OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 4, No. 5, May 2010, p. 681 - 684

Effect of doping concentration on photovoltaic property of ZnO:Al/Si heterojunction

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N-ZnO:Al(ZAO)/P-Si heterojunctions were prepared by direct current reactive sputtering. Al dopant concentrations of ZnO films were altered by varying the sputtering targets. The crystal structure, electrical property and photovoltaic effect were examined by XRD, Hall effect measurement, open circuit voltage and short circuit current. The results demonstrated that all the samples had a strong preferred *c*-axis orientation, and the crystal quality was destroyed with the increasing of Al concentration. The Hall effect measurement shows that the carrier concentration increased with the addition of Al dopant. It was worth emphasizing that the photovoltaic effect was improved obviously by increasing Al concentration. In order to further investigate the mechanism of the influence of Al contents, the response spectra of these samples were analyzed in detail.

(Received March 01, 2010; accepted May 20, 2010)

Keywords: Photovoltaic property, ZnO/Si, Al concentration

1. Introduction

Among various types of solar cells, the P-N junction solar cells of single crystalline silicon are undoubtedly preferred because of their high conversion efficiencies (above 20%). However, these monocrystalline silicon solar cells require very elaborate configurations for the realization of high efficiency, and thus have a serious shortcoming that the manufacturing cost is very high. On the other hand, low-cost solar cells have obtained more and more attention recently, even though they have relatively low conversion efficiencies.

Among many different low-cost solar cells, one interesting heterojunction solar cell is the transparent conductive oxide semiconductor hererojunction. The solar cells have a number of potential advantages such as an excellent blue response, simple processing and low deposition temperature[1] simple structure. Although they have a very simple structure, relatively high conversion efficiencies in the 12~15% range have been obtained using indium tin oxide (ITO) films[2]. Nevertheless, on the earth source of indium (In) is limited. As a wide band gap semiconductor, zinc oxide (ZnO) thin films have good electrical/optical properties and lower in cost comparable to the ITO films. Besides, it has attracted much attention because of their effective use in the fabrication of solar cells[3,4], solid state luminescent device and electronic devices[5,6] in the last decade. So it is possible to use the ZnO films to make ZnO/Si heterojunction solar cells. A.A. Ibrahim et al.[1] had reported ZnO/Si heterojunction produced by spray pyrolysis method. The solar cells showed relatively high conversion efficiency of 6.6%. As far as we know, the effect of Al doping concentration on photovoltaic(PV) property of ZnO/Si junction has not been reported.

ZnO films can be produced by DC reactive and magnetron sputtering[7,8], metal-organic chemical vapor deposition (MOCVD)[9,10], vacuum evaporation[11], sol-gel method [12], pulsed laser deposition [13]and spray pyrolysis[14]. The conversion efficiency of ZnO/Si solar cell depends greatly on the properties of ZnO films which are dominated by the growth conditions including deposition temperature, growth pressure and deposition time. We had studied these problems in previous articles[15,16]. According to the previous results, conversion efficiency can be improved by Al doping in ZnO films. In this work, the N-ZnO/P-Si heterojunction solar cell was prepared by DC sputtering, and the effect of Al doping concentration on the PV effect was investigated in detail.

2. Experiment

Al doped ZnO films were prepared by direct current reactive sputtering on P-Si (100) substrates with resistivity of 6-12Ω·cm. Si substrates with an area of $1\times1cm^2$ were treated by a standard wet cleaning procedure. In order to study the optical and electrical properties, the quartz substrates were also placed into the chamber at the same time. During deposition, argon and oxygen were introduced to keep the pressure at 8×10^{-2} Torr ($Ar:O_2$=6:2). The distance from target to substrate was maintained at 5cm and the substrate temperature at 300℃. The sputtering time was 1.5h. To compare the Al-doped ZnO with pure ZnO film, five groups of samples (marked A-E) were grown with different sputtering targets. The targets of A-E were pure Zn (99.99%), 0.4% Al-mixed Zn (Al pieces on Zn target surface, area percent), 0.7% Al-mixed Zn, 0.9% Al-mixed Zn and 1.6% Al-mixed Zn.

The crystal structure was measured by X-ray diffraction (XRD) technique using MXPAHF type system. The films resistivity was measured by Four-probe method and carrier concentration and mobility were measured by Hall measurement in Van der Pauw configuration at room temperature. The measurement of PV effect were performed keeping the light irradiation area a constant (φ=6mm), Optical response spectra of the heterojunctions had been tested by monochromator (DS-5 type) with Xe lamp(LHX, 150W).

3. Results and discussion

In order to study the effect of Al concentration on microstructural properties of Al-doped ZnO thin films , we measured the XRD patterns of sample A-E on Si (100) substrates which were shown in Fig. 1 (A. 0%; B. 0.4%; C. 0.7% D. 0.9% E. 1.6%). It can be seen that all the samples exhibit only the (002) diffraction peaks besides the diffraction peak from Si(100) substrates, the results indicate that they all grow along the *c*-axis perpendicular to Si substrates due to its self-texturing phenomenon. Thus, it can be concluded that import of Al dopant don't change the crystal structure of ZnO. However, the peak position and full-width at half-maximum (FWHM) of (002) diffraction peak changed with Al doping concentration obviously, as mentioned in Table 1.

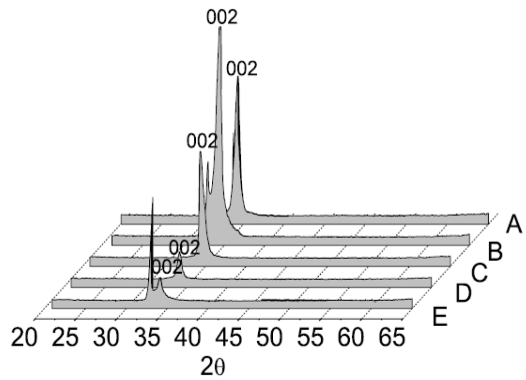

Fig. 1. XRD patterns of ZnO films on Si(100) with different Al doping concentrations. A. 0%; B. 0.4%; C. 0.7% D. 0.9% E. 1.6%.

Table 1. This shows the comparison between calculated c values, grain size, the estimated percentage strain, and the FWHM of the (002) peak of ZnO for sample A-E.

S. No.	FWHM (002) (^{0})	Diffraction (θ)	Grain size (nm)	Strain (%)	*c* value (Å)
A	0.73	17.17	11.4	1.73	5.216
B	0.46	17.255	18.1	-2.88	5.192
C	0.68	17.2	12.2	…	5.207
D	0.7	17.1	11.8	5.76	5.237
C	0.8	17.06	10.4	8.06	5.249

In addition, the calculated values of the "lattice parameter *c*", grain size and the estimated percentage strain were also shown in it. From figure 1 and table 1, several points should be mentioned. Firstly, the intensity of (002) peak weakens and the FWHM becomes wider with increasing doping concentration. So, the crystal quality of films is deteriorated with increasing of Al doping concentration, which may be due to the formation of stresses by the difference in ion size between zinc and the dopant and the segregation of dopants in grain boundaries for high doping concentrations. Secondly , the crystal structure of ZnO films are also changed due to addition of Al atom. Thus, the sample B has the minimum value of $FWHM_{(002)}$ and the biggest grain size. The ionic radius of Al^{3+}(53pm) are smaller than Zn^{2+}(72pm) [17], the *c* value will shorten comparing to pure ZnO when introducing a little Al atom, and with the Al concentration increase, superabundance Al atoms would hold the grain boundaries and make the lattice stretch; accordingly, the *c* value becomes bigger. So, the position of (002) peak shifts from 34.51^o to 34.12^o with the increase of Al doping concentration.

Table 2. Hall datas of ZnO thin films with different Al concentration.

S. No.	Carrier concentration (cm^{-3})	Electrical resistivity (Ω cm)	Hall mobility (cm^2/v s)
A	8.90×10^{15}	1.84×10	38.16
B	6.80×10^{16}	1.92×10^{0}	47.87
C	9.10×10^{17}	4.20×10^{-1}	16.35
D	5.79×10^{18}	9.20×10^{-2}	11.73
E	1.02×10^{19}	3.46×10^{-2}	17.71

The electrical resistivity ρ of all ZnO films was measured by four probes method as shown in Table 2. Table 2 shows the ρ for ZnO films with different Al doping concentration. It can be seen that ρ of the ZnO films decrease by introducing Al atom into ZnO film, and decrease from 1.92×10^{0} to 3.46×10^{-2}Ωcm with increase of Al concentration. Moreover, carrier concentration *N* and mobility *μ* were obtained by Hall measurements in Van der Pauw configuration at room temperature. The carrier concentration *N* and mobility *μ* for ZnO thin films with different Al/Zn ratios were listed in Table 2. It can be seen that the carrier concentration of ZnO film increase from 8.90×10^{15} to 1.02×10^{19}cm^{-3} with increasing Al concentration. The decrease of electrical resistivity and increase of carrier concentration are due to the substitution of Zn by Al, the redundant electron would decrease the electrical resistivity and increase the carrier concentration.

Table 3. Open circuit voltage and short circuit current for heterojunctions with different Al doping concentrations in ZnO films.

S. No.	Al concentration (%)	V_{OC}(mV)	I_{SC}(μA)
A	0	215	43
B	0.4	240	99
C	0.7	267	120
D	0.9	295	161
E	1.6	320	194

Table 3 shows the open circuit voltages and short circuit currents of ZAO/Si heterojunctions with different Al doping concentrations. It can be seen that the open circuit voltage and short circuit current increase with the increase of Al doping concentration, it means that PV effect is enhanced by introducing Al atom into ZnO film. From the results of Hall effect measurement, the carrier concentration increases with the increasing of Al dopant. Thus, the built-in potentials in the heterojunctions become higher with the increase of Al contents. Accordingly, open circuit voltage was also enhanced. Besides, the carriers under the action of high built-in potential would result in the big short circuit current.

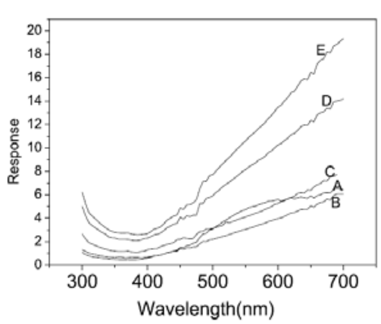

Fig. 2. Response spectra of heterojunctions with different Al doping concentrations in ZnO films.

In order to further investigate the effect of doping concentration on PV effect, the response spectra of them are examined which is shown in Figure 2. It can be seen that all the samples have a good response in the ultraviolet and visible region, and there is a dip region around 370-400nm which is in according with the band gap (3.37ev) of ZnO film. In the ultraviolet region, it clearly shows that it has higher response intensity for shorter wavelength, so, the advantage of ZnO who has a strong ultraviolet response emerges. On the other hand, in visible region, photon through ZnO is absorbed in Si substrate to generate electrons and holes. Thus, the advantage of Si who has a strong response in long wavelength has been appeared.

Moreover, for samples B-E, the response intensity is enhanced with increasing Al content in ZnO film, consistent to the tendency of PV property. These result from the increase of free carrier concentration of ZnO films and the potential barrier of heterojunction.

4. Conclusions

In summary, a series of ZnO thin films with different Al doping concentration on P-Si (100) substrates have been prepared by DC sputtering. The XRD patterns show that all the films just have a (002) diffraction peak, indicating that the samples grow along preferential *c*-axis orientation. Furthermore, the PV effect and spectrum response intensity are enhanced distinctly with the increase of Al doping concentration, this is possibly responsible for the increase of electron concentration in ZnO films and the increase of potential barrier in heterojunctions. It provides a new idea for novel solar cell with low cost and ultraviolet detector with strong response intensity.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 50532070) and the Funds of Chinese Academy of Sciences for Knowledge Innovation Program under (No. KJCX3.5YW.W01)

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