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Transport and magnetic properties of $ZnCo_2O_4$/Si heterostructures grown by radio frequency magnetron sputtering

Z. Chen [a,*], X.L. Wen [b], L.W. Niu [a], M. Duan [a], Y.J. Zhang [a], X.L. Dong [a], R.L. Zhang [a], C.L. Chen [a]

[a] Key Laboratory of Space Applied Physics and Chemistry (Ministry of Education), School of Science, Northwestern Polytechnical University, Xi'an 710072, China
[b] State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, Xi'an 710072, China

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ABSTRACT

We report a growth of $ZnCo_2O_4$/Si heterostructures by using radio frequency magnetron sputtering (RFMS) method, and characterizations of their transport and magnetic properties. It is found that the $ZnCo_2O_4$/Si heterostructures exhibit a good rectifying behavior at four measured temperatures of 100 K, 150 K, 200 K, and 290 K. The energy band structure reveals that the electron is the mainly contributing factor to the current of the $ZnCo_2O_4$/Si heterostructures. The transport behaviors of these heterostructures can be qualitatively explained by diffusion or recombination in the space charge region at low voltages ranging from 0.16 V to 0.3 V, and the space-charge-limited current conduction mechanism plays a main role when the voltage is higher than 0.3 V. The magnetic measurements of the $ZnCo_2O_4$/Si heterostructures indicate a strong ferromagnetic behavior at oxygen pressures ranging from 1.333 Pa to 6.665 Pa. It is believed that this work would open perspectives for $ZnCo_2O_4$/Si heterostructure-based devices.

1. Introduction

ZnO/Si heterostructures have gained substantial interest in the integration of optoelectronic devices [1–4], which take advantage of the hybrid merits of ZnO thin films and the cheapness of Si substrates [5–8]. Recently, a number of reports [9–11] work on visible and ultraviolet photoresponse properties of ZnO/p-Si heterostructures. For example, n-ZnO/p-Si heterostructure prepared by sol–gel method was proved to have strong photovoltaic responses illuminated by either ultraviolet or visible light [12]. However, a common problem is that the photovoltaic efficiency of ZnO/Si heterostructures is still very low. Element doped ZnO/Si heterostructures are expected to be a potential way to improve the photovoltaic efficiency. $ZnCo_2O_4$ thin film is recently confirmed to be one of good candidates [13]. Nevertheless, their transport behaviors have not been reported yet. It is significant and important to understand physical properties and transport mechanisms of $ZnCo_2O_4$/p-Si heterostructures for expanding their applications.

The ferromagnetic nature places the cobalt-doped ZnO in the realm of ferromagnetic semiconductors, which can be considered for spintronics applications [14–17]. $ZnCo_2O_4$, which is a spinel oxide with strong ferromagnetism and high Curie temperatures (Tc) greatly exceeding room temperature [13,18–20] constitutes another class of ferromagnetic semiconductors. Although there are numbers of studies on cobalt doped ZnO [21–26], the ferromagnetism of n-type and p-type $ZnCo_2O_4$ is a continuous debate and the microscopic origins of this ferromagnetism remain poorly understood. Moreover, there is no consensus on whether the observed ferromagnetism is intrinsic. A detailed understanding of high Tc ferromagnetism in $ZnCo_2O_4$ thin film is helpful to promote their applications in spintronics.

In this work, we present a fabrication of $ZnCo_2O_4$/p-Si heterostructures by using RFMS method. Detailed investigations on their microstructure, transport behaviors and magnetic properties have been performed and the results have been discussed. It is believed that our work is important to expand the $ZnCo_2O_4$/p-Si heterostructures into high-effective spintronic and optoelectronic application.

2. Experimental details

The $ZnCo_2O_4$ thin films were deposited on p-Si(100) substrates by RFMS method. The stoichiometric $ZnCo_2O_4$ ablation target was made by pressed powder of evenly mixed ZnO and Co_3O_4 with 1:1 composition, and sintered in air at 1000 °C. Before the deposition, the substrate was treated by ultrasonic cleaning with acetone followed by ethanol, and finally dried by blowing purity nitrogen. The substrates were fixed in the substrate holder, and the distance between the target and the substrate was 5 cm. Then, the chamber was evacuated lower than 1×10^{-5} Pa and the substrate was annealed at 750 °C for 30 min to clean the carbon contamination and form a high crystalline surface. During the deposition, the substrates were kept at 450 °C, the RFMS power is 110 W, and Ar/O_2 keeps the ratio of 1 to 2 and partial pressures of oxygen are 1.333 Pa, 2.666 Pa, 6.665 Pa and 13.33 Pa, separately. The

* Corresponding author. Tel.: +86 29 8843 1670.
E-mail address: zhaoch17@hotmail.com (Z. Chen).

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deposited films were annealed at 450 °C in the oxygen atmosphere for 1 h and then cooled to the room temperature with a rate of 5 °C/min with 101325 Pa oxygen pressure.

The phase structures of the $ZnCo_2O_4$/p-Si heterostructures were characterized by X-ray diffraction (XRD, Cu K_α radiation, D/max2200PC, Rigaku) using $\theta - 2\theta$ scans mode. The valence states of Co ions in $ZnCo_2O_4$ were characterized with an X-ray Photoelectron Spectroscopy (XPS, PHI-5400, PE). In the process of measurement, Mg Kα radiation operated at 250 W and the high voltage was kept at 14 kV with a detection angle at 54°. The measurement was conducted at a base pressure of over $3 \times 10^{-}8$ Pa and the sample was sputtered by an argon ion beam with a 3.0 keV and an ion beam density of 0.44 μA/0.5 cm × 0.5 cm for 10 min. All the spectra were calibrated with C 1 s standard spectrum. Microstructure and surface morphology of the sample were examined by atom force microscopy (AFM, Olympus, AC240TS MFP-3D, Asylum Research) in tapping mode. To investigate the electrical properties of these films, circular Pt electrodes (diameter 0.20 mm) were sputtered on the film surface using a shadow mask. The thicknesses of the films measured by using a spectroscopic ellipsometer (SPECEI-2000-VIS, Mikropack) are about 213 nm. The transport properties of the films were performed under different temperatures using a Keithley Sourcemeters (2400) in low temperature Hall system. Magnetic properties of the thin films were characterized by a temperature-dependent superconducting quan-tum interference device (SQUID, Quantum Design Inc.).

3. Results and discussion

Fig. 1(a) shows a representative X-ray diffraction pattern of $ZnCo_2O_4$/p-Si heterostructures grown at 450 °C and various oxygen partial pressures. It is observed that all samples show similar diffraction pattern, of which peaks can be well indexed with a cubic spinel structure. There is no discernable impurity peak in the diffraction pattern at four various oxygen pressures. And, the lattice spacing did not change with oxygen pressures. The surface morphology of $ZnCo_2O_4$/p-Si heterostructures grown at 450 °C and 2.666 Pa measured by atom force microscope (AFM) is shown in Fig. 1(b), revealing a flat surface and uniform distribution of grains. The root mean square roughness was 7 nm over a 1 μm^2 area, and the average grain size is less than 100 nm. In order to determine the valency of Co element in $ZnCo_2O_4$ thin film, the high resolution XPS scan of the Co peak $2p_{3/2}$ and $2p_{1/2}$ locations in a $ZnCo_2O_4$ film grown at 450 °C and 6.665 Pa O_2 is shown in Fig. 2. It is noted that the stoichiometric $ZnCo_2O_4$ ablation target in our experiment was made by pressed powder of evenly mixed ZnO and Co_3O_4 with 1:1 composition. In principle, the valency of Co in $ZnCo_2O_4$ films should be determined by whether Co occupies the A-site or B-site in the AB_2O_4 spinel structure. The spinel Co_3O_4 has +2 and +3 valence states due to occupancy at both cation sites. As shown in Fig. 2, the XPS data shows a large height of the $2p_{3/2}$ and a $2p_{1/2}$ satellite peaks, which experimentally indicates a Co^{+2} in the $ZnCo_2O_4$ films and suggests that some of the Co in the $ZnCo_2O_4$ films does reside on the Zn site. This finding is different from the others' reports [27,28], of which intrinsic reason originate from the target composition.

The current–voltage (*I*–*V*) characteristics of the $ZnCo_2O_4$/p-Si heterostructures at various temperatures ranging from 100 K to 290 K are shown in Fig. 3, of which inset reveals a schematic circuit of the heterostructure. The convention of the applied bias polarity is defined as negative at the $ZnCo_2O_4$ side and positive at the p-Si side. It can be seen that all of *I*–*V* curves in Fig. 3 show a well-defined rectifying diode-like behavior at four temperatures, revealing a conventional semiconductor p–n junction. In order to further confirm the semiconductor type of as-grown $ZnCo_2O_4$ film, we carried out Hall measurement of the $ZnCo_2O_4$ thin film grown at 6.665 Pa. The relevant data are shown in Table 1, which shows that the $ZnCo_2O_4$ films grown at 6.665 Pa are n-type under low magnetic field and P-type under high magnetic field. Because we fabricated $ZnCo_2O_4$ films by using commercial P-type Si substrates, the carriers of P-type Si can affect the measurement result of experiment under high magnetic field. In addition, the *I*–*V* curves in our experiments show that the $ZnCo_2O_4$/p-Si heterostructure

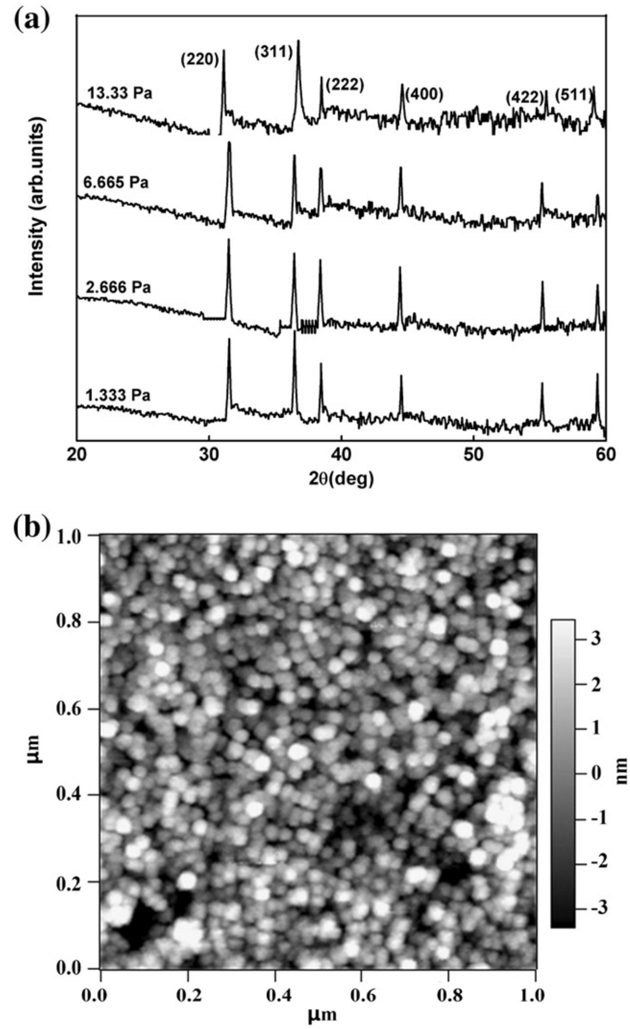

Fig. 1. (a) A representative X-ray diffraction pattern of $ZnCo_2O_4$/Si heterostructures at different partial pressures of oxygen. (b) A typical AFM image of the $ZnCo_2O_4$/Si heterostructures at 450 °C and 2.666 Pa.

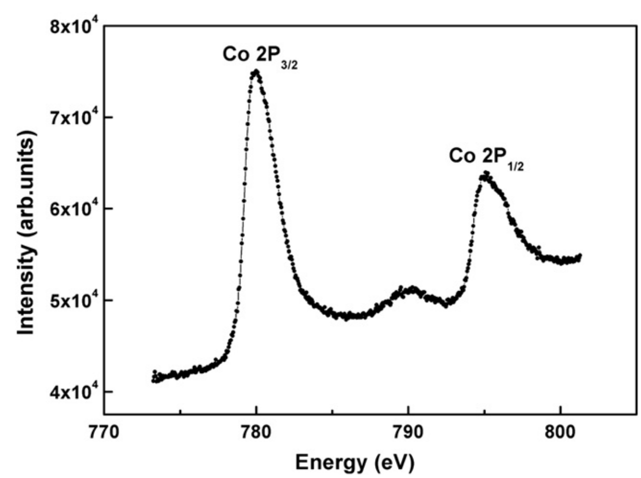

Fig. 2. X-Ray Photoelectron Spectroscopy spectrum for a ZnCo2O4 film grown at 450 °C and 6.665 Pa oxygen, showing the Co 2p3/2 and 2p1/2 peaks.