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The influence of pH value and annealing temperature on the characteristics of ZnO–Ru composite films and their application in thin film transistors

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ABSTRACT

ZnO–Ru thin films were prepared using a sol–gel spin coating method. We investigated the effects of the Ru-doping concentration, the pH value of precursor and the annealing temperature on the characteristics of the ZnO–Ru thin films. The crystallinity of ZnO–Ru films decreases as the Ru-concentration increases. The surface morphology of the ZnO–Ru films is also related to the pH of the precursors. The optical energy band gap is a function of Ru-doping concentration and the annealing temperature. The correlations among the Zn/Ru ratio, the pH value of the pre-solutions, the annealing temperature and the characteristics of ZnO–Ru films are derived. In addition to the material properties, the application of ZnO–Ru films as a channel layer in thin film transistors is also discussed.

1. Introduction

Zinc oxide (ZnO) is a common oxide semiconductor with a hexagonal wurtzite structure and a wide direct band gap (E_g ~ 3.37 eV). It is widely used in transparent electrodes in displays, dye-sensitized solar cells, sensors and electronics. In order to meet the needs of a diverse range of applications, ZnO-based semiconductors are usually formed by introducing transition metal ions or rare earth ions into the host semiconductor. A number of studies have investigated ZnO films that are doped with different transition metal ions, such as Ni-doped ZnO [1], Co-doped ZnO [2] and (Fe, Ag)-doped ZnO [3]. RuO_2 is a deep blue-black tradition metal oxide with a tetragonal rutile structure and good conductivity. RuO_2 is used for a variety of applications, such as diffusion barriers [4], as the bottom electrode of ferroelectric thin films that are used in dynamic random access memories [5], thin-film resistors [6] and electrochemical capacitors [7], because they exhibit good conductivity (the resistivity of RuO_2 is 35 μΩ-cm in bulk single crystal.), good thermal stability [8,9], excellent diffusion barrier properties [10] and high resistance to chemical corrosion [11]. A ZnO–Ru composite film can be fabricated by doping Ru into a ZnO film. It is thus possible for ZnO–Ru composite films to provide a class of transparent conducting and semiconductor materials.

Compared with conventional vacuum-based techniques, the sol–gel method is relatively simple and cheap. The stoichiometry is also easy to control and adjust, and it can be processed at relatively low temperatures [12]. This study thus fabricated ZnO–Ru composite film using the sol–gel process. The surface morphology, crystal structure, elemental composition, transmittance and band gap of ZnO–Ru composite films are also studied. The correlations among the Zn/Ru ratio, the pH of the pre-solution, the annealing temperature and the characteristics of ZnO–Ru composite films are derived.

2. Material and methods

A ZnO–Ru composite film with a thickness of 100 nm was prepared using a sol–gel process in combination with the spin-coating method. Hydrated zinc acetate ($Zn(CH_3COO)_2 \cdot 2H_2O$) and hydrated ruthenium (III) chloride ($RuCl_3.3.5H_2O$) were respectively used as precursors for the ZnO and RuO_2. $Zn(CH_3COO)_2 \cdot 2H_2O$ and $RuCl_3 \cdot 3.5H_2O$ were dissolved in ethylene glycol monomethyl ether (EGME) to form two pre-solutions. $Zn(CH_3COO)_2 \cdot 2H_2O$ (1 mmol) was hydrolyzed in EGME (30 ml) and stirred for 6 h. For the RuO_2 sols solution (deep purple), different amounts of $RuCl_3 \cdot 3H_2O$ (according to the Ru/Zn molar ratio) were first mixed with 30 ml EGME and then stirred for 1 h at room temperature, using a magnetic stirrer. The two pre-solutions were mixed at various Ru/Zn molar ratios (i.e., 0%, 1%, 2%, 3%, 4% and 6%) and stirred for 1 h. The pH values (4.86 and 10) of the mixed solutions were adjusted by adding different amounts of concentrated acetic acid (99.7%) and ammonia (0.1 N). The mixed solutions were spin-coated onto cleaned silicon with 100 nm thick SiO_2 and quartz glass substrates. After spin-coating, the films were baked at 80 °C for 5 min. Finally, the coatings were annealed in an O2 flow [150 sccm (standard cubic centimeter per minute)] ambient in a horizontal quartz-tube furnace, at 600 °C for 30 min. For use in thin film transistors, the thickness of the ZnO–Ru composite film is 20 nm. The film thickness was adjusted by varying

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the spin speed. The Al source and drain electrodes (300 nm thick) were then evaporated by e-beam evaporation through a shadow mask, to define the TFT channel width (2000 μm) and length (100 μm). The Si substrate, the ZnO–Ru composite film and the SiO_2 respectively function as the gate electrode, the active layer and the gate dielectric.

The characteristic crystal phases of the ZnO–Ru composite films were identified using glancing-incident angle x-ray diffraction (GIAXRD, Rigaku D/MAX2500), using Cu Kα radiation at an incident angle of 2°. The surface morphology and the film thickness of the ZnO–Ru composite films were determined using field emission scanning electron microscopy (FE-SEM, Philips XL-40FEG). The composition of the ZnO–Ru composite films was determined using Electron probe microanalysis (EPMA). The optical transmittance of the ZnO–Ru composite films that were deposited on a glass substrate was measured at normal incidence, from 1100 to 300 nm, using a Hitachi U-2001 UV/Visible Spectrophotometer. All of the electrical characteristics of the ZnO–Ru TFTs were measured using a semiconductor parameter analyzer (Agilent 4156 C) in ambient atmosphere in a dark box.

3. Results and discussion

In order to determine the phases present in the samples, before and after annealing at 600 °C, the sample was analyzed using GIAXRD. The GIAXRD patterns for the as-deposited films do not exhibit any characteristic peaks, which demonstrates that all of the as-deposited films are amorphous (data not shown). Fig. 1 shows the GIAXRD patterns for ZnO films that are annealed at 600 °C and doped with different molar ratios of Ru. There are several characteristic diffraction peaks in the figure, which pertain to the ZnO phase (JCPDS Card NO. 36–1451). The intensity of the ZnO diffraction peaks for all of the films decreases as the Ru-concentration of the ZnO films increases, as shown in Fig. 1. This demonstrates that the crystallinity decreases when ZnO films are doped with Ru.

In order to determine the way in which the acidity and basicity of the precursors affect the thin film morphology, ZnO films doped with 2% of Ru with pH values of 4.86 and 10 were spun from the pre-solutions. The surface morphologies of the 600 °C-annealed ZnO films doped with a Ru molar ratio of 2% and spun at pH values of 4.86 and 10 are shown in Fig. 2. Fig. 2(a) shows that the surface morphology of the 2%-doped ZnO film that was prepared at a pH of 4.86 is smooth and continuous, when observed using SEM. When the pH value is increased to 10, the sol–gel ZnO–Ru film exhibits a rugged surface, as shown in Fig. 2(b). When the magnification is increased to 20000×, the network-like surface

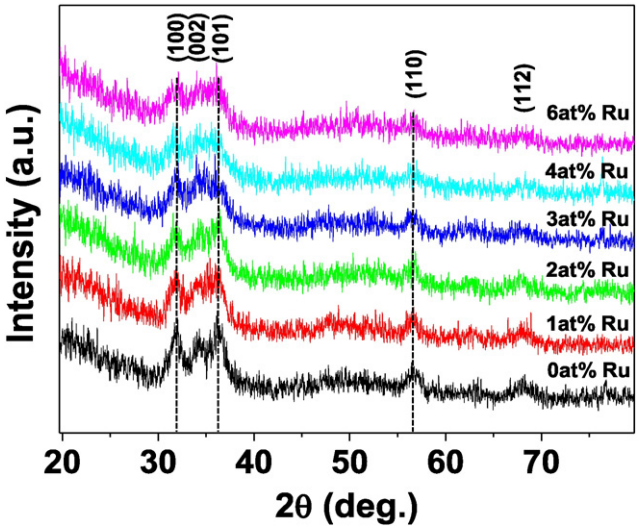

Fig. 1. GIAXRD patterns for ZnO films doped with different Ru molar ratios.

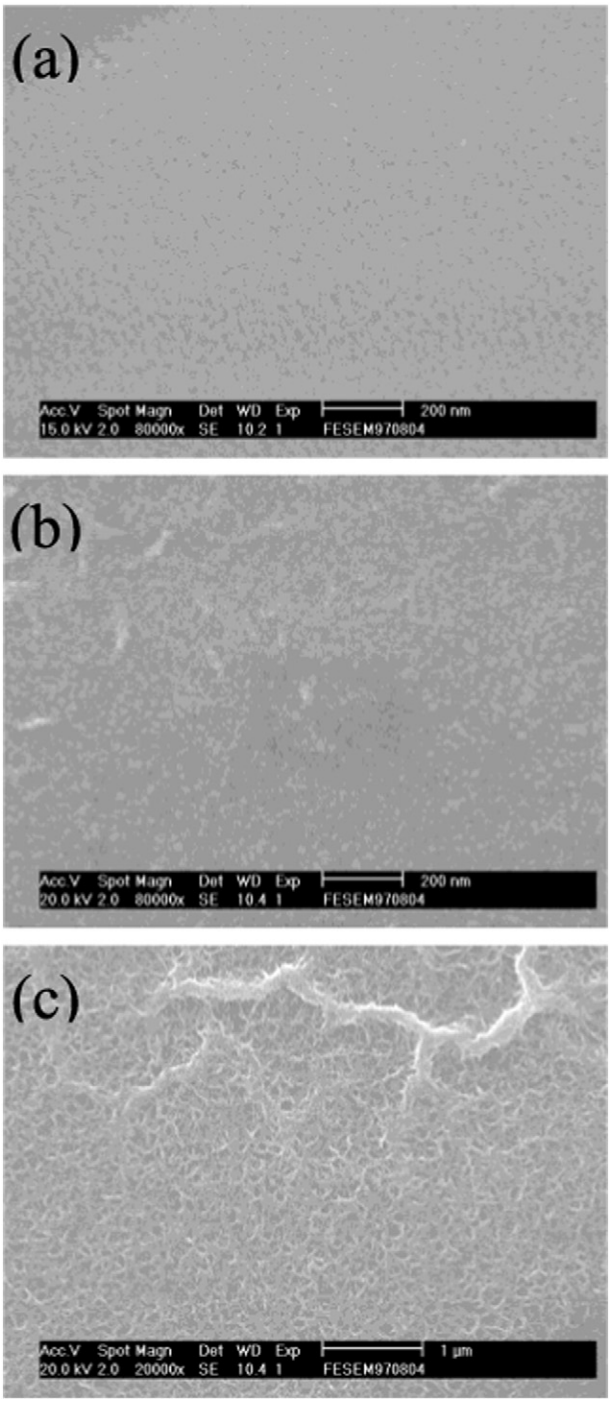

Fig. 2. Surface morphologies of ZnO films that are annealed at 600 °C and doped with Ru molar ratios of 2%: (a) prepared from an acidic precursor (pH = 4.86), (b) prepared from a basic precursor (pH = 10), and (c) an enlargement of Fig. 2(b).

becomes more apparent (see Fig. 2(c)). In general, the rate of hydrolysis increases under acidic conditions, but the condensation rate increases under basic conditions [13]. Therefore, the surface of 2% Ru-doped ZnO film that was annealed at 600 °C has a smooth and flat surface when the thin film is prepared from a precursor with a pH of 4.86. In contrast, the surface of the same film is network-like when it is prepared from a precursor with a pH of 10. In addition, EPMA was used to quantitatively examine the Ru/Zn molar ratio of the sol–gel ZnO–Ru films, as shown in Table 1. It is seen that the Ru/Zn ratios for the films are very close to the molar ratio of the hydrate ruthenium (III) chloride to the hydrate zinc acetate solutions. After annealing at 600 °C, the Ru/Zn ratios