Rectifying and photovoltaic properties of $ZnCo_2O_4$/Si heterostructure grown by pulsed laser deposition*

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$ZnCo_2O_4$/Si heterostructures have been fabricated by a pulsed laser deposition method, and their transport behaviors and photovoltaic properties have been characterized. The $ZnCo_2O_4$/Si heterostructures show a good rectifying behavior at five different temperatures ranging from 50 K to 290 K. The measurements of the photovoltaic response reveals that a photovoltage of 33 mV is generated when the heterostructures are illuminated by a 532 nm laser of 250 mW/cm^2 and mechanically chopped at 2500 Hz. Both the photocurrent and the photovoltage clearly increase with the increase of the laser intensity at room temperature. However, the heterostructures' photovoltage peak decreases with the increase of the temperature. This work may open new perspectives for $ZnCo_2O_4$/Si heterostructure-based devices.

Keywords: $ZnCo_2O_4$/Si heterostructure, rectifying behavior, photovoltaic properties, pusled laser deposition

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1. Introduction

$ZnCo_2O_4$ has attracted much attention in recent years due to its unique magnetic and electrical properties and chemical stabilities.[1–3] These properties are significant not only from a fundamental point of view, for example, ferromagnetism[1] and the ability to control the carrier types via the growth atmosphere of oxygen,[4] but also for their potential applications, such as dilute magnetic semiconductors,[5] spinelectronics,[6,7] optoelectronics,[8,9] and anode materials.[10] Its crystal structure is a spinel with Zn^{2+} occupying the tetrahedral sites and Co^{3+} occupying the octahedral sites.[11] Various methods, including physical[12] and chemical techniques,[13,14] have been used to prepare microscale, nanoscale, and thin film $ZnCo_2O_4$. The majority of the reported works focused on the growth of p-type $ZnCo_2O_4$ and the characterization of their electrical and magnetic properties.[2,14] And until now, there is no report on $ZnCo_2O_4$ heterostructures.

The heterostructures, such as ZnO/Si heterostructures, have gained substantial interest in the integration of optoelectronic devices,[15,16] which take advantages of the hybrid merits of ZnO thin films and the cheap costs of Si substrates.[17–20] Moreover, the heterostructures can efficiently collect solar energy through the double-band structure, where the ZnO layers can absorb the high energy photons in the ultraviolet (UV) region, and the depletion region of the p-Si substrates can collect the low-energy photons in the visible range after the light has passed through the ZnO layers. Recently, many works have reported the investigation of the photoresponse properties of ZnO/p-Si heterostructures under visible and UV illuminations.[21–23] For example, an n-ZnO/p-Si heterostructur prepared by the sol–gel method, illuminated by visible and UV lights, demonstrated a strong photoresponse phenomenon.[24] However, a common problem is that the efficiency of the ZnO/Si heterostructures is still very low. Element doped ZnO/Si heterostructures are expected to improve the photovoltaic efficiency. A $ZnCo_2O_4$ thin film was recently confirmed to be one of the good candidates. The study of the photovoltaic effect of the $ZnCo_2O_4$/p-Si heterostructures has not been reported yet. It is well known that $ZnCo_2O_4$ yields a bandgap of approximately 2.63 eV, which is far less than the 3.36 eV bandgap of ZnO. The sensitivity of the $ZnCo_2O_4$/p-Si heterostructures thus could be quite different from that of the ZnO/p-Si heterostructures.

Here, we present the fabrication of $ZnCo_2O_4$/p-Si heterostructures by using a pulsed laser deposition method and report the measurements of their transport and photovoltaic properties. It is believed that our work is important to the study of the application of $ZnCo_2O_4$/p-Si heterostructures in high-effective spinelectronic and optoelectronic devices.

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2. Experiment

The $ZnCo_2O_4$ thin films were deposited on p-Si (100) substrates by using a pulsed laser deposition method. The stoichiometric $ZnCo_2O_4$ ablation target was made of pressed powder of evenly mixed ZnO and Co_3O_4 with 1:1 composition ratio, and sintered in air at 1000 °C. Before the deposition, the substrates were 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. The chamber was evacuated lower than 2×10^{-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 temperature of the substrate was kept at 450 °C and the pressure of oxygen was 20 mTorr. A KrF excimer laser (248 nm) operating with a repetition rate of 2 Hz was used for ablation. The energy density of the laser was approximately 1.5 J/cm^2. The deposited film was annealed at 500 °C in an oxygen atmosphere for 1 h and then cooled to room temperature with a cooling rate of 5 °C/min under 1 atm of oxygen pressure.

The phase structure of the $ZnCo_2O_4$/p-Si heterostructures was characterized by X-ray diffraction (XRD, Cu Kα radiation D/max2200PC, Rigaku) using the θ–2θ scan mode. The thickness of the film measured by a spectroscopic ellipsometer (SPECEI-2000-VIS Mikropack) was about 213 nm. To investigate the electrical and photovoltaic properties, two circular electrodes (diameter 0.20 mm) were sputtered on $ZnCo_2O_4$ and Si surfaces using a shadow mask. Their current–voltage (I–V) characteristics under dark background and light illumination were measured at 290 K using a Keithley sourcemeter (2400). The light source used in the photovoltaic experiment was a 532 nm green laser with a tunable intensity ranging from 0 mW to 300 mW and modulated by a chopper at 2500 Hz. The photovoltaic signals were gathered by using a Tektronix digitizing oscilloscope (MSO4054) with 500 MHz bandwidth and 1 MΩ input impedance. All of the various temperature experiments were performed in a low temperature Hall system.

3. Results and discussion

Figure 1(a) shows a representative X-ray diffraction pattern of the $ZnCo_2O_4$/p-Si heterostructures, of which the peak intensities are normalized with respect to the highest intensity of the Si (200) peak. The Si (200) peak is not shown here. It is seen that the heterostructure has a (111) preferential orientation and there is no second phase or other preferential orientations detected. The surface morphology of the $ZnCo_2O_4$ heterostructures measured by atomic force microscopy (Olympus, AC240TS MFP-3D, Asylum Research) in tapping mode is shown in Fig. 1(b), revealing a flat surface and a uniform distribution of grains. The average grain size is less than 50 nm, and the roughness is 3.6 nm.

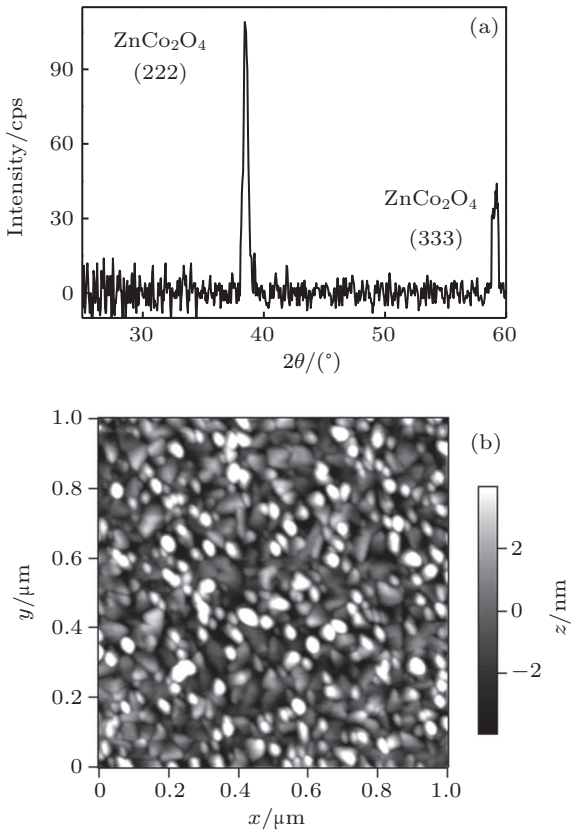


Fig. 1. (a) A representative X-ray diffraction pattern of the $ZnCo_2O_4$/p-Si heterostructure. (b) A typical AFM image of the heterostructure.

The dark current–voltage characteristics of the $ZnCo_2O_4$/p-Si heterostructures at various temperatures ranging from 50 K to 290 K are shown in Fig. 2, and the inset shows a schematic circuit of the heterostructures. 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 in Fig. 2 that all of the I–V curves at the five temperatures show a well-defined rectifying diode-like behavior, revealing a conventional semiconductor p–n junction.

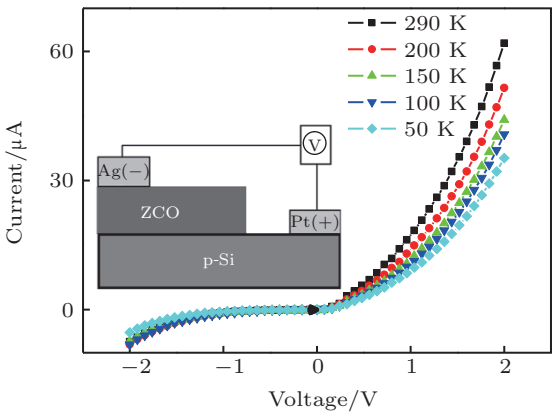


Fig. 2. (color online) Current–voltage curves of the $ZnCo_2O_4$/p-Si heterostructure at five temperatures. Solid lines are the exponential fits according to the expression $I \propto (qV/\eta kT)$. The inset shows the schematic circuit of the heterostructure.

The turn-on voltages of the $ZnCo_2O_4$/p-Si heterostructures gradually decrease as the temperature increases at the same applied voltage. On the contrary, the currents increase. This phenomenon indicates a negative temperature coefficient between the resistivity of the $ZnCo_2O_4$/p-Si heterostructures. It is derived from a lower potential barrier and a narrower depletion region present in the heterostructure with an increasing temperature. The current, which corresponds to the positive potential of the substrate, can be expressed as[25,26]

$$I = I_0 \left[\exp(AV) - 1\right], \tag{1}$$

with

$$A = \frac{q}{\eta k_B T}, \tag{2}$$

where q is the electronic charge, η is the ideality factor, k_B is the Boltzmann constant, and I is the reverse saturation current. The ideality factor η describes a deviation of the diode from an ideal p–n junction and can be evaluated by fitting the experimental data using Eq. (1). In our case, η varies from 5.43 to 3.62 when the temperature increases from 50 K to 290 K. It is known that η typically varies from 1 to 2 for an ideal p–n heterostructure according to the Sah–Noyce–Shockley theory.[27] Our experimental η is clearly much higher than that of the ideal p–n heterostructure. It may be that it originated from some defective states existing in the $ZnCo_2O_4$/p-Si junction interface. Furthermore, the coefficient A is a linear function of the reciprocal of the temperature, which indicates that the current is dominated by diffusion or recombination in the junction space charge region.

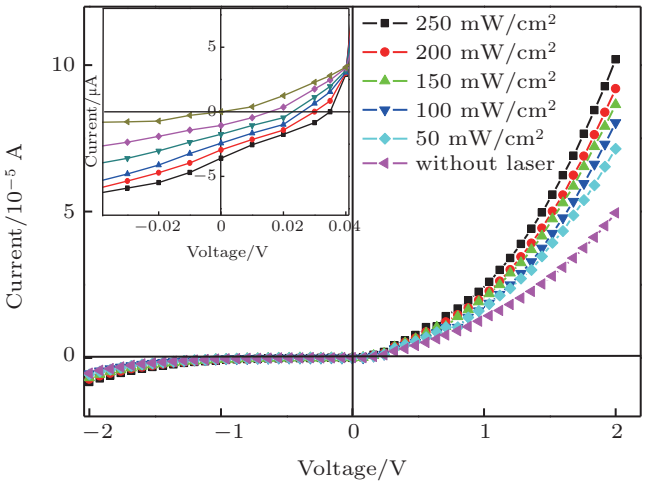


Fig. 3. (color online) Current–voltage curves of the $ZnCo_2O_4$/p-Si heterostructure in the dark and under the illuminations of 532-nm laser with different intensities. The inset shows the photovoltaic characteristics at low biases.

The current–voltage characteristics of the $ZnCo_2O_4$/p-Si heterostructures in the dark and under the illuminations of 532 nm green laser with different intensities, measured at room temperature are illustrated in Fig. 3. The photocurrents under various illuminations are far larger than that in the dark. In particular, the inset of Fig. 3 shows that the short-circuit photocurrent and photovoltage of the $ZnCo_2O_4$/p-Si heterostructures remarkably increase with the increasing laser intensity, which indicates that the carrier concentration is determined by the incident laser intensity. It is reasonable to believe that the photovoltaic effect of the heterostructures is related to the laser-induced carriers as well as the carrier separation by the built-in electric field at the interface between the $ZnCo_2O_4$ film and the p-Si substrate.[28,29]

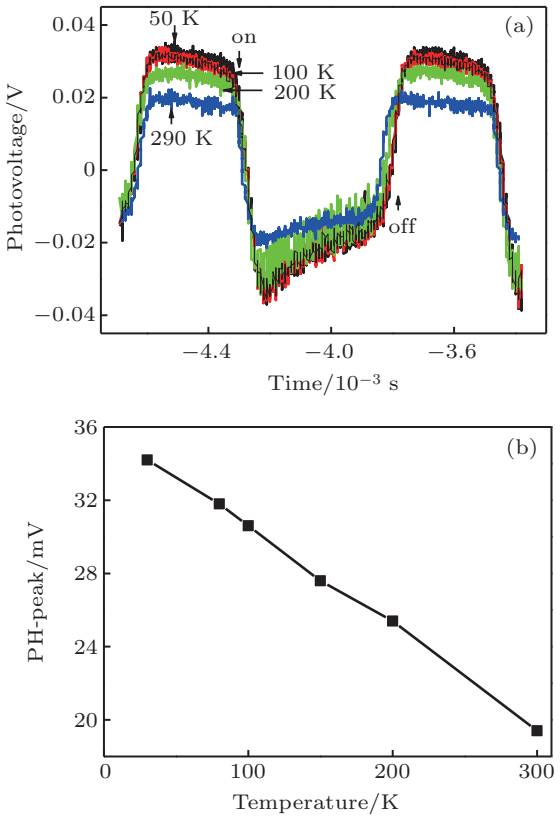


Fig. 4. (color online) (a) The time dependence of the photovoltage measured at four temperatures, where the heterostructures are illuminated by a 532 nm green laser with 100 mW/cm^2 intensity and zero bias chopped at 2500 Hz. (b) The peak photovoltage as a function of temperature.

In order to measure the photovoltaic responses of the $ZnCo_2O_4$/p-Si heterostructures, a mechanical chopper was used to chop the light of a 532 nm green laser with 100 mW/cm^2 intensity and zero bias at 2500 Hz. The relevant results detected at 50 K, 100 K, 200 K and 290 K are shown in Fig. 4(a). It is clearly seen that the induced photovoltage suddenly increases to a transient maximum and then reaches a steady state in each period measured at all four temperatures. A peak photovoltage appears after approximate 90 μs in each period. When the laser beam is blocked, the photovoltage quickly drops and then inclines to the initial value. The peak photovoltage of the $ZnCo_2O_4$/p-Si heterostructures ver-

sus the temperature is plotted in Fig. 4(b), revealing that the peak photovoltage decreases with the increasing temperature.

The photovoltage of the $ZnCo_2O_4$/p-Si heterostructures versus the intensity of the incident laser was also studied as shown in Fig. 5(a). It is clearly seen that the photovoltage of the heterostructures is proportional to the increase of the laser intensity ranging from 50 mW/cm^2 to 250 mW/cm^2. A 33 mV peak photovoltage is achieved under 250 mW/cm^2 illumination. The peak value as a function of the laser intensity at room temperature is plotted in Fig. 5(b), which shows a linear relation similar to the p–n junction behavior. Therefore, we adapt the semiconductor theory for a standard p–n junction to analysis our experimental data, in which the expression is[30]

$$V_{\rm p} = \frac{k_{\rm B}T}{{\rm e}^{\ln(1+\alpha P)}}, \tag{3}$$

where $k_{\rm B}$ is the Boltzmann constant and P is the illumination intensity. The value of α is fitted to be about 7.2 from the experimental data in Fig. 5(b).

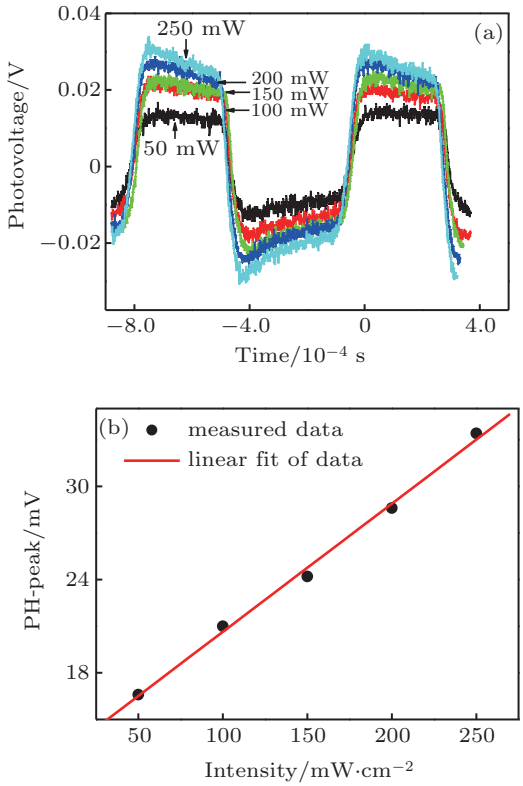


Fig. 5. (color online) (a) The time dependence of the photovoltage under different laser intensities at room temperature. (b) The peak photovoltage as a function of the laser intensity.

We now discuss the physical origin of the photovoltaic effect in the $ZnCo_2O_4$/p-Si heterostructures. Our heterostructures built with the $ZnCo_2O_4$ thin film sputtered on a p-Si substrate are a conventional p–n junction. When the electrons in the $ZnCo_2O_4$ thin film flow into the Si substrate, the holes in the Si substrate simultaneously inject into the $ZnCo_2O_4$ thin film because of diffusion. In this process, the recombination of electrons and holes produces a depletion layer and induces a built-in electric field. The electron affinity and the band gap of $ZnCo_2O_4$ are about 4.35 eV and 2.6 eV, respectively.[2] The electron affinity and the band gap of the p-Si are 4.05 eV and 1.1 eV, respectively. The photon energy of the 532 nm laser is about 3.75 eV, which is larger than the band gaps of the $ZnCo_2O_4$ film and the Si substrate. Therefore, when the 532 nm laser is incident on the surfaces of our specimens, a large number of photon-induced electron–hole pairs can be generated. Under the effect of the built-in electric field at the interface of the $ZnCo_2O_4$/p-Si junction, the holes in the $ZnCo_2O_4$ thin film shift to the P region, meanwhile the electrons in the Si substrate move to the N region. As a consequence, the potential in the P region rises, and that of the N region is reduced, which inevitably form a photovoltaic potential at the opposite ends of the $ZnCo_2O_4$/p-Si p–n junction. In addition, as we know that the pyroelectric effect is a transient effect, it converts a temperature change into electric current and voltage, which causes an unstable photovoltage[31] in our case. Thus, in Fig. 4(a), the initial spike of the induced photovoltage in each period may be attributed to the pyroelectric effect, and the steady-state photovoltage (Fig. 4(a)) should originate from the photogenerated carriers. In a semiconductor, the minority carrier concentration increases exponentially with the increase of the temperature, which promotes the increase of the photocurrent. It is well known that the photovoltage is related to the accumulation of the photogenerated carriers and the depletion layer width.[32–34] On one hand, when the temperature increases, the accumulation of the photo-generated carriers is reduced because of thermal fluctuations. On the other hand, when the temperature increases, the Fermi level in the semiconductor will be far away from the extrema of the energy band, which causes difference reductions of the Fermi energy in the semiconductor on both sides of the P–N heterostructure. As a result, the depletion layer width decreases with the increase of the temperature. Therefore, these two facts eventually lead to the decrease of the peak photovoltage with the increase of the temperature.

4. Conclusion

In summary, $ZnCo_2O_4$/p-Si heterostructures have been fabricated and their transport behaviors and photovoltaic properties have been investigated. The $ZnCo_2O_4$/p-Si heterostructures show a well-defined rectifying diode-like behavior at various temperatures ranging from 50 K to 290 K. The induced photocurrents and photovoltages are proportional to the intensity of the incident laser. However, the photovoltages increase with decreasing temperature. The peak photovoltage linearly increases with the increase of the laser intensity. The photovoltaic effect of the $ZnCo_2O_4$/p-Si heterostructures may rely

on the accumulation of the photogenerated carriers at the interface between the $ZnCo_2O_4$ thin film and the p-Si substrate. Our work has proved that the $ZnCo_2O_4$/Si heterostructures can be applied to photovoltaic devices, which is significant and important for the development of photovoltaic materials.

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