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Formation of randomly dispersed pores in Ga-doped ZnO between Al_2O_3 and glass via promoted atomic diffusion: Experimental and computational study

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ABSTRACT

Kirkendall diffusion, an unbalanced interdiffusion process through an interface of two materials, has attracted attention for decades as one of the promising techniques to fabricate nanoporous materials. In particular, a lot of efforts have been focused on the study of Kirkendall diffusion occurred in ZnO-based material couples due to the unique optoelectronic properties of ZnO. In this study, we fabricate nanoporous planar multilayered structures composed of Al_2O_3/Ga-doped ZnO (GZO)/Glass with different Ga concentrations by utilizing Kirkendall effect-induced diffusion. It is demonstrated that Ga-doping leads to the formation of internal (not interfacial) voids in the GZO layers, and the features of formed voids clearly depend on the Ga concentration. Through atomistic computational analyses, we elucidate that grain boundaries (GBs) whose density increases as the Ga doping concentration increases promote the local atomic diffusivity, and consequently act as the initiators of voids formed in the GZO layers. In addition, the doped Ga atoms and GBs induce a compressive stress within the GZO layers, which suppresses the growth rate of each individual void. Fundamental understandings of atomic diffusion mechanism demonstrated in this study may provide a simple approach to fabricate nanoporous materials with controlled porosity by modulating the Ga doping concentration.

1. Introduction

Nanoscale porous structures play a key role in numerous applications including high-efficiency catalysts [1–3], drug-delivery systems [4–6], and optical devices [7,8]. Since accurate control of the pore structures is crucial for utilizing the nanoporous materials in a wide range of applications, nanostructure engineering has attracted a lot of attention in the nanoscience and technology field. Researchers have reported various techniques for the fabrication of nanoporous structures including not only top-down [9–11] but also bottom-up approaches [12–16]. Since the top-down techniques such as nanolithography suffer from the imperfection of the surface structure (e.g. impurity, defects, rough surface, etc.) caused by the processes of etching and template removal, bottom-up approaches have been magnified for decades. Among a variety of bottom-up techniques, Kirkendall effect, caused by unequal diffusion of elements at the interface in a material couple resulting in interfacial nanovoids, has been promising for the fabrication of nanoporous materials with not only hollow [17–19] and tubular [20–22] structures but also buried porous structures [13,23,24]. The planar structures with buried pores are particularly useful as internal light scattering/absorption layers in optoelectronic devices. For instance, flat internal light extraction layers containing optically effective nanovoids without additional planarization prior to the deposition of the electrodes are highly desirable for OLED devices.

ZnO-based material couples such as ZnO/Al_2O_3 [23–26], ZnO/TiO_2 [25,27], ZnO/Fe_2O_3 [25,26] and ZnO/SnO_2 [25] have been most commonly utilized for the formation of nanotubes and hollow nanoparticles by the Kirkendall effect and diffusion processes because of the high diffusivity of Zn atoms. The ZnO is a well-known transparent conducting oxide (TCO) that has been intensively studied for application in electronics, optoelectronics and laser technology [28,29] due to its remarkable properties such as wide band gap (3.37 eV) [30–35], high exciton binding energy (60 meV) [30–33] and strong green luminescence [35]. The group III-doped ZnO films have also received attention over the years [36–42] since the electrical conductivity and optical transmittance of ZnO films can be improved by introducing group III elements such as Al and Ga. Numerous studies on the Kirkendall effect using ZnO-based material couples have been focused on understanding the Kirkendall effect-related phenomena including void formation and growth at the interfaces and the diffusion mechanism [23–27]. However, no one has reported the occurrence of voids induced by Kirkendall effect in doped ZnO-based materials and the roles of dopants in Kirkendall diffusion.

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In this study, we first presented the internal void formations caused by Kirkendall effect-based diffusion in planar multilayered structures composed of Al_2O_3/Ga-doped ZnO (GZO)/Glass with different Ga concentrations, and captured how the features of the voids formed in the GZO layers are different from those of the common Kirkendall voids. In order to understand the mechanism of the void formations in GZO layers at the atomic-level, molecular dynamics (MD) simulations and first-principles calculations were utilized to explore how the atomic mobility of Zn is affected by the presence of the doped Ga atoms and the consequently formed grain boundaries (GBs) in GZO. This systematic study on the Ga-doping concentration dependence of void features in GZO layers can bring advances in engineering of porous films with controlled porosity.

2. Methods

2.1. Experimental details

Al_2O_3/GZO films were deposited on boroaluminosilicate glass substrates. 400 nm-thick GZO films were formed directly on the substrate by atmospheric pressure chemical vapor deposition (APCVD) using three precursors of DEZ (Diethyl Zinc), alcohol and TMG (Trimethyl Gallium) for Zn, O, and Ga, respectively. The substrate temperature was kept at 500 °C during the GZO deposition and the Ga doping rate was controlled by changing the flow rate of the Ga precursor from 80 to 120 sccm. 200 nm-thick Al_2O_3 film deposition on top of GZO was successively carried out at room temperature via DC magnetron sputtering using pure ceramic targets of Al_2O_3. The fabricated samples of Al_2O_3(200 nm)/GZO(400 nm)/Glass(0.7 mm) were annealed in a horizontal tube furnace at atmospheric pressure at a temperature of 800 °C for 5 h to generate Kirkendall voids in GZO. X-ray diffraction was performed with a Cu Kα1 radiation ($\lambda = 1.5406$ Å) for phase identification of all the deposited films. The morphologies of the prepared samples were characterized using field-emission scanning electron microscopy (SEM) and transmission electron microscopy (TEM). High-resolution elemental depth profiles were obtained from line scans of cross-sections using TEM-energy dispersive X-ray spectroscopy (EDX).

2.2. Simulation details

MD simulation that describes the time dependent behavior of atomic/molecular systems is a widespread tool to explore the materials properties [43–45] and physical/chemical processes [46–49]. Despite of the limitation of its small time and length scales due to the computational cost, it has been demonstrated that MD simulation can successfully carry out the investigations of atomic diffusivities [47–49]. From the atomic trajectories of MD simulations, mean squared displacement (MSD) of atoms can be calculated as

$$\mathrm{MSD} = \left\langle (r(t) - r_0)^2 \right\rangle, \quad (1)$$

where $r(t)$ is the position of the atom at time t, and r_0 is the initial position of the atom. Atomic diffusivity is directly related to MSD of the atom. For instance, if an atom undergoes Brownian motion in an isotropic liquid phase, MSD grows linearly with time and the diffusion coefficient of the atom can be estimated from the slope of the time-MSD curve. If the system is a crystal solid as the case of GZO studied in this work, MSD saturates to a finite value because the atoms in the system vibrate around the lattice points, and cannot escape from the points within the MD time-scale. In this case, the saturated value can be used as an indicator of atomic mobility [50]. In other words, the higher the saturated value of MSD, the higher the atomic mobility.

During the MD simulations, the temperature and the pressure were kept constant at 300 K and 0 GPa using a Nosé–Hoover thermostat [51,52] and a Parrinello–Rahman barostat [53,54], respectively. The integration time step was 1 fs. The MSDs of ZnO and GZO systems were calculated by utilizing the classical and ab initio MD simulations, respectively. The classical MD simulations were performed using large-scale atomic/molecular massively parallel simulator (LAMMPS) [55,56] with the Buckingham potentials parameterized by Binks to model the Zn-Zn, Zn-O, and O-O interactions [57]. The structural optimizations and ab initio MD simulations were carried out using the plane-wave pseudopotential method implemented in Cambridge serial total energy package (CASTEP) [58–61]. Core and valence electrons were described by ultrasoft pseudopotentials, and Perdew–Burke–Ernzerhof (PBE) function of the generalized gradient approximation (GGA) was adopted for the exchange and correlation contributions [62]. Monkhorst–Pack scheme were used with $1 \times 1 \times 1$ k-mesh to sample the electronic Brillouin zone and the plane-wave cutoff energy was set at 400 eV.

3. Experimental observations of nanovoids formed in Al_2O_3/GZO/Glass multilayers

Three samples of Al_2O_3/GZO/Glass multilayered structures were prepared with 3.8 wt.%, 4.3 wt.%, and 5.6 wt.% of Ga concentrations in order to investigate the effects of dopant concentration on the void formations. The results of X-ray diffraction analysis (not shown in this paper) revealed that the GZO layers were the wurtzite crystal structure, whereas the Al_2O_3 layers were amorphous state. The cross-sectional morphologies of as-deposited GZO layers with different Ga concentrations before growing Al_2O_3 layers on top of the layers are shown in Fig. 1a. It is observed that the higher the Ga doping concentration, the higher the GB density in the GZO layers. Fig. 1b shows morphological changes of GZO in Al_2O_3/GZO/Glass multi-layered structures with different Ga concentrations after the heat treatment at 800 °C for 5 h. After the heat treatment, voids were formed in the all GZO layers and were 10–250 nm in size. It is expected that these nanovoids were formed by imbalance of atomic diffusion between Zn and Al [21]. Since Zn atoms move faster than Al atoms, there would be a net atomic flux from GZO layer to Al_2O_3 layer, resulting in the formation of nanovoids in the GZO layer composed of elements with a relatively faster diffusivity.

We note that the voids are dispersed over the entire GZO layers after the heat treatment as presented in Fig. 1b. This is clearly distinguishable from the previously reported features of Kirkendall voids observed in undoped ZnO/Al_2O_3 multilayers [23,24]. For undoped ZnO/Al_2O_3 multilayers, the Kirkendall voids were mostly found near the ZnO/Al_2O_3 interface rather than in the entire ZnO layers. This indicates that Ga doping likely promotes the mobility of Zn atoms located inside the GZO layers, resulting in highly porous structures after the heat treatment. If the atomic mobility of Zn in GZO layers is expedited as the Ga concentration increases, it is not surprising that the GZO layer with the higher Ga concentration resulted in the higher number density of voids. Interestingly, the size of each void, however, decreased with increasing dopant concentration, as seen in Fig. 1b. The higher Ga concentration may provide more seeds of the void formation on the one hand, but suppress the growth rate of the voids on the other hand. Since it is known that the mechanical stress can enhance the rate of atomic diffusions [63,64], the Ga doping concentration is expected to affect the stress development in GZO layers, inducing a change in void growth rate.

In order to further understand the void formation in Al_2O_3/GZO/Glass multilayered structures at the atomic level, TEM analyses were performed for two Al_2O_3/GZO/Glass samples with 3.8 wt.% and 5.6 wt.% of Ga concentration. Fig. 2 shows the TEM images of the samples before (Fig. 2a and c) and after (Fig. 2b and d) the heat treatment. The corresponding atomic depth-profiles are also presented on the right of the TEM images. The atomic depth profiles in Fig. 2b and d clearly show the formation of the intermediate layers at both Al_2O_3/GZO and GZO/Glass interfaces due to the atomic interdiffusion near the interfaces