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Structural and Raman properties of silver-doped ZnO nanorod arrays using electrically induced crystallization process

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ABSTRACT

The vertically-aligned ZnO:Ag nanorods doped by the electrically induced crystallization (EIC) process at a low temperature, 200 °C, were investigated. The XRD analysis revealed that the EIC process significantly improved the crystallinity and quality of the resulting ZnO nanorods/ZnO thin film. Spectroscopy coupled with XPS confirmed that Ag elements were doped into the ZnO nanorods. The Raman spectrum indicated the strong blue shift of the A_1(TO) and A_1(LO), and there emerged a new Raman mode at 482 cm^{-1}, termed the "TH mode" which is believed to have been created by silver nanoballs appearing on the surface of the silver films. This study demonstrated that EIC is a viable approach to dope the metal elements into nanostructures, and can thus help to produce optical devices with a 1D ZnO *p*-type structure.

1. Introduction

Zinc oxide (ZnO) is a piezoelectric ceramic material and the *c*-axis oriented ZnO thin film has high optical transparency and good optical characteristics [1]. In addition to serving as a transparent material for conducting electricity, the rough surface or potholes of ZnO can enhance the light trapping effect, and thus improve the efficiency for use in solar cells and other optical devices [2,3].

A number of studies have presented the methods to synthesize one-dimensional (1D) nano-materials, such as nanotubes, nanowires, and nanorods, with these then being applied to micro-nano semiconductor devices [4]. ZnO nanorods are II–VI semiconductors [5], and doping metal elements into its structure can enhance its optical features and *p*–*n* junctions [6,7]. Most 1D optical devices are based on *n*-type ZnO and few studies have examined 1D *p*-type ZnO optical devices, and thus there remain considerable difficulties in producing stable *p*-type ZnO.

Conventional solid doping techniques have a number of defects. For example, the thermal diffusion method requires a temperature of at least 400 °C, which can reduce the reliability of the resulting nanostructure. It is thus, crucial to explore low temperature crystallization processes.

In this study, we choose silver films as the conductive metal layer for the electrically induced crystallization (EIC) process since silver has a high thermal conductivity (4.29 W cm^{-1} K^{-1}), the best electrical resistivity and lower work function (4.3 eV) than that of zinc oxide (5.3 eV) [8]. Ag belonging to group-IB is a suitable choice for being doped into *p*-type ZnO [9]. The structure of ZnO doped with Ag has *p*-type properties and outstanding optical characteristics, and thus can be applied to produce optical devices [10]. When the silver layer contacts the zinc oxide layer in the EIC process, the electric power drives the migration of Ag atoms from the layer into the ZnO nanorods, ultimately enabling the Fermi level of the dual-layer system to become balanced.

Using the low temperature aqueous solution method [11] to synthesize ZnO nanorods, the nanorods grow vertical and evenly arrayed on the ZnO/Ag structure. EIC is a process that works by exerting voltage and current on conductive layers of metals to drive the metal atoms to the ZnO film and nanorods [12,13]. This study carried out EIC in an atmospheric environment with a low temperature of 200 °C and by manipulating the *I*–*V* condition to control the concentration and deepness of the doping metal. The crystallization of the resulting nanostructure and concentration of the doping metals are then analyzed, as these, are important characteristics with regard to optical applications. This doping technique can be applied to produce many 1D nanostructures for *p*-type ZnO optical devices.

2. Experimental procedures

Fig. 1 shows a schematic illustration of the EIC process. The EIC process was applied to the ZnO NRs/ZnO/Ag structure to obtain a

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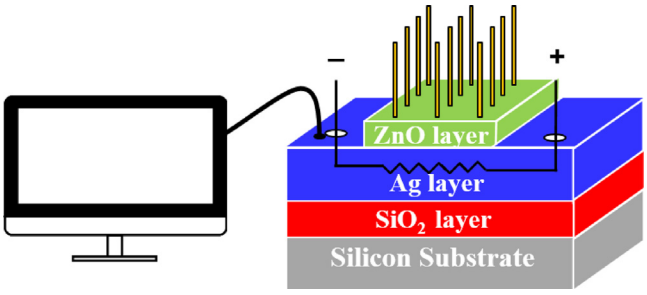

Fig. 1. Schematic illustration of EIC process on ZnO NRs/ZnO/Ag/SiO_2/Si structure.

ZnO nanostructure with silver doped into it. The 200 nm Ag film was deposited on the SiO_2/Si substrate by DC sputtering (Helix HLLS-87). The Ag film was a conductive channel to facilitate the electrically induced crystallization. The 100 nm ZnO film was prepared by RF magnetron sputtering (Helix HLLS-87). The ZnO nanorods grew on a ZnO seed layer by using aqueous solution method. In detail, equimolar aqueous solution (35 mM) of zinc nitrate and methenamine was added to a flask and heated at the low temperature of 90 °C for 1 h [14,15]. During the EIC process, the sample temperature was monitored by placing a K-type thermocouple (40 AWG) in the vicinity of the sample.

The XRD measurements were carried out with the Rigaku 18 kW rotating anode X-ray generator (2θ: 30–90°). The morphologies of the nanostructures were analyzed on a Carl Zeiss AURIGA (FIB-SEM). The morphology of the ZnO/Ag NBs studied in this study was analyzed using TEM (JEM-2010, JEOL Co.). XPS (Probe-5000, PHI Versa) was used to determine elemental depth profile of the ZnO NRs/ZnO/Ag structure. Micro-Raman spectral analysis was carried out by using a LABRAM-HR micro-Raman spectrometer (excitation line $\lambda_0 = 633$ nm) and the spectral range was 300–800 cm^{-1}.

3. Results and discussion

Fig. 2(a) shows the hexagonal-shaped ZnO nanorod arrays grown on the surface of the sample, with diameters of about 58 nm. This shows that the structure of the silver film was stable and the silver atoms had no interaction with the growing structure of the nanorods. Fig. 2(b) shows the cross section of the nanostructure. It indicates that the interface between the ZnO nanorods and ZnO thin film was well-bonded and that the nanorods had a length of around 860 nm and grew perpendicular to the substrate. Fig. 2(c) is a TEM image of ZnO NRs/ZnO/Ag, and shows the same morphology as that in Fig. 2(b).

Previous studies found that the EIC process significantly influences the relation between structural stability and the induced joule heating [11], and thus we need to obtain an appropriate current-voltage condition for the EIC process. We conducted an experiment using the EIC process with different voltage conditions and the resulting *I–V* curve is shown in Fig. 3(a). It can be seen that the breakdown voltage was 4.5 V. Based on results from the *I–V* curve (Fig. 3(a)), we set the condition of 4 V–0.8 A to conduct the EIC process. The temperature curve of EIC process (*I–V* condition: 4 V–0.8 A) is shown in Fig. 3(b), and it can be seen that the surface temperature was stable starting from 7 min and the average surface temperature was about 200 °C. The EIC process used a temperature controlled sensor to keep the temperature during the experiment at 195 °C ± 5 °C (*I–V* condition: 4 V–0.8 A), and the experiment lasted for one hour. Joule heating and electro-migration were induced in the EIC process and both of them influenced the nanostructure in the following tests.

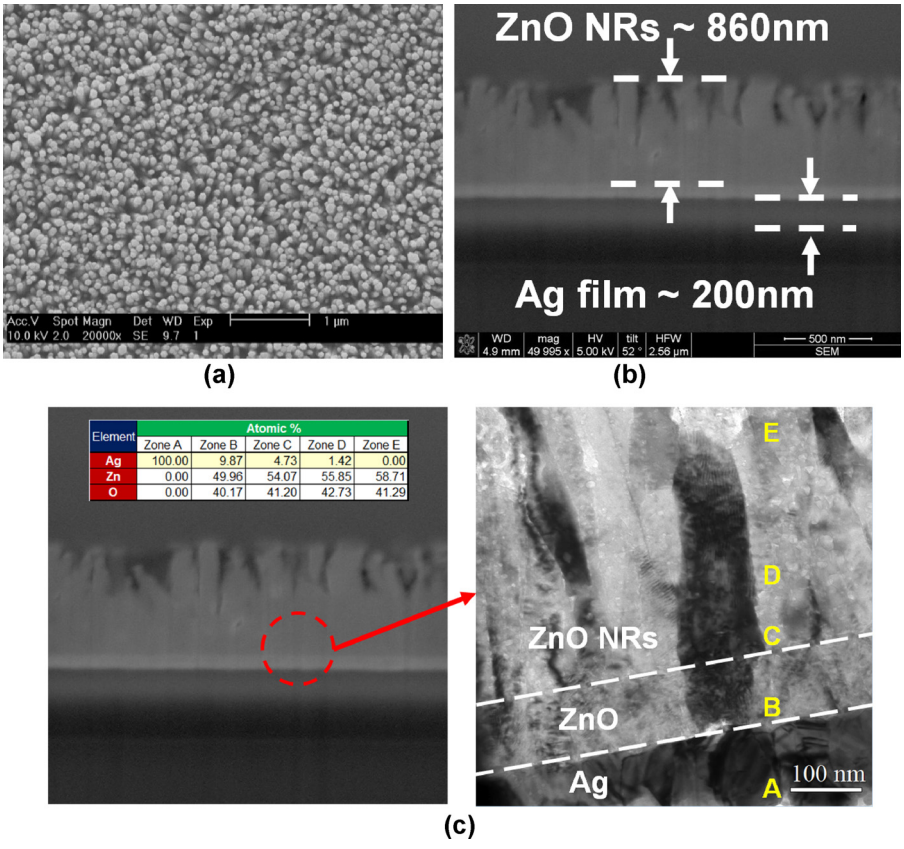

Fig. 2. Structural characterizations of the ZnO NRs/ZnO/Ag structure. (a) top- view SEM image; (b) cross-section and (c) TEM image of a ZnO nanorod arrays on ZnO/Ag layer.