntheses, e.g. hydrothermal methods [17–20] and vapor-based syntheses typically as conventional chemical vapor deposition [17,21–23], have been developed to synthesize various ZnO nanowires. Besides these mentioned methods, some special techniques for growth of epitaxial films including metalorganic chemical vapor deposition (MOCVD) [24,25], laser ablation (LA) [26], and pulsed laser deposition (PLD) [27] have been extended to fabricate well aligned ZnO nanowire arrays assisted by metal catalysts. The merits of the epitaxial film-related techniques are the well controllable growth properties and excellent crystalline nature of the as-synthesized ZnO nanowires. Recently, pulsed electron beams deposition (PED) is emerged as a novel film technique, and has been widely used in the preparation of poly-component oxide films [28]. PED can produce high energy density electron beam on the surface of target, and the thermodynamical properties of target such as melting point and specific heat are not important in the PED process, which redounds to synthesize high-quality epitaxial films. Lei et al. [29] utilized Au catalyst-assisted PED technique to fabricate GaN nanowires on the 6H-SiC substrates. We deduce that the method may be extended to prepare other semiconductor nanowires such as ZnO. In this paper, we utilize a novel PED method to fabricate well aligned ZnO nanowire arrays on Au-coated indium tin oxide (ITO), 6H-SiC and Si substrates, respectively. The structure and photoluminescence (PL) properties of the nanowire arrays are investigated in detail.

2. Experimental

Well aligned ZnO nanowire arrays were grown on Au-coated ITO, 6H-SiC and Si substrates by using a novel PED technique. The target was produced by using the commercial ZnO powders pressed into solid tablet at a pressure of 20 MPa. ITO substrates coated with 10 nm of Au were glued on a stainless steel heater for the growth of ZnO nanowire arrays. In the deposition process, the chamber was purged with oxygen vapor and maintained at a deposition pressure of 200 mTorr. The pulse frequency and the voltage of the electron beam were 4 Hz and 15 kV, respectively. The electron ablation process had been performed for 30 min and the substrate temperature was fixed at 750 °C. After the temperature was cooled to room temperature, the deposit was taken out for further characterization. The morphology of the as-synthesized product was examined by field-emission scanning electron microscope (FEI XL30 S-FEG). Powder X-ray diffraction (XRD) data used for structural analysis were collected on PaNalytical X'Pert Pro MPD X-ray diffractometer with Cu Kα radiation. The transition electronic microscopy (TEM) and high-resolution TEM (HRTEM) images of samples were collected on the JEOL 2010F transmission electron microscope equipped with energy-dispersive X-ray spectroscopy (EDS). Photoluminescence (PL) spectra of the nanowires were measured by using the 325 nm line of a He–Cd laser with an output power of about 2 mW as the excitation source.

3. Results and discussion

A typical low-magnification SEM image of the ZnO nanowires grown on ITO substrates is shown in Fig. 1a. All the nanowires are straight and aligned on the substrates via definite angles. The nanowires are high uniformity across the entire substrate, indicat-

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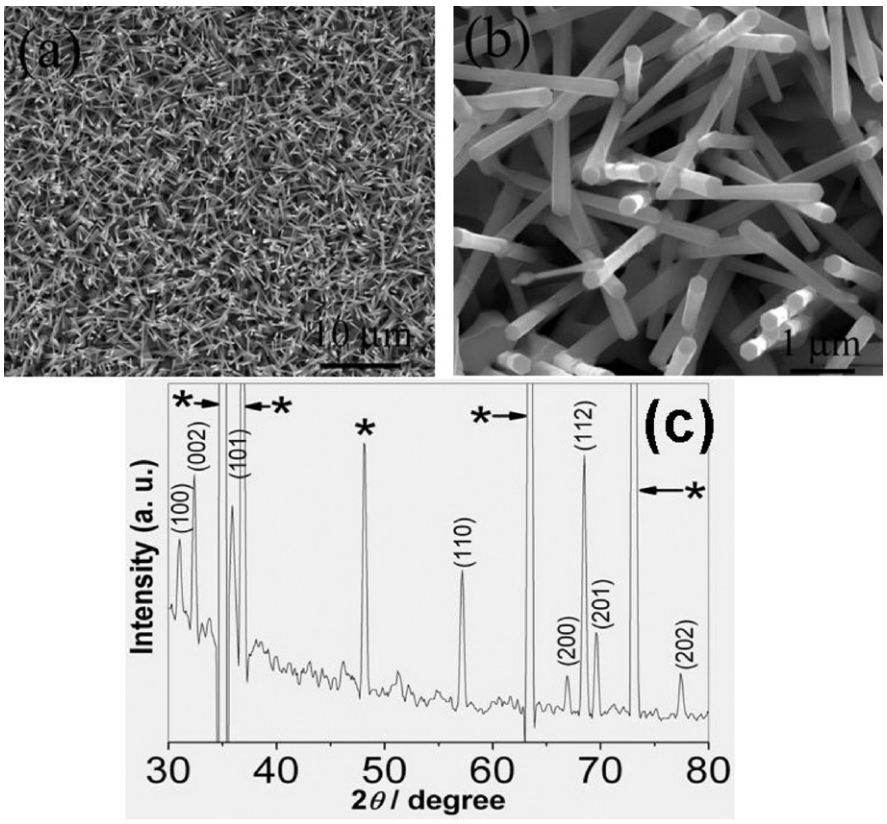

Fig. 1. (a and b) SEM and enlarged SEM images of the deposits, respectively and (c) XRD patterns of the deposits. The symbol * denotes the diffraction peaks detected from the ITO substrates.

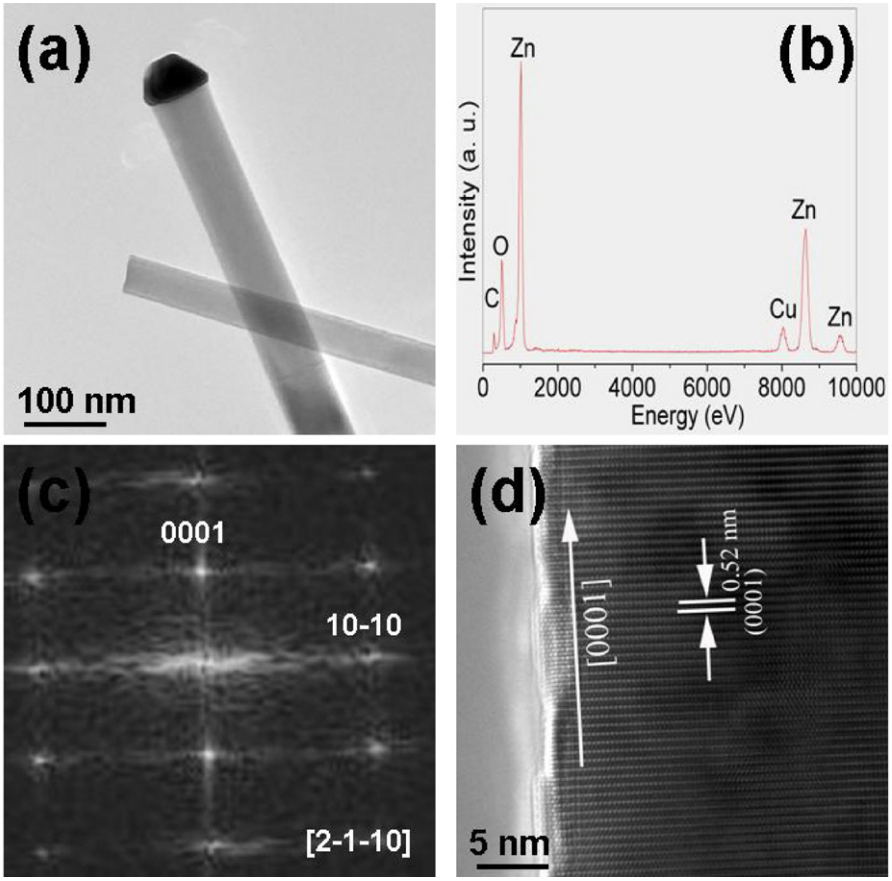

Fig. 2. (a) TEM image of an individual nanowire, (b) EDS spectrum of the nanowire and (c) FFT pattern of the nanowire; (d) HRTEM image of the nanowire.

ing the PED technique can be scaled up for large-area production. As shown from an enlarged image in Fig. 1b, the ZnO nanowires exhibit uniform diameter with 80 nm and regular hexagonal cross section. The corresponding XRD pattern of the nanowire arrays is shown in Fig. 1c. In addition to diffraction peaks detected from ITO substrates that denoted as symbol *, the other peaks (1 0 0), (0 0 2), (1 0 1), (1 1 0), (2 0 0), (1 1 2), (2 0 1), and (2 0 2) are well consistent with that of the standard ZnO patterns (JCPDS card no. 36-1451), revealing the nanowires are ZnO with hexagonal wurtzite structure.

The TEM image clearly reveals a typical morphology of an individual ZnO nanowire, as shown in Fig. 2a. The nanowire is straight and rather uniform in diameter along growth direction and has smooth surface. A nanoparticle confirmed as Au is observed to attach on the tip of the nanowire, revealing that the growth process follows a typical vapor–liquid–solid (VLS) mechanism. The corresponding EDS spectrum (Fig. 2b) indicates the nanowire is mainly composed of Zn and O elements with atomic ratio of 1:0.916, close to the chemical formation of ZnO. The fast Fourier transformation (FFT) pattern (Fig. 1c) recorded along [2-1-10] zone axis is indexed, well consistent with diffraction spots of the hexagonal ZnO. The measured spacing of the lattice fringes is *ca.* 0.52 nm (Fig. 1d), corresponding to the (0 0 0 1) planes of wurtzite ZnO. Based on HRTEM image and FFT pattern, it is determined that the growth direction of the nanowire is along [0 0 0 1] and no bulk defects such as stacking faults, dislocations and twinning defects are observed, revealing the well crystalline nature of the ZnO nanowire. We also investigate the growth of ZnO on other substrates such as 6H-SiC and Si synthesized by the PED technique. We found that aligned ZnO

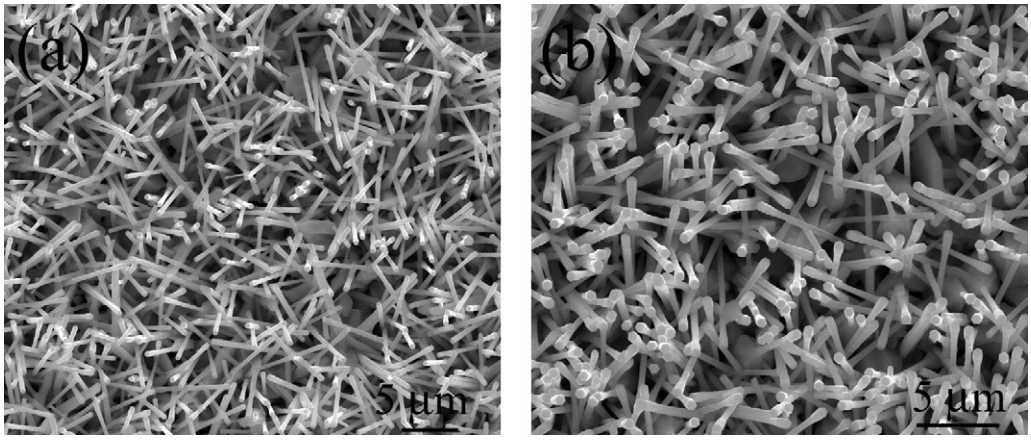

Fig. 3. SEM images of the ZnO nanowires grown on (a) 6H-SiC and (b) Si substrates.

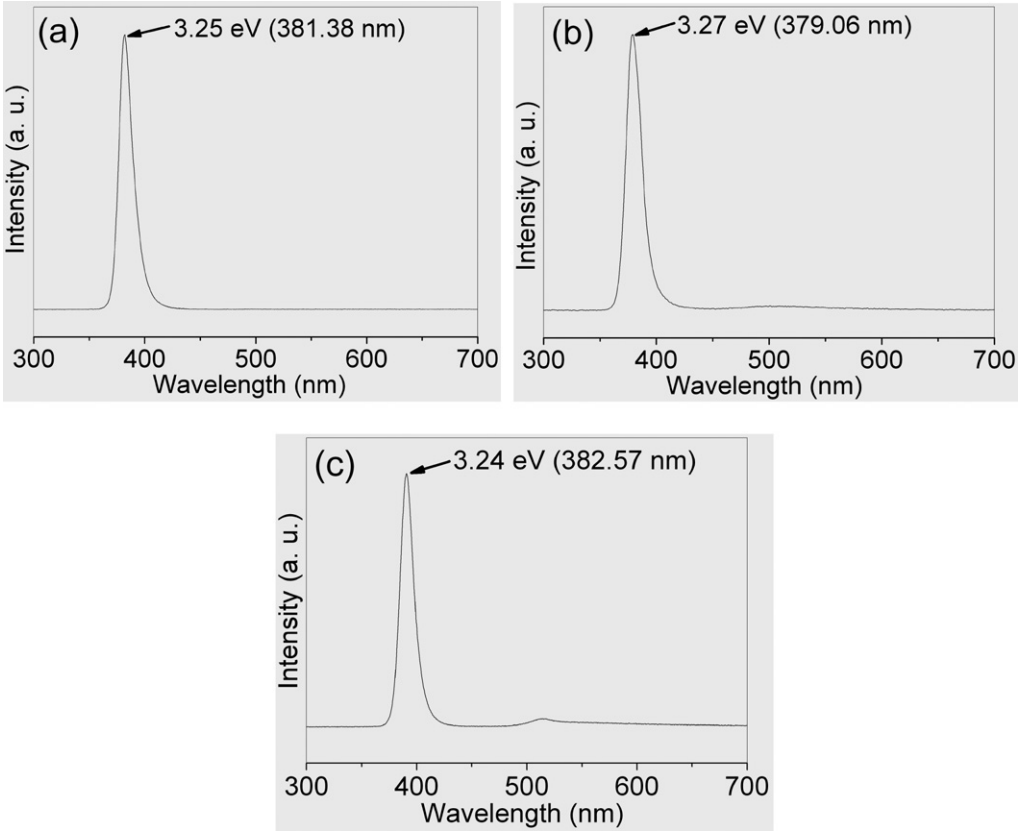

Fig. 4. PL spectra of the ZnO nanowires grown on (a) ITO, (b) 6H-SiC and (c) Si substrates.

nanowires with similar morphology are also observed in the 6H-SiC and Si substrates, as shown in Fig. 3a and b, respectively. The corresponding microstructures also indicate well crystalline nature of the nanowires (HRTEM images are not shown here). It is demonstrated that aligned ZnO nanowires can be fabricated on some common substrates assisted by Au catalysts via the PED technique.

Fig. 4 shows the room-temperature PL spectra of the ZnO nanowires grown on different substrates, which exhibits excellent optical properties in these nanowires. Sharp and strong UV emission bands centered at 3.25, 3.27 and 3.24 eV are observed in the ZnO nanowires grown on the ITO, 6H-SiC and Si substrates, respectively, as shown in Fig. 4a–c. The UV emission originates from the excitonic recombination corresponding to the band edge emission. However, rather weak defect-relative green emission is observed in the ZnO nanowires grown on the Si substrates. We deduce that the green emission originates from the impurity deposition on the Si Substrates. Nevertheless, the exact reason is needed to be further investigated.

4. Conclusions

In summary, we utilize a novel PED technique to synthesize well aligned ZnO nanowire arrays on ITO, 6H-SiC and Si substrates, respectively. XRD and TEM characterizations indicate that the nanowires are of well crystalline single-crystal hexagonal wurtzite structure, and their growth direction is along [0 0 0 1]. The nanowires have uniform diameter and length with 80 nm and 5 μm, respectively. Au nanoparticles were observed at the tip of the nanowires, revealing the growth process follows a typical VLS mechanism. PL spectra reveals similar strong UV emission bands centered at 3.25, 3.27 and 3.24 eV in the ZnO nanowires grown on the ITO, 6H-SiC and Si substrates, respectively, indicating well crystalline nature of the nanowires synthesized by the PED technique.

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