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Superhydrophobic Al-doped ZnO nanorods-based electrically conductive and self-cleanable antireflecting window layer for thin film solar cell

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ABSTRACT

A simple strategy, based on the Al-doped ZnO nanorods (NRs), to get an antireflective, self-cleanable and electrical conductive window layer for the thin film solar cell was demonstrated. The length and diameter of Al-doped ZnO NRs were optimized by controlling Al precursor concentration and growth time and an average reflectance of 2.9% was achieved. Al-doped ZnO NRs simultaneously having the rugged surface morphology with the micrometer- and nanometer-scale roughness also exhibited superhydrophobicity and extremely small water contact angle (WCA) hysteresis below $\Delta 1^\circ$ after treatment of hydrophobic self-assembled monolayer (SAM). Finally, in spite of the existence of the SAM, the enhancement of the electrical contact with silver from Schottky to Ohmic for various Al doping concentrations was confirmed. Self-cleanable and electrically conductive antireflecting layer introduced in this work would be expected to increase photovoltaic efficiency in a thin film solar cell.

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1. Introduction

As a window layer in most thin film solar cells, the several hundreds of nanometer-thick transparent conducting metal-doped zinc oxide (ZnO) films have been used. There are many studies to give functional surface properties to the window layer of the solar cells for high efficient solar energy harvesting, for examples, a film with an intermediate refractive index, micro-texturing, absorption nanostructure switch photonic crystals and embedding metallic nanoparticles for surface plasmonic scattering between air and the window layer of the solar cell and so on [1–8].

Recently, for the antireflection of light incident surface on a thin film solar cell, we suggested the direct growth of vertically aligned ZnO NRs on the window layer *via.* a low temperature aqueous chemical process that is the most cheap and simple strategy, because the grain size of the layer is large enough and well oriented along *c*-axis to grow ZnO NRs with a high density [9–13]. Furthermore, to reduce the contact resistance between the NRs and the current collecting top silver electrode, a strategy exchanging the naturally n-type ZnO NRs showing Schottky contact with silver into aluminum (Al)-doped ZnO NRs showing Ohmic contact was introduced in our previous work [14].

To maximize surface functionality in the window layer for high efficient solar energy harvesting, we reinforced the Al-doped ZnO NRs to have a self-cleaning properties based on the top structures of the NRs in this work. Inherently, there is the rugged surface morphology with the micrometer- and nanometer-scale roughness from arbitrary narrowing vertically aligned Al-doped ZnO NRs in diameter by the adsorption of Al^{3+} on the NR's prismatic surface [14]. This hierarchical structure treated by fluorinated siloxane SAM showed the superhydrophobicity with the WCA hysteresis below $\Delta 1^\circ$. As a result, we demonstrated a multi-functional window layer which possessed antireflecting, electrical conducting and self-cleaning properties at the same time.

2. Experimental procedure

Ga-doped ZnO (GZO) film was used as a seed layer for growing ZnO NRs. A 750 nm-thick GZO film using a ZnO target containing Ga 5 wt% was deposited on a glass substrate by RF sputter at the RF power of 3 kW, a working pressure of 3 mTorr, an Ar flow rate of 30 sccm and a substrate temperature of 230 °C. In the typical method, undoped ZnO NRs were grown on the GZO film by using a hydrothermal method. 0.2 g of zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) dissolved in the 25 mL deionized (DI) water was mixed with 1 mL of ammonium hydroxide solution. ZnO NRs grown at 90 °C for different times were washed with DI water and

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dried at 60 °C for 6 h. In this work, doping concentration of Al in ZnO NRs was controlled by changing the concentration of aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$) during the above mentioned hydrothermal process.

To provide the NRs with the self-clearing function, the SAM of 1H, 1H, 2H, 2H -perfluorodecyltriethoxysilane (PFDTES) was coated on ZnO NRs. Before SAM treatment, ZnO NRs were treated by O_2 plasma at 60 W for 2 min. Then, this sample was put on the square dish ($125 \times 125 \times 20$ mm) and a PFDTES was dropped near the sample. Here, vapor deposition of PFDTES was processed for 30 min and it was finally stabilized at room temperature for 8 h.

Shape and morphology of the NRs were observed by field-emission scanning electron microscope (FESEM, S-5200, HITACHI). Electrical contact properties between NRs and Ag were investigated by using a semiconductor parameter analyzer system (Agilent B1500A, Agilent Technologies). Optical properties of the window layer were measured in wavelength range of 400–1200 nm by using a UV–vis spectrometer (JASCO, V-670). Static and dynamic contact angles of the water were measured by a contact angle analyzer (Phoenix-300, SEO).

3. Results and discussion

By increasing the concentration of $Al(NO_3)_3 \cdot 9H_2O$ from 0 to 6 mM, the morphological changes of the vertically aligned ZnO NRs grown for 90 min on GZO films are shown in Fig. 1(a)–(d). Without addition of $Al(NO_3)_3 \cdot 9H_2O$, undoped ZnO NRs were vertically, densely and uniformly grown with a length of about 2.62 μm as shown in Fig. 1(a). The origin of the vertical alignment

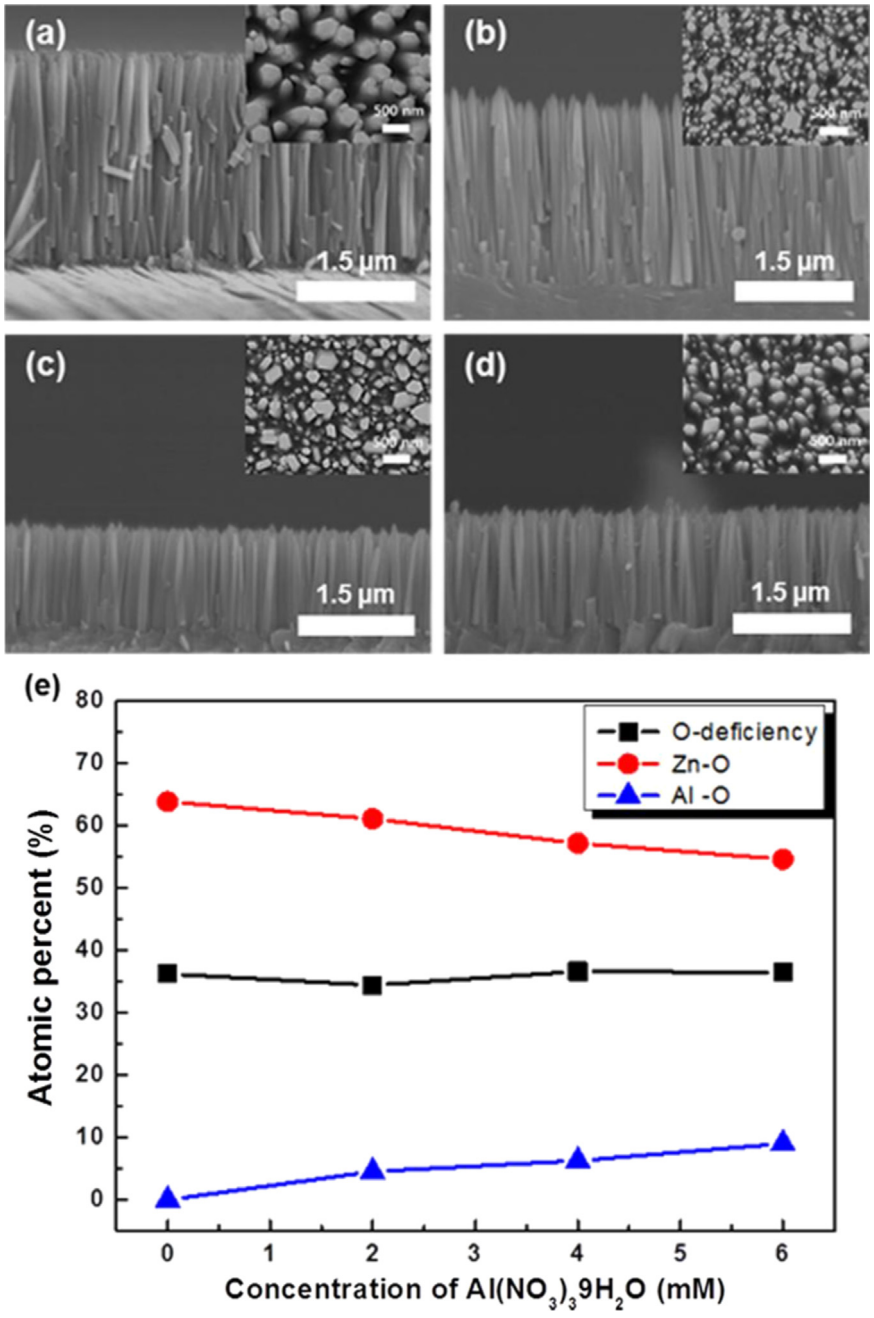

Fig. 1. Top and 90° cross-sectional SEM images of the Al-doped ZnO NRs grown for 90 min on Ga-doped ZnO films with different Al $(NO_3)_3 \cdot 9H_2O$ concentrations at (a) 0, (b) 2, (c) 4 and (d) 6 mM. (e) Atomic percents of Zn–O, Al–O and O-deficient in the same NRs with different Al $(NO_3)_3 \cdot 9H_2O$ concentrations.

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