World Academy of Science, Engineering and Technology
International Journal of Physical and Mathematical Sciences
Vol:8, No:7, 2014

Interfacial Layer Effect on Novel p-$Ni_{1-x}O$:Li/n-Si Heterojunction Solar Cells

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Open Science Index, Physical and Mathematical Sciences Vol:8, No:7, 2014 publications.waset.org/9998912.pdf

Abstract—This study fabricates p-type $Ni_{1-x}O$:Li/n-Si heterojunction solar cells (P^+/n HJSCs) by using radio frequency (RF) magnetron sputtering and investigates the effect of substrate temperature on photovoltaic cell properties. Grazing incidence x-ray diffraction, four point probe, and ultraviolet-visible-near infrared discover the optoelectrical properties of p-$Ni_{1-x}O$ thin films. The results show that p-$Ni_{1-x}O$ thin films deposited at 300 °C has the highest grain size (22.4 nm), average visible transmittance (~42%), and electrical resistivity (2.7 Ωcm). However, the conversion efficiency of cell is shown only 2.33% which is lower than the cell (3.39%) fabricated at room temperature. This result can be mainly attributed to interfacial layer thickness (SiO_x) reduces from 2.35 nm to 1.70 nm, as verified by high-resolution transmission electron microscopy.

Keywords— Heterojunction, nickel oxide, solar cells, sputtering.

I. INTRODUCTION

PHOTOVOLTAIC energy conversion is used today for both space and terrestrial solar energy conversion. The success of solar cells in space applications is well known (communications satellites, manned space laboratories), and need for the increased use of solar cells in terrestrial applications becomes clearer with the growing, widespread demand for a renewable and environmentally acceptable terrestrial energy resource [1]. Since the first silicon (Si) solar cell was reported in 1954 [2], the conversion efficiency of crystalline Si solar cells has been drastically improved. Nowadays, by using four important techniques (back side field, light trapping by surface texturization, surface passivation, and contact passivation), the highest efficiency to date of 24.7% (passivated emitter rear locally-diffused (PERL)) has recently been demonstrated by UNSW [3]. However, the fabrication of cell requires many photomask processes and high-temperature cycling of furnace steps that result in an increase in complexity and manufacturing cost [4]. Therefore, to enable solar cells to significantly contribute to the world's energy resources, further cost reduction must be accomplished as soon as possible.

Transparent conducting oxide (TCO) thin film as an emitter layer deposited on n-type single-crystal silicon (c-Si) substrate (TCO/n-Si) is a promising Si-base heterojunction (HJ) solar cell because of its simple device structure, low fabrication cost, and low processing temperature [5]-[10]. Currently, the optimal conversion efficiency for n-type ZnO-base/n-Si heterojunction solar cells (HJSCs) and n-type indium tin oxide (ITO)/n-Si HJSCs is 9.4% achieved in our previous study (Al–Y codoped ZnO, AZOY) [11] and 16.5% achieved by Kobayashi *et al.* [12], respectively. In 2013, our study [13] proposed that low-cost p-type $Ni_{1-x}O$:Li thin film was a promising material candidate for n-ZnO-base or n-ITO in HJSCs applications because its work function (approximately 5.3 eV) was higher than that of ZnO (approximately 4.4 eV) or ITO (approximately 4.7 eV), yielding increased built-in potential and open circuit voltage (V_{oc}). However, the results show that conversion efficiency is only 2.33%. We propose that reduce interface states and improve the optoelectrical properties of p-$Ni_{1-x}O$:Li thin films are two important issues because they can directly and significantly affect the conversion efficiency of cell. In our knowledge, the substrate temperature is a key issue for HJSC performance. Therefore, in this study, the effect of substrate temperatures on the optoelectrical properties of p-$Ni_{1-x}O$:Li thin films were first investigated and its influences on the cell performance were also discussed.

II. EXPERIMENT

P-type Li-doped $Ni_{1-x}O$ (p-$Ni_{1-x}O$:Li) thin films were deposited on glass and n-type silicon (100) substrates with a resistivity of 1-10 Ωcm and a 250 μm thickness by RF magnetron sputtering with a 3 inch NiO:Li_2O (98.5:1.5 wt.%, 99.9% purity) ceramic target. A turbo molecular pump reduced the base pressure to 2×10^{-6} Torr prior to deposition. A 120 W sputtering source power and 6 mTorr working pressure were used for p-$Ni_{1-x}O$:Li thin film deposition. The substrate temperature was varied in the range of RT-300°C (called NiO_{RT}-NiO_{300}).

For p-$Ni_{1-x}O$:Li/n-Si HJSC fabrication, the p-$Ni_{1-x}O$:Li thin film (NiO_{RT} and NiO_{300}) was deposited on the n-Si substrate. Subsequently, high conductivity AZOY thin film was deposited by using RF magnetron sputtering and a finger-shape Al layer served as the front electrode. And then, before back electrode Al deposition, an ultra-thin LiF was thermally deposited onto the back surface of n-Si to provide a good ohmic contact. Finally, the cell area was fixed at 0.56 cm^2 (8 mm x 7 mm) by cutting for four edges.

The thickness of p-$Ni_{1-x}O$:Li thin films were measured by

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ellipsometry. The structural, electrical, and optical properties of p-Ni$_{1-x}$O:Li thin films were measured by grazing incidence x-ray diffraction (GIXRD), four point probe, and UV-visible-NIR spectrophotometer, respectively. The microstructures of the interface of cell were analyzed using high-resolution transmission electron microscopy (HR-TEM). The photovoltaic characteristics of the device were tested using an AM 1.5 standard Newport #96000 solar simulator (Peccell PEC-L11) with an illumination intensity of 100 mW/cm^2.

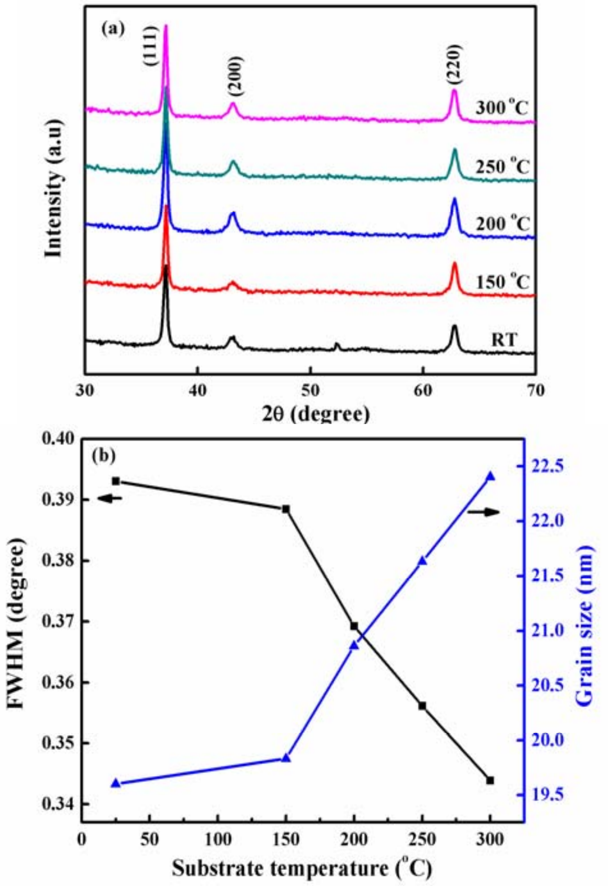

Fig. 1 (a) X-ray diffraction θ–2θ scan data and (b) FWHM and grain size of NiO (111) diffraction peak for p-Ni$_{1-x}$O:Li thin films prepared at various substrate temperatures

III. RESULT AND DISCUSSION

A. P-Type Ni$_{1-x}$O: Li Thin-Film Properties

Fig. 1 (a) shows the GIXRD spectra of p-Ni$_{1-x}$O:Li thin films deposited at various working pressures. In the 2θ range under investigation, films exhibit cubic NaC-type NiO with (111), (200), and (220) diffraction peaks. Also, the (111) plane has maximum intensity in this study, indicating that the (111) orientation minimizes the surface free energy in growing p-Ni$_{1-x}$O:Li thin films. Fig. 1 (b) shows the full-width at half-maximum (FWHM) value and grain size of film deposited at various substrate temperatures. It is seen that the grain siz slightly increases from 19.6 nm to 22.4 nm with the increase of substrate temperature. Also, the crystalline quality is improved by applying substrate temperature. The dependence of p-Ni$_{1-x}$O:Li thin films on substrate temperature for quality can be explained mainly by the different kinetic energies of adsorption atoms to move around the substrate surface at various substrate temperatures [8], [14]. Increases in substrate temperature provided more kinetic energy for the mobility of adsorption atoms to scatter to suitable positions on the substrate surface. Thus, films deposited at higher substrate temperature achieve enhanced crystal growth, thereby resulting in better crystalline quality and larger grain size.

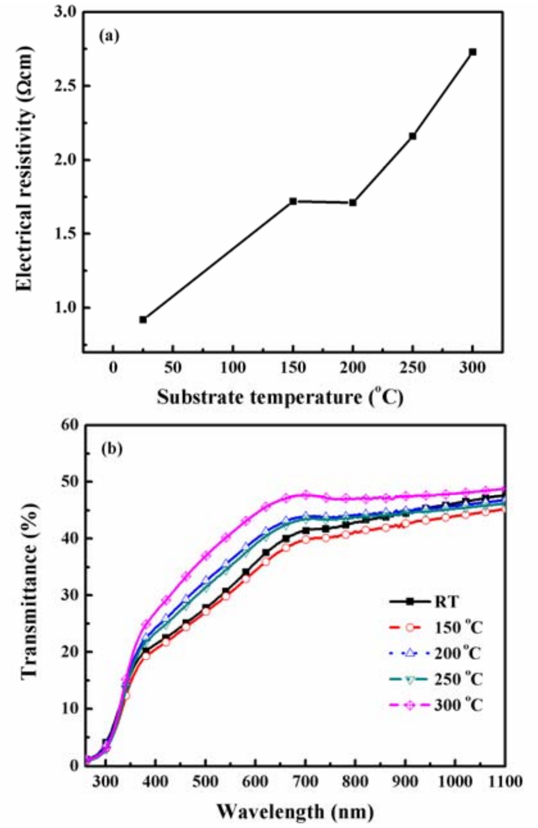

Fig. 2 (a) Electrical resistivity and (b) optical transmittance spectra of p-Ni$_{1-x}$O: Li thin films (with glass substrate) deposited at various substrate temperatures

Fig. 2 shows the electrical resistivity (ρ) and optical transmittance of p-Ni$_{1-x}$O:Li thin film as a function of substrate temperature. All p-Ni$_{1-x}$O:Li thin films show the p-type conductivity. In addition, the electrical resistivity and average visible transmittance of films increase with the increase of substrate temperature. The electrical resistivity can be written as follows:

$$\rho = \frac{1}{qp\mu_p} \tag{1}$$

where q is the electronic charge, p is the hole concentration, and μ_p is the hole mobility. As seen in Fig. 1 (b), the grain size increases with the increase of substrate temperature. The enlarging in grain size will decrease grain boundary scattering, resulting in increase of carrier mobility [15], [16]. However, it is in contrary to our experiment results. Therefore, a simple inference for increase of electrical resistivity is due to the decrease of carrier concentration. It is known that the predominant defects in NiO thin films are Ni^{2+} vacancies (V_{Ni}) [13], [17]. When V_{Ni} exists in NiO thin films, a broken Ni-O bond can easily combine with the Ni 3d electron, inducing the loss of a 3d electron from two nearby Ni^{2+} atoms. Thus, to achieve charge neutrality, two nearby Ni^{2+} atoms are oxidized to Ni^{3+}. This produces two hole carriers in the valence band, and corresponds to a forbidden gap existing in a shallow acceptor level. Base on the knowledge, a possible reason for increase of electrical resistivity is that the improvement in crystallinity decreases the native defects. Another possible reason is the insufficient amount of Li doping. It is known that the additional thermal energy will promote the activation of dopants. This in turn reduces the hole concentration caused by the incorporated Li^{+} occupying V_{Ni}. Therefore, the electrical resistivity increases with the increase of substrate temperature. In addition, the presence of Ni^{3+} in Ni_2O_3 acts as color centers in NiO films [18]. Thus, an increase in visible transmittance (Fig. 2 (b)) with the increase of substrate temperature can be attributed to a decreased Ni^{3+} presence in the p-Ni_{1-x}O:Li thin films.

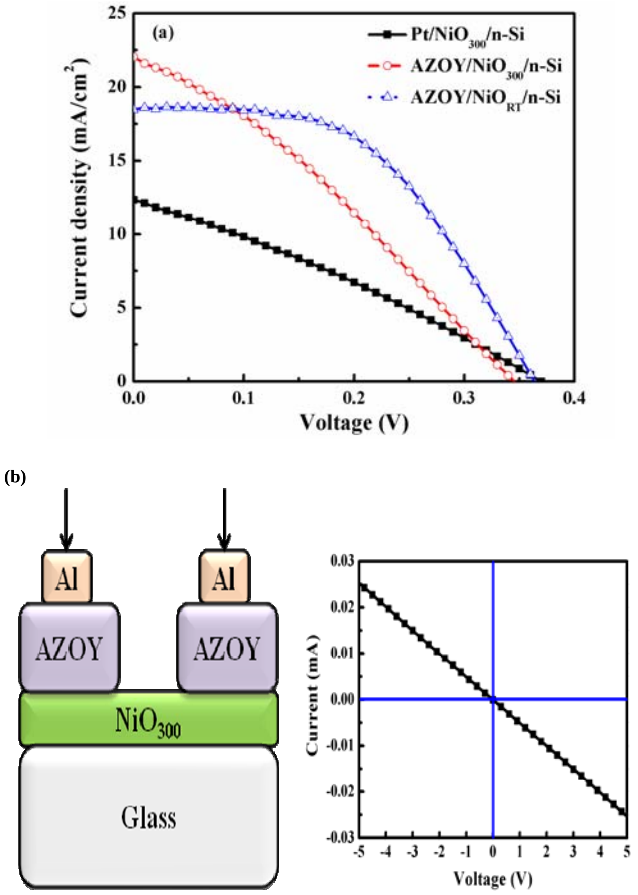

Fig. 3 (a) *J-V* characteristics of cells measured under 100 mW/cm^2 illumination (AM1.5 condition) for Pt/NiO_{300}/n-Si, Al/AZOY/NiO_{300}/n-Si, Al/AZOY/NiO_{RT}/n-Si, repressively. (b) *I –V* characteristics of Al/AZOY/NiO_{300} HJ

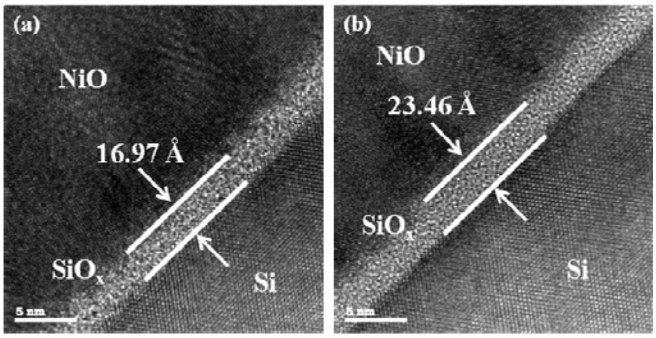

Fig. 4 Cross-sectional TEM micrographs of p-Ni_{1-x}O:Li/n-Si HJSC prepared at substrate temperatures of (a) RT (b) 300 ^{o}C

B. p-Ni_{1-x} O:Li/n-Si Heterojunction Solar Cell Performance

Fig. 3 (a) shows the light current density-voltage (*LJ-V*) characteristic of p-Ni_{1-x}O:Li/n-Si HJSC. A very low conversion efficiency of 1.34% (V_{oc}: 0.37 V, J_{sc}: 12.35 mA/cm^2, and *FF*: 0.29) was observed when the high work function platinum (Pt) contacted on NiO_{300} thin film as a front electrode. After a high conductivity AZOY thin films deposition, the conversion efficiency of cell increases to 2.33% (V_{oc}: 0.35 V, J_{sc}: 22.08 mA/cm^2, and *FF*: 0.31). Fig. 3 (b) shows the linear *I-V* behavior for AZOY contacts on NiO_{300} thin films, indicating the formation of ohmic contacts. The increase of conversion efficiency can be mainly attributed to the low sheet resistance of AZOY thin films (~70 ohm/square) as a front electrode contact layer, which leads to a great decrease of the lateral resistance due to the larger surface area electrode of AZOY layer. Therefore, the photo-generated hole can easily flow through AZOY layer entering the Al front contact, resulting in higher J_{sc} and *FF*.

In our knowledge, the emitter layer material should theoretically produce better crystalline quality and excellent optoelectrical properties. The results show that the NiO_{300} should be the best chosen due to its largest grain size and highest optical transmittance. However, the highest conversion efficiency of 3.39% (V_{oc}: 0.36 V, J_{sc}: 18.46 mA/cm^2, and *FF*: 0.51) was achieved in NiO_{RT} due to the higher FF value, as seen in Fig. 3 (a). It is believed that p-Ni_{1-x}O:Li deposited at different substrate temperature will influence the interface properties between film and n-Si. The microstructures of the interface of cell (NiO_{RT} and NiO_{300}) were shown in Fig. 4. It is seen that a clear interfacial layer is existed at the interface. Possible reason for this phenomenon is to form a SiO_x layer because the bond energy of Si-O (452 kJ/mol) is larger than Ni-O (372 kJ/mol). In addition, the thickness and denseness of SiO_x layer increase with the increase of substrate temperature, indicating that its properties can be influenced by varying substrate temperature. In our device, the photo-generated hole needs to through this ultra-thin SiO_x layer by tunneling process. When SiO_x layer is too thick (> 2 nm), the carrier tunneling will be significantly impeded [19], [20]. Therefore, the *FF* increases with increase of substrate temperature for NiO film deposition, presumably due to the decreasing thickness of SiO_x layer. In fact, the decrease of SiO_x thickness will also increase J_{sc}.

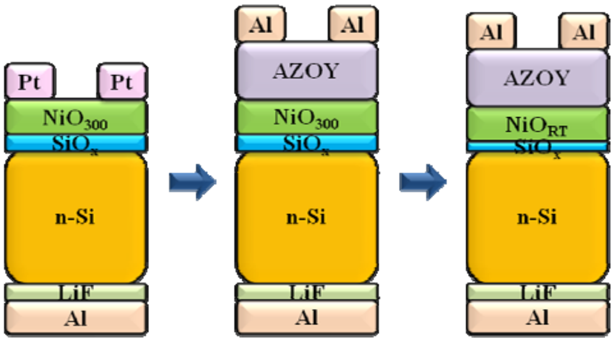

Fig. 5 Improvement structures of p-$Ni_{1-x}O$:Li/n-Si HJSC

However, the lower optical transmittance of NiO_{RT} (~35%) directly leads to the reduction in photo-generated carriers. This causes the lower J_{sc} value of NiO_{RT}/n-Si than NiO_{300}/n-Si. The improvement structures of p-$Ni_{1-x}O$: Li/n-Si HJSC were shown in Fig. 5.

IV. CONCLUSION

This study reports the successful improvement of conversion efficiency of p-$Ni_{1-x}O$:Li/n-Si from 1.34% to 3.39%. The results show that the NiO_{300} has the largest grain size (22.4 nm), highest optical transmittance (~42%), and highest electrical resistivity (2.7 Ωcm). The increase in conversion efficiency from 1.34% to 2.33% is due to the high conductivity AZOY thin films as a front electrode contact layer resulting in decrease of lateral resistance. And then, the conversion efficiency increases further from 2.33% to 3.39% which can be mainly attributed to the decrease in thickness of SiO_x, resulting in increase of tunneling probability of photo-generated carriers. In the future, we will continue to investigate this low cost cell structure, and will also propose higher conversion efficiency by improving optoelectrical properties of NiO thin films.

ACKNOWLEDGMENT

The authors gratefully acknowledge the financial support from the National Science Council of Taiwan, ROC (Grant Nos. NSC 102-2221-E-006-242-MY3 and NSC 101-2221-E-230-015).

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