Physica B 404 (2009) 3519–3524

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Enhancement of electrical conductivity by Al-doped ZnO ceramic varistors

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ARTICLE INFO

Article history:
Received 17 March 2009
Received in revised form
20 May 2009
Accepted 28 May 2009

Keywords:
Al doping
Wurtzite structure
Breakdown
Conductivity and Upturn region

ABSTRACT

$Zn_{1-x}Al_xO$ ceramic samples with various x values ($0.00 \le x \le 0.20$) are sintered in air at temperatures of 850 °C for 10 h and then quenched to room temperature. Structural, surface morphology and *I–V* characteristics of the samples are investigated using X-ray diffractometer (XRD), scanning electron microscope (SEM) and dc electrical measurements. It is found that addition of Al up to 0.05 does not influence the well-known peaks related to wurtzite structure of ZnO ceramics, and other unknown peaks could be formed above 0.05 of Al. The cell parameters of Al-doped samples are a little shorter than the undoped ZnO, and also the shape and size of grains are clearly affected. Average crystalline diameters, deduced from XRD analysis, are between 39.90 and 47.18 nm, which are 25 times lower than those obtained from SEM micrographs. Although breakdown field, nonlinear coefficient and barrier height are generally decreased by Al addition, the electrical conductivity is improved. These results are discussed in terms of the interaction mechanism between atoms of Al and Zn in both under and over-doped regions.

1. Introduction

Electrical conductivity of oxide semiconductors such as ZnO ceramic varistor depends on the amount and nature of oxygen vacancies that are generated during its synthesis [1,2]. These oxygen vacancies are normally controlled by several dopants added to ZnO such as Bi, Ni, Ga, Mn, Co, Sb, Al, Fe and Cr [3–7]. Therefore, it is very important to understand effects of these dopants on structural and nonlinear properties of this type of ZnO varistor. However, the effect of Al doping on the electrical properties of ZnO varistor has been investigated by several reports [8–11]. It has been observed that Al increased the current density in the upturn region and shifted its onset to lower fields, and consequently the grain conductivity of ZnO is increased. Since the conductivity in the upturn region depends on the grain conductivity of ZnO, a systematic study of the effect of Al doping on the conductivity of ZnO is, therefore, necessary.

With this purse in mind, a range of $Zn_{1-x}Al_xO$ ceramic samples with various x values are sintered in air at temperature of 850 °C for 10 h and then quenched from sintering temperature down to room temperature. Structural and grain morphology of the samples are investigated using X-ray diffractometer (XRD) and scanning electron microscope (SEM) techniques; while *I–V* characteristics are obtained using dc electrical measurements.

2. Experimental details

$Zn_{1-x}Al_xO$ samples with various x values ($0.00 \le x \le 0.20$) are synthesized using the conventional solid-state reaction method [7,12]. The powders of ZnO and Al_2O_3 (Aldrich 99.999 purity) are thoroughly mixed in required proportions and calcined at a temperature of 1000 °C in air for a period of 12 h. The resulting powders are ground, mixed, pressed into pellets and sintered at temperatures of 850 °C for 10 h in air. Finally, the samples are quenched from sintering temperature down to room temperature. The bulk density of the samples is measured in terms of their weight and volume. The phase purity and surface morphology of the samples are examined using X-ray diffractmeter and scanning electron microscope. *I–V* characteristics are obtained with an electrometer (model 6517, Keithley), 5 kV dc power supply and digital multimeter. The samples are well polished and sandwiched between two copper electrodes and the current is measured relative to the applied voltage. High-quality silver paint is used on the samples surfaces for electrical contact.

3. Results and discussion

It is noted that color of pure ZnO sample is white and it changed to yellow with Al addition. The bulk density of the samples, listed in Table 1, is generally decreased by Al. The structure of $Zn_{1-x}Al_xO$ samples, shown in Fig. 1(a), with $x \le 0.05$ is Wurtzite structure, and no additional peaks could be formed. When Al content is increased above 0.05, some of unidentified

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doi:10.1016/j.physb.2009.05.054

Table 1
ρ, D, a, c and average crystalline diameter versus Al content for Al-doped ZnO samples.

Al content	ρ (gm/cm^3)	D (SEM) (nm)	a (Å)	c (Å)	D_{100} (nm)	D_{002} (nm)	D_{111} (nm)	D_{102} (nm)	D_{110} (nm)	Average (nm)
0.00	6.35	1560	3.252	5.208	43.36	40.60	41.53	54.63	55.77	47.18
0.025	4.31	920	3.247	5.201	43.40	44.78	35.32	39.12	48.78	42.28
0.05	5.24	840	3.242	5.196	39.46	44.78	32.71	37.76	44.81	39.90
0.10	5.05	1020	3.231	5.188	36.11	37.22	38.36	49.68	55.84	43.44
0.20	4.31	1120	3.225	5.181	36.11	44.73	38.07	54.69	60.97	46.91

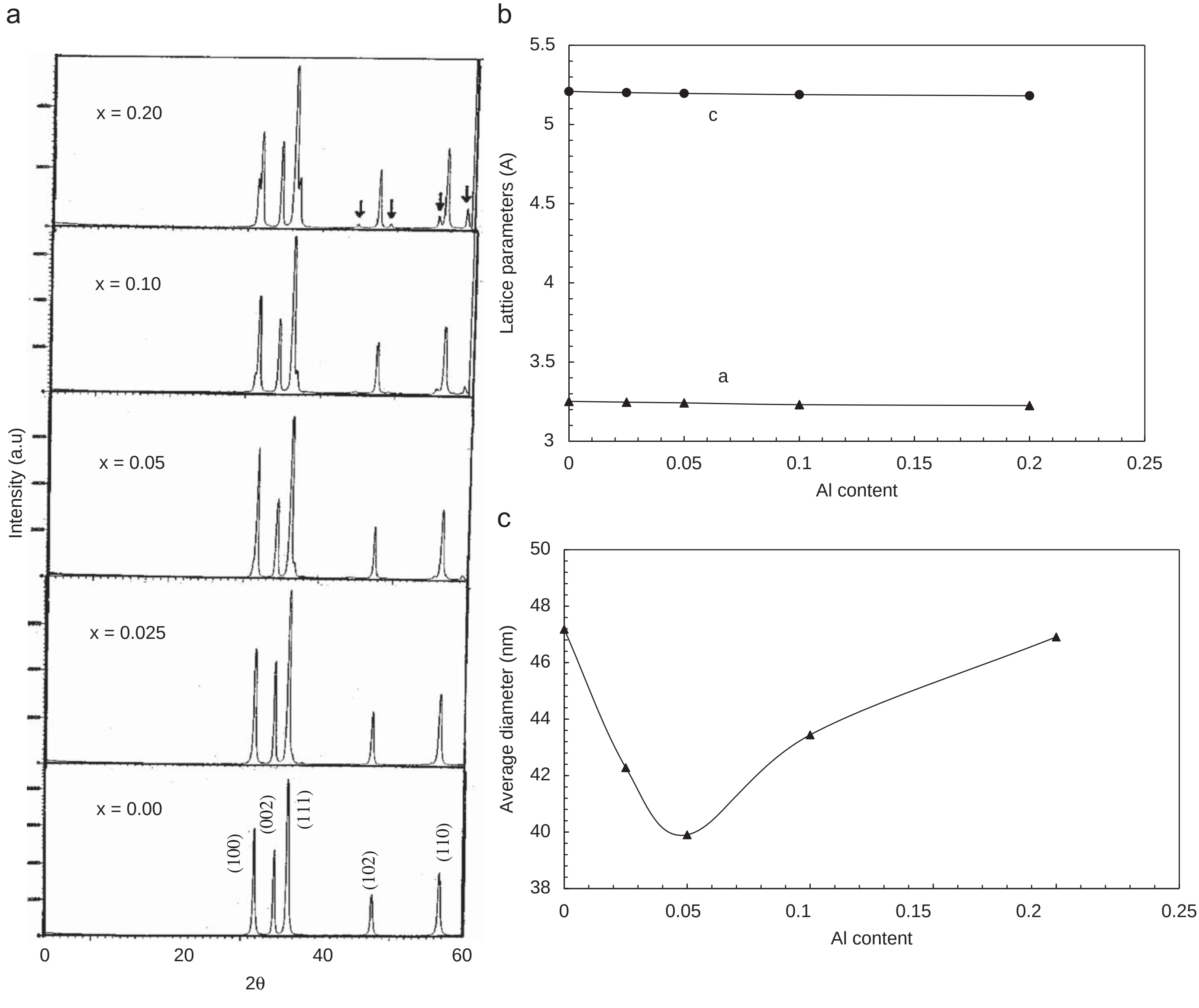

Fig. 1. (a) X-ray diffraction patterns of pure and Al-doped ZnO samples. (b) Lattice parameters of pure and Al-doped ZnO samples. (c) Average crystalline diameter deduced from XRD analysis of pure and Al-doped ZnO samples.

very low-intensity peaks denoted by arrowhead could be seen in the XRD pattern. This is because that with increasing Al content above 0.05, the solubility limit of Al through Zn lattice is reached, and some of Al atoms could be localized at the interstitial position. To further confirm that Al^{3+} has been substituted for Zn^{2+} in the unit cell, the lattice parameters of the samples are calculated and listed in Table 1. As shown in Fig. 1(b), the lattice parameters are decreased by Al addition, probably due the smaller ionic size of Al^{3+} (0.51 Å) than that of Zn^{2+} (0.74 Å). On the other hand, the average crystalline diameter D_{hkl} is evaluated in terms of X-ray line broadening described by the following Scherer's equation [13]:

$$D_{\mathrm{hkl}} = \frac{k\lambda}{\Delta\theta \cos\theta} \qquad (1)$$

where λ is X-ray wavelength ($\lambda = 1.5418$ Å), $\Delta\theta$ is half-maximum line width, θ is Bragg angle and K is constant ($K = 0.9$ for this type of ceramics). Average crystalline diameter versus Al content is shown in Fig. 1(c). Similar values are listed in Table 1. It is clear that values of D_{hkl} are decreased by Al addition up to 0.05,