Structural and Optical Properties of Cu-, Ag, and Al-doped Zinc Oxide Nanorods

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Abstract

We investigated structural and optical properties of Cu-, Ag-, and Al-doped zinc oxide (ZnO) nanorods grown on ZnO seed layers. Cu-doped ZnO (ZnO:Cu) nanorods showed increased length and improved crystallinity, compared to undoped ZnO nanorods, where the average transmittance in the visible region is lower than that of ZnO nanorods. Meanwhile, the Ag incorporation led to quite opposite behaviors: decreased length and crystallinity of nanorods. It was also found that Ag-doped ZnO (ZnO:Ag) nanorods exhibited high transparency. The incorporation of Al dopant led to a marked morphological variation, with randomly oriented microrods grown on the surface of the ZnO seed layer, instead of nanorods. Al-doped ZnO (ZnO:Al) microrods exhibited excellent transparency over the visible region. The present results thus show that incorporation of Cu, Ag, and Al dopants has a critical effect on structural and optical properties of ZnO nanorods.

Keywords; ZnO, Nanorods, Cu, Ag, Al, Dopant

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1. Introduction

Zinc oxide (ZnO) is a direct wide bandgap (3.37 eV) semiconductor with high exciton binding energy (60 meV) at room temperature [1-4]. Its numerous applications include polariton lasers, light emitting diodes (LEDs), photovoltaics, thin film transistors (TFTs), chemical sensor, and piezoelectronics [1-7]. Among many possible structures (plates, whiskers, dumbbells, etc.), well-aligned nanorods have attracted increasing interest due to strong exciton-photon coupling with high internal quantum efficiency (IQE) for application in nano-electronic and nano-optoelectronic devices [4-11].

The growth of ZnO nanorods is strongly influenced by the seed layer conditions [7,8]. In our previous paper, we investigated the structural properties of ZnO nanorods grown on ZnO seed layers with various seed annealing temperatures, ranging between 150 ºC and 450 ºC [8]. The length and crystallinity of ZnO nanorods increased with increasing seed annealing temperature up to 350 ºC, and then slightly decreased with further temperature increases.

On the other hand, it is well known that n-type (Al, Ga, etc.) and p-type (Cu, Li, etc.) dopants effectively modify the physical properties of ZnO film [12-17]. However, there are not many systematic comparative study of Cu, Ag, and Al doping effect on the properties of ZnO nanorods.

In the present study, the effect of Cu, Ag, and Al dopants on the structural and optical properties of ZnO nanorods grown on ZnO seed layers was investigated by comparison to the corresponding properties of undoped ZnO nanorods.

2. Experimental

The ZnO seed layers were prepared by sol-gel spin-coating. Zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$, 0.25 M, Wako) precursor was dissolved in ethanol (C_2H_5OH, Wako), 2-methoxethanol (ME) ($C_3H_8O_2$, Wako) and Milli-Q solvents. After spin-coating of the sol on fluorine-doped tin oxide (FTO) coated glass substrates, the seed layers were annealed at 350 ºC for 30 min in ambient air. The mean thickness of the seed layers was 35 nm.

The ZnO nanorods were fabricated by a chemical solution deposition with an aqueous solution of zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, 0.01 M, Sigma-Aldrich) and hexamethylenetetramine (HMT) ($C_6H_{12}N_4$, 0.01 M, Sigma-Aldrich). Copper acetate monohydrate ($Cu(CO_2CH_3)_2 \cdot H_2O$, Wako), silver nitrate ($AgNO_3$, Sigma-Aldrich), and aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$, Wako) were added as the dopants with Cu/Zn, Ag/Zn, and Al/Zn atomic ratios of 10. The seed layers were vertically immersed in the solution at 90 ºC for 6 h. The samples were then washed with deionized water and dried at 120 ºC for 10 min.

The crystal structure and orientation were observed by X-ray diffraction (XRD, Bruker, D8ADVANCE) operating at a voltage of 40 keV and a current of 40 mA. Surface morphology was examined by field emission scanning electron microscopy (FESEM, JSM-6701F). Optical transmittance were investigated by ultraviolet-visible (UV-vis) spectroscopy (HITACHI, U-2910).

3. Results and discussion

3.1 Properties of ZnO seed layer

Fig. 1 shows the XRD pattern of the ZnO seed layer, consistent with the hexagonal wurtzite structure (JPCDS card no. 36-1451). The diffraction peaks at 31.77º, 34.42º, 36.25º, and 47.53º were indexed to the (100), (002), (101), and (110) planes, respectively. The FESEM image (not shown) highlights uniformly distributed nanocrystals with a mean size of 20 nm.

3.2 Effects of Cu and Ag dopants on growth of ZnO nanorods

Fig. 2 shows the cross-sectional and top-view FESEM images of the nanorods grown on ZnO seed layers prepared on the FTO coated glass substrates. The growth behavior is strongly dependent on the dopants. As shown in Fig. 2(a,b), the length, diameter, and surface density of undoped ZnO nanorods are 1.2 μm, 35 ± 10 nm, and 168 ± 5 μm^{-2}, respectively. Fig. 2(c,d) shows that the length, diameter, and surface density of the Cu-doped ZnO (ZnO:Cu) nanorods are 2.1 μm, 40 ± 10 nm, and 130 ± 5 μm^{-2}, respectively. Compared to undoped ZnO nanorods, Cu incorporation thus leads to nanorods of longer length and lower surface density. With incorporation of Ag dopant (Fig. 2(e,f)), the length of nanorods decreases to 0.6 μm, while, the surface density increases to 254 ± 5 μm^{-2}. Zhang *et al.* reported that Ag doping on the ZnO nanorods has no remarkable effects on the morphology and growth behavior of nanorods [18]. On the contrary, some studies reported that the morphology of ZnO nanorods was affected by metal dopants [19,20]. Lupan *et al.* reported that the growth rate in the (101) direction of ZnO nanorods was enhanced in the presence of Ag^{+} ions in the ZnO [19]. Raja *et al.* reported that Cu dopant has effect on the morphology of the ZnO nanorods and bunch like nanorods were grown by introduction of Cu dopant [20]. In our case, with incorporation of Cu and Ag dopants, no marked change in the morphology is observed, whereas, the length and surface density are significantly related to the dopants in ZnO nanorods.

Fig. 3 shows the XRD patterns of ZnO nanorods, ZnO:Cu nanororods, and Ag-doped ZnO (ZnO:Ag) nanorods grown on ZnO seed layers. All samples show peaks corresponding to the hexagonal wurtzite structure of ZnO, with no other impurity phases. All nanorods show a highly preferential (002) orientation with their *c*-axis perpendicular to the surface of the FTO substrates, and no shift in peak position (2θ = 34.44° for all samples). This reflects the very similar ionic radii of Cu^{2+} (0.073 nm) and Zn^{2+} (0.074 nm) [21,22]. It also indicates that Ag (10 at%) could systematically substitute Zn without deteriorating crystalline structure although the lattice mismatch between radii of Zn^{2+} (0.074 nm) and Ag^{+} (0.126 nm) is large [19]. The intensity of the (002) peak increases going from ZnO:Ag nanorods, to ZnO nanorods, to ZnO:Cu nanorods, showing that Cu doping improves the crystallinity of the ZnO nanorods. The relative intensity ratio of the (002) peak (defined as $i_{(002)} = I_{(002)}/[I_{(100)} + I_{(002)} + I_{(101)} + I_{(102)}]$) of ZnO nanorods, ZnO:Cu nanorods, and ZnO:Ag nanorods is 0.94, 0.97, and 0.90, respectively. These results are in good agreement with the FESEM results.

The optical transmittance spectra of the nanorods are shown in Fig. 4. The ZnO nanorods and ZnO:Ag nanorods show high transparency over than 80% in the visible region. Consistent with the observation of previous studies on ZnO:Cu films, the transmittance of the ZnO:Cu nanorods decreases in the visible wavelength region and the absorption edge red-shifts with respect to the ZnO nanorods [23,24]

3.3 Effects of Al dopants on growth of ZnO nanorods

With the addition of Al dopant, Fig. 5(a) shows that nanorods are infrequently grown on the ZnO seed layer; instead, hexagonal-shaped microrods with length ~ 8 μm are found randomly distributed on the surface of the ZnO seed layer. The diameter of microrods were in rage of ~ 1 μm at the base side and 200 - 300 nm at the top side. The surface density of these Al-doped ZnO (ZnO:Al) microrods is ~ 0.1 μm^{-2}. Leem *et al.* reported a change from hexagonal to prism-like shape in ZnO nanorods doped with Al [16]. However, Fang *et al.* reported that the length of ZnO nanorods increased and their diameter decreased with incorporation of Al dopant without remarkable change in morphology [13].

The optical transmittance spectrum of the ZnO:Al microrods is shown in Fig. 5(b). It is found that ZnO:Al microrods show excellent transparency in the visible region.

4. Conclusions

We investigated the effects of Cu, Ag, and Al dopants on the properties of ZnO nanorods on the FTO coated glass substrates prepared by a chemical solution deposition.

In comparison to the undoped ZnO nanorods, length and crystallinity of nanorods were significantly enhanced with addition of Cu dopant on nanorods, without structure deterioration, whereas their visible transmittance was slightly lower than ZnO nanorods. With incorporation of Ag dopant, the length and crystallinity of nanorods were decreased, meanwhile the transmittance of ZnO:Ag nanorods was high. The surface morphology considerably changed upon incorporation of Al dopants. Randomly oriented microrods were found distributed on the surface of the seed layer and showed excellent transparency. The incorporation of Cu, Ag, and Al dopants on nanorods and seed layers thus represent facile and effective methods to tune structural and optical properties of nanorods.

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Figure captions

Fig. 1. XRD pattern of ZnO seed layer on glass substrate.

Fig. 2. FESEM images of ZnO nanorods (a,b), ZnO:Cu nanororods (c,d), and ZnO:Ag nanorods (e,f) grown on ZnO seed layers on the FTO/glass substrates. (a,c,e) and (b,d,f) figures show cross-sectional and top views, respectively. The insets in figures (b,d,f) are high-magnification images.

Fig. 3. XRD patterns of ZnO nanorods, ZnO:Cu nanorods, and ZnO:Ag nanorods grown on ZnO seed layers prepared on the FTO/glass substrates.

Fig. 4. UV-Vis transmittance spectra of ZnO nanorods, ZnO:Cu nanorods, and ZnO:Ag nanorods grown on ZnO seed layers prepared on the FTO/glass substrates.

Fig. 5. Cross-sectional (a) FESEM image and transmittance spectrum (b) of ZnO:Al microrods.

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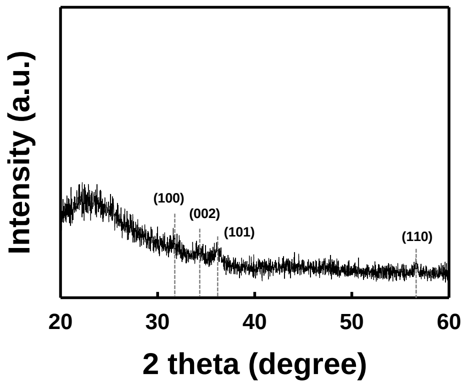
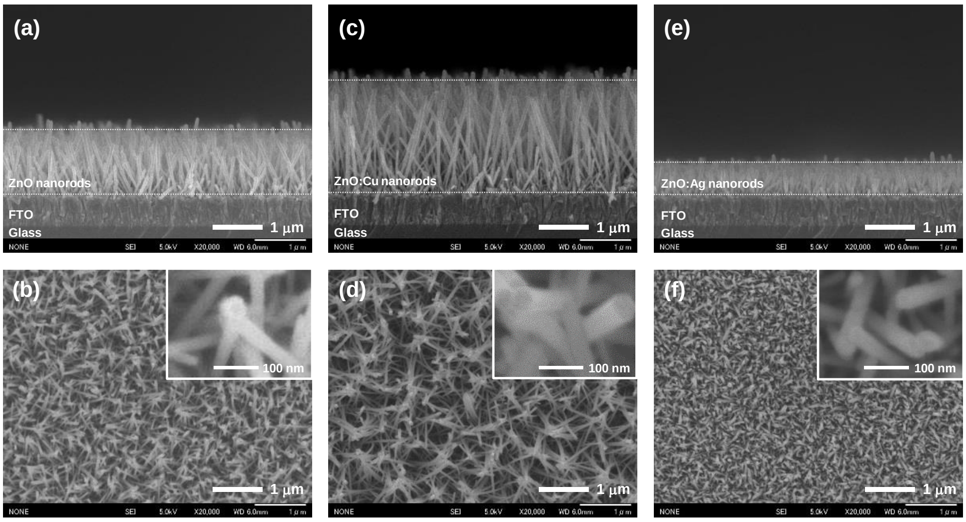
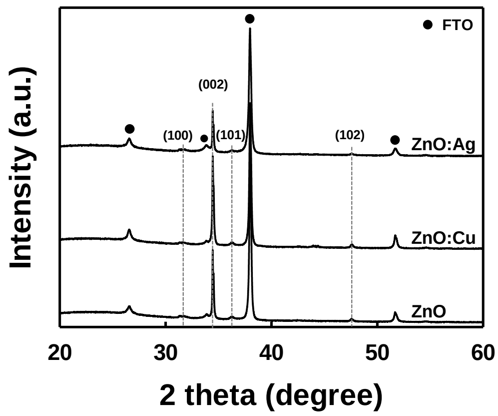


Fig. 1.



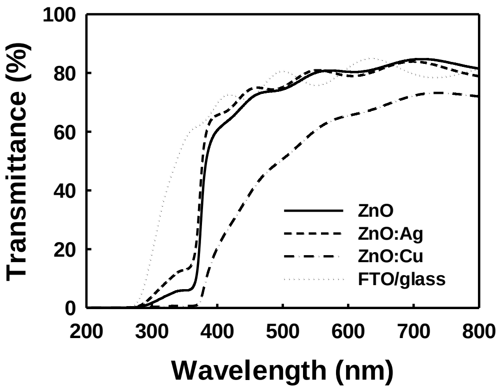
(a)
ZnO nanorods
FTO
Glass
1 µm
(b)
100 nm
1 µm
(c)
ZnO:Cu nanorods
FTO
Glass
1 µm
(d)
100 nm
1 µm
(e)
ZnO:Ag nanorods
FTO
Glass
1 µm
(f)
100 nm
1 µm

Fig. 2.



● FTO
(002)
(100)
(101)
(102)
ZnO:Ag
ZnO:Cu
ZnO
Intensity (a.u.)
20
30
40
50
60
2 theta (degree)

Fig. 3.



100
80
60
40
20
0
Transmittance (%)
200
300
400
500
600
700
800
Wavelength (nm)
ZnO
ZnO:Ag
ZnO:Cu
FTO/glass

Fig. 4.

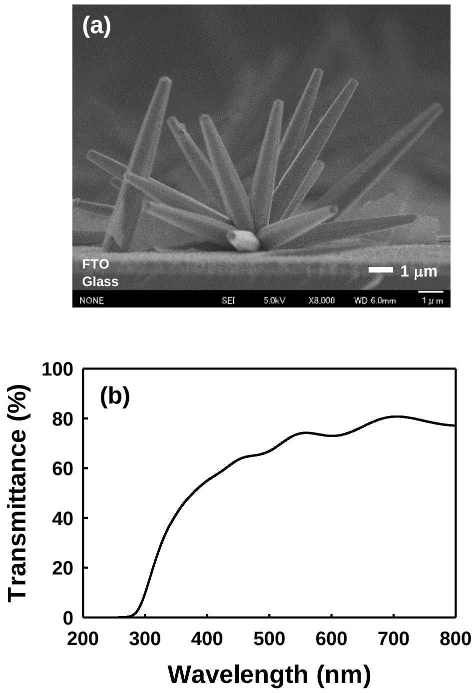

(a)
FTO
Glass
1 μm
NONE SEI 5.0kV X8,000 WD 6.0mm 1 μm
(b)
Transmittance (%)
0
20
40
60
80
100
200 300 400 500 600 700 800
Wavelength (nm)

Fig. 5.