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Thickness dependence of the properties of magnetron sputtered ZnO : Al films and its application in a-Si:H thin film solar cell

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Abstract . Transparent conducting ZnO:Al films with various film thicknesses have been prepared under Ar-ambient at substrate temperature 100°C by RF-magnetron sputtering. The resistivity of ZnO film decreases from 7.2×10^{-2} ohm-cm to 8.2×10^{-4} ohm-cm with the increase of film thickness. The minimum sheet resistance is ~10 ohm/□ and maximum carrier concentration and Hall mobility are 1.36×10^{20} cm^{-3} are 55.7 m^2/volt sec respectively. All the films are highly transparent (above 90% visible transmission) in visible wavelength region and IR-transmission is very sensitive with film thickness. The crystallinity has been greatly improved with increase of film thickness upto certain limit, confirmed from X-ray diffraction pattern (XRD) and Transmission Electron Microscopy (TEM) analysis. Surface morphologies are different for different thicknesses confirmed by Scanning Electron Micrograph (SEM). The effect of variation of ZnO thickness as back reflector on the a-Si solar cell performance is significant.

Keywords . Zinc oxide (ZnO), magnetron sputtering, thickness variation, material property, solar cell performance

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1. Introduction

ZnO thin films are technologically important due to their superior electrical properties and high optical transmission over wide range of wavelength, which makes it suitable for thin film solar cell applications. Highly transparent films with a resistivity of the order of 10^{-4} ohm-cm have been prepared by RF-magnetron sputtering by several workers [1-3]. Using thin layer of ZnO films as back reflector in a-Si single and double junction solar cell, the cell performance has been improved significantly [4,5]. Absorption in the i-layer increases due to insertion of thin ZnO layer at the n/metal interface. Therefore, the i-layer thickness can be reduced which will help to increase the electric field across p-n junction and the degradation of thin film a-Si:H solar cell reduces. Thus, the ZnO film thickness is an important factor for device applications. The electrical-optical as well as structural properties of ZnO:Al films are strongly dependent on film thickness.

Up to date, there are several reports regarding the effect of oxygen pressure and growth temperature on the properties of ZnO films grown by sputtering technique. Jae-Min Myoung *et al* [6] reported the effect of thickness variation on the material properties of ZnO films prepared by Pulsed Laser Deposition technique. In this work, resistivity increased and carrier concentration decreased with increase of film thickness. However, there has been no report on the effect of film thickness on the properties of Al doped ZnO films grown by sputtering technique. In this study, the effects of thickness variation on the electrical, optical properties, surface morphology and structural properties of ZnO thin films have been discussed. This ZnO films with different thicknesses has been applied as back reflector in a-Si:H single and double junction solar cell. Finally, the cell performance with different ZnO thicknesses has been investigated.

2. Experimental

ZnO:Al films were prepared on glass substrate by RF-magnetron sputtering using Ar as sputtering gas. For this purpose, a sintered ceramic disc of ZnO (purity 99.99%) with 2 wt% Al_2O_3 (purity 99.99%) was used as target (diameter of 4 inches). During each deposition, the chamber pressure was kept constant with the help of a throttle valve and the gas flow was maintained by

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a mass flow controller. Substrates of corning 7059 glass were placed parallel to the target surface at a distance of 7cm. The rf-power is applied between two capacitively coupled electrodes. Before each deposition, the base pressure inside the deposition unit was brought down to 3×10^{-6}Torr by water-cooled oil diffusion pump through a liquid nitrogen trap. Prior to sputtering, the substrates were heated at above 200^{0}C for degassing. In order to investigate the effect of thicknesses variation on the properties of ZnO, a series of ZnO films with various thicknesses were prepared with 100 watt rf-power, 4mT chamber pressure at a substrate temperature T_s = 100^{0}C.

The electrical resistivity, sheet resistance, carrier concentration and Hall mobility of the film were measured at room temperature by the van der Pauw point probe technique using a square configuration. Resistivity has been measured by interchanging the current and potential terminals as per the usual practice in four probe measurements. Relevent expression of resistivity for this configuration is

$$\rho = (\pi d/2\ln 2)(V_1/I_1 + V_2/I_2)\, f \text{ and } R_{sh} = (\rho/d),$$

where V_1, V_2 are the measured voltages of any two terminals; I_1, I_2 are the current passing through the other two terminals and f is the van der Pauw correction factor. R_{sh} is the sheet resistance of the films. The Hall measurements were carried out utilizing a magnetic field (B) of several kilo-Gausses, in the transverse direction of the applied current (I). Several Hall voltage readings were taken changing the current and keeping the magnetic field constant. Carrier concentration and Hall mobility have been calculated using the formulas

$$n_e = (IB/V_H ed) \text{ and } \mu = 1/(\rho\, n_e e),$$

where, V_H and μ are Hall voltage and mobility respectively. The optical transmission, reflection and absorption coefficient for ZnO films were measured by a double beam UV-VIS-NIR spectrophotometer (Hitachi, 330) at room temperature with unpolarised light in the spectral range 185-2600 nm. X-ray diffraction (XRD) pattern and Transmission Electron Micrograph (TEM) were taken for structural analysis of ZnO:Al films with different thicknesses. For TEM study, carbon coated grid were used as substrate. Crystallite sizes were measured from XRD data using Scherrer's formula. The changes in surface morphology of the films were evaluated by Scanning Electron Micrograph (SEM).

Single junction (a-Si:H) thin film solar cell (1 cm^2) have been fabricated with the following structure in a multichamber PECVD system. Glass/ textured SnO_2:F/ p-a-SiC:H/ a-SiC:H/ i-a-Si:H/ n-a-Si:H/Al or ZnO/Al with different ZnO layer thickness. Zinc Oxide layers of different thicknesses have been deposited on p-i-n structure by magnetron sputtering. Double junction (a-Si/a-Si) solar cells have also been fabricated with the structure Glass/ textured SnO_2: F/p-a-SiC: H/ a-SiC: H/ i-a-Si: H/n-μc-Si: H/p-a-SiC: H/ a-SiC: H/i-a-Si: H/n-a-Si: H/ZnO/Al. In some cells, ZnO:Al has been introduced in between n-a-SiH and Al layers and in some cases, only Al is introduced as back contact. The I V characteristics of these cells were taken under a calibrated AM 1.5G solar simulator.

3. Results and discussion

The electrical properties of ZnO:Al films were measured at room temperature. The substrate temperature was kept fixed at 100°C since the film will be used for the application on amorphous Si or microcrystalline-Si based solar cells as back reflector. Figure 1 shows the variation of resistivity and carrier concentration with film thickness. The values of resistivity, carrier concentration and mobility are depicted in Table-1. There is a sharp decrease of resistivity from 7.2×10^{-2} ohm-cm to 4.1×10^{-3} ohm-cm as the film thickness increases from 45nm to 170nm. Then the resistivity changes slowly and the lowest resistivity *i.e* 8.23×10^{-4} ohm-cm is achieved at a thickness of 610nm. But, one interesting result has been achieved for 1175nm thick film. Here, the resistivity is of slightly higher value compared to the former film.

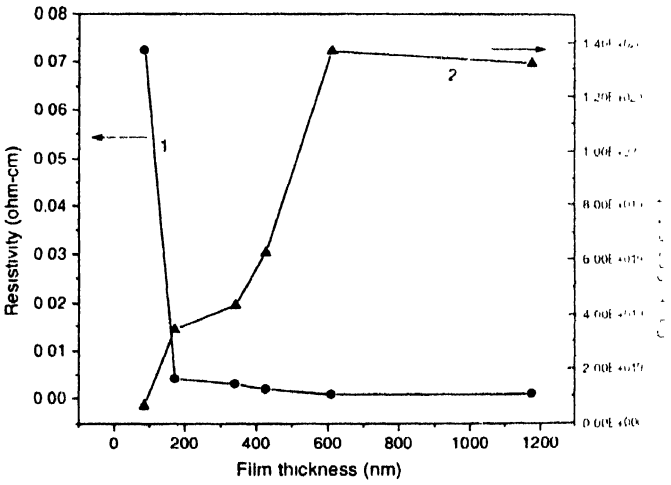

Figure 1. Variation of resistivity and carrier concentration with film thickness.

On the other hand, with increase of film thickness, carrier concentration increases and at 610nm, it reaches the maximum value (shown in Figure 1). The maximum carrier concentration and mobility are 1.36×10^{20} cm^{-3} and 55.7 cm^2/volt.sec respectively. The electrical sheet resistance (R_s) of ZnO film in Figure 2 shows a sharp fall as the film thickness increases from 85nm to170nm and after that the curve continues to fall at a much slower rate, showing near saturation beyond 340nm. The lowest sheet resistance of ZnO film is 9.75 ohm/ . The thickness dependence of electrical parameters of ZnO film is shown in Table 1.

Figure 3 shows the optical transmission and reflection spectra of ZnO films. It is evident that the transmission in visible region is above 90% for very thin films (with thickness ≤ 170nm) and between 85-90% for all other films. The near infrared transmission is sensitively dependent on film thickness. The

transmission of 85nm film at 1500nm is 95% whereas it is below 60% for 610nm film. At 1000nm, the change is much lower i.e from 95% to 85% with increase of ZnO film thickness from 85 to

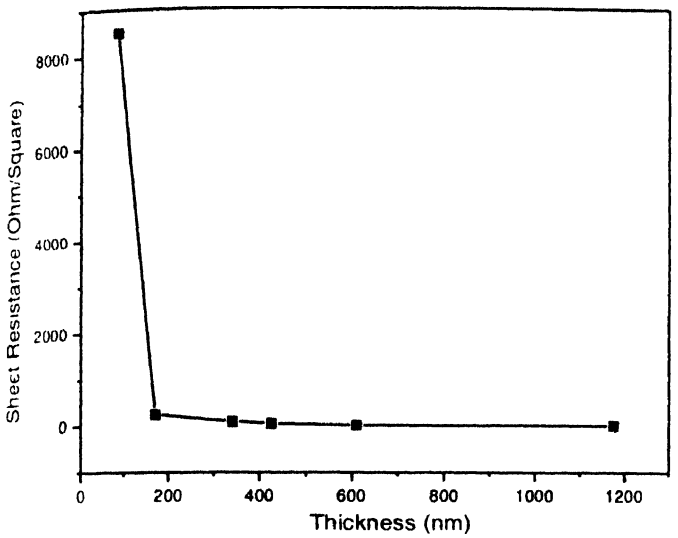

Figure 2. Variation of sheet resistance with the film thickness.

610nm. For microcrystalline-Si solar cell, transmission upto 1000nm is important. The reflection spectra of the ZnO films are also shown in Figure 3. It is almost same for films of different

Table 1. Variation of electrical parameter of ZnO films with different thickness deposited at substrate temperature T_s= 100°C

Substrate temperature (T_s)°C	ZnO film thickness (nm)	Resistivity (ohm-cm)	Carrier concentration (cm^{-3})	Mobility (cm^2/ sec.volt)
100	85	7.2×10^{2}	6.2×10^{18}	13.9
	170	4.1×10^{-1}	3.4×10^{19}	45
	340	3×10^{-1}	4.33×10^{19}	48.5
	425	1.9×10^{-1}	6.2×10^{19}	53
	610	8.2×10^{-4}	1.36×10^{20}	55.7
	1175	8.8×10^{-4}	1.32×10^{20}	53.8

thicknesses in visible range and varies within 10% to 20%. However, %reflection at longer wavelength (λ>1500nm) changes with film thickness. Plasma resonant frequency is defined by the wave number at which transmission and reflection spectra intersect. It is proportional to the carrier concentration, which is corroborated by the recent observation. The plasma resonant frequency has been shifted towards shorter wavelength side initially with increase of film thickness upto 610nm but after further increase of film thickness, plasma frequency shifts towards longer wavelength. The variation of reflectance is not the function of thickness, but the function of carrier concentration. From Hall effect studies, it was also found that carrier concentration increases upto a film thickness of 610nm. The band gap of ZnO film deposited under Ar-ambient at substrate temperature T_s= 100 °C has been calculated from α^2 *vs* $h\nu$ plot. The value of band gap of ZnO film is 3.5eV and it does not vary with film thickness significantly.

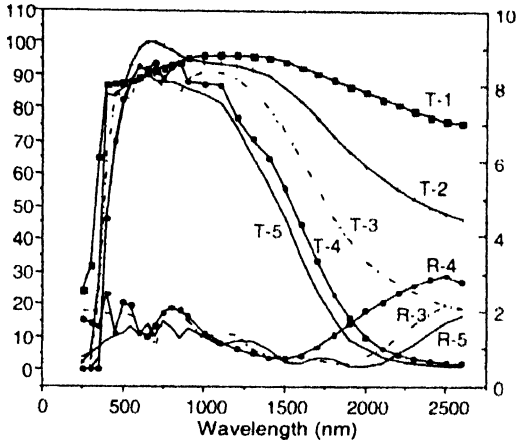

Figure 3. Variation of optical transmission with the thickness T-1 85nm, T-2 170nm, T-3 340nm, T-4 425nm and T 5 1175nm and reflection with the film thickness R-3 340nm, R 4 425nm and R 5 1175nm

A series of X-ray diffraction pattern of ZnO film with different thicknesses have been shown in Figure 4. All the films exhibit the <002> diffraction since ZnO film grows with strong <001> preferred orientation as the surface free energy is minimum [7].

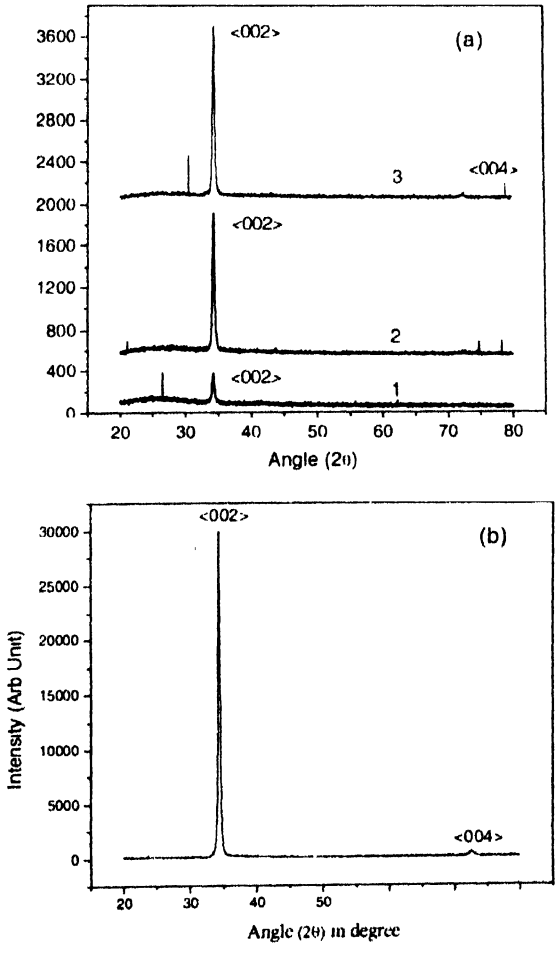

Figure 4. X-Ray diffraction pattern of ZnO.Al films of thickness (a) (1) 170nm, (2) 340nm, (3) 425nm and (b) 1175nm.

The film with thickness 85nm exhibits the weak ZnO <002> diffraction but with increase of film thickness, the intensity sharply increases. For all the films, the ZnO <002> peak position slightly shifts towards the higher angle sides than that of the bulk ZnO and it clearly implies that the films are under tensile strain. As glass is amorphous material, the film strain has been originated due to the mismatch of thermal expansion coefficient of ZnO and glass. The strain values (ξ) has been calculated by using the equation, $\xi = [\lambda/\delta\cos\theta) - \beta] \times 1/\tan\theta$ [8,9], where λ, δ and β are the wavelength of the x-ray, crystallite size and Full Width Half Maxima (FWHM) respectively. The values of microstructural parameters are enlisted in the Table 2. With increase of the film thickness from 170nm to 425nm, the FWHM decreases and as a result, the crystallite size increases. The average crystallite sizes vary from 19.8nm to 24.2nm. Further increase of the film thickness does not affect the value of FWHM. So crystallite sizes get saturated. The film strain decreases with increase of film thickness. On the other hand, dislocation density decreases with increase of crystallite size and saturates at 610nm thickness. The dislocation density (D), which is defined as the length of dislocation lines per unit volume, has been calculated from the formula, $D = 1/\delta^2$ [9]. Lattice spacing (d) is obtained from the Bragg's law given by $d = \lambda/2\sin\theta$. The lattice parameters have been calculated by the equations, $1/d^2 = (h^2 + k^2 + l^2)/a^2$ and $1/d^2 = 4(h^2 + hk + k^2)/3a^2 + l^2/c^2$ which are valid for hexagonal system [9].

Table 2. Variation of microstructural parameters of ZnO:Al films with film thickness deposited at 100°C

ZnO film thickness (nm)	XRD peak	Peak position (2θ) in degree	Crystallite size (δ) in (Å)	Micro-structural strain (ξ)	Dislocation density (D) lines/m²× 10^{14}	Lattice constant (d) in (Å)
170	<002>	34 26	19.8	2.93×10^{-3}	2.55×10^{9}	2.617
340	<002>	34.3	22 2	2.63×10^{-3}	2.03×10^{9}	2 614
425	<002>, <004>	34 32	24 2	2.37×10^{-3}	1.7×10^{9}	2 612
1175	<002>, <004>	34.4	24.5	2.34×10^{-3}	1.66×10^{9}	2.606

Figure 5 shows the TEM micrographs of ZnO films of thicknesses 45nm and 80nm. For both the films, the crystallite sizes are small, but it is clear that with increase of film thickness, the number density of crystallite increases. The average crystallite size as estimated from Transmission Electron Micrograph is around 15nm.

Figure 6 shows the surface morphologies of ZnO films with thicknesses 85nm, 340nm and 1175nm as observed by Scanning Electron Micrographs. The film with thickness 85nm (shown in Figure 6a) shows the non-uniform distribution of small grains. The density of grains increases as the of ZnO film thickness is 340nm. Here, grain size is bigger, granular and round shaped with different sizes (80-120nm). The above fact clearly illustrates that with increases of film thickness, surface roughness has

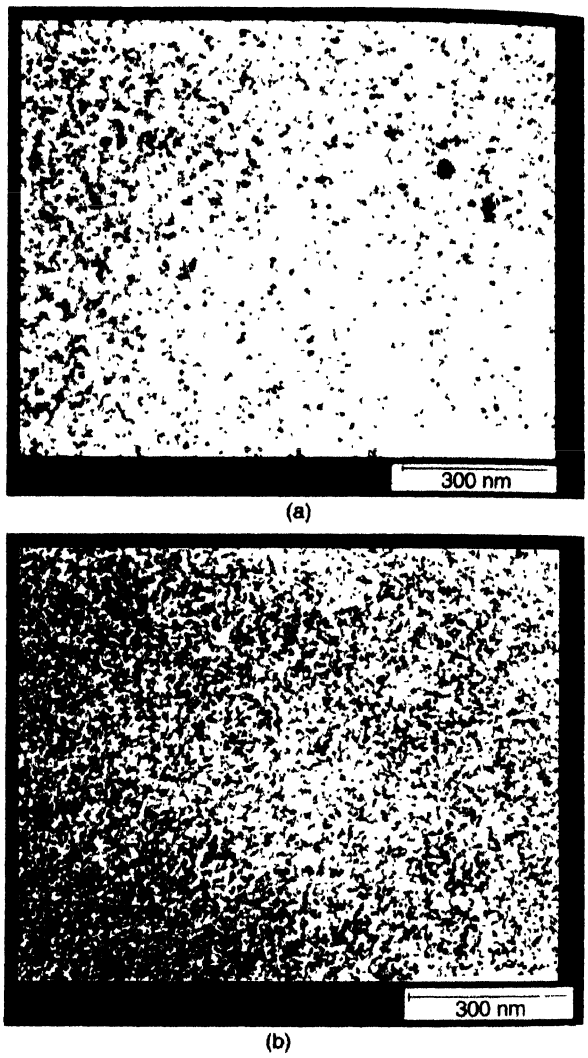

Figure 5. Transmission electron micrograph of ZnO film with film thickness (a) 43nm and (b) 85 nm

increased. For the film of thickness 1175nm (shown in Figure 6c), the grains are closely packed with average grain size 60nm.

On the basis of SEM, TEM and XRD analysis, we can explain the variation of electrical properties with film thickness of ZnO film with thickness. Initially, the growing film is discontinuous and non-uniform. During the film growth, some islands come into mutual contact and coalescence like two droplets. Large islands grow faster and small ones partly disappear due to the coalescence with larger ones. In this way, uniform films are formed. That means, very thin films are inhomogeneous where spatially separated crystallites are formed. Due to incomplete coalescence of the crystallite, the current carriers cannot complete the percolation path and as a result, the film shows high resistivity. With increase of film thickness, proper percolation

path formed as the number density of carriers and grain size increases. The increase in mobility is observed from Hall effect measurement with thickness. This together with the increase in carrier concentration explains the sharp fall of resistivity as well as the sheet resistance of the film with increase of thickness

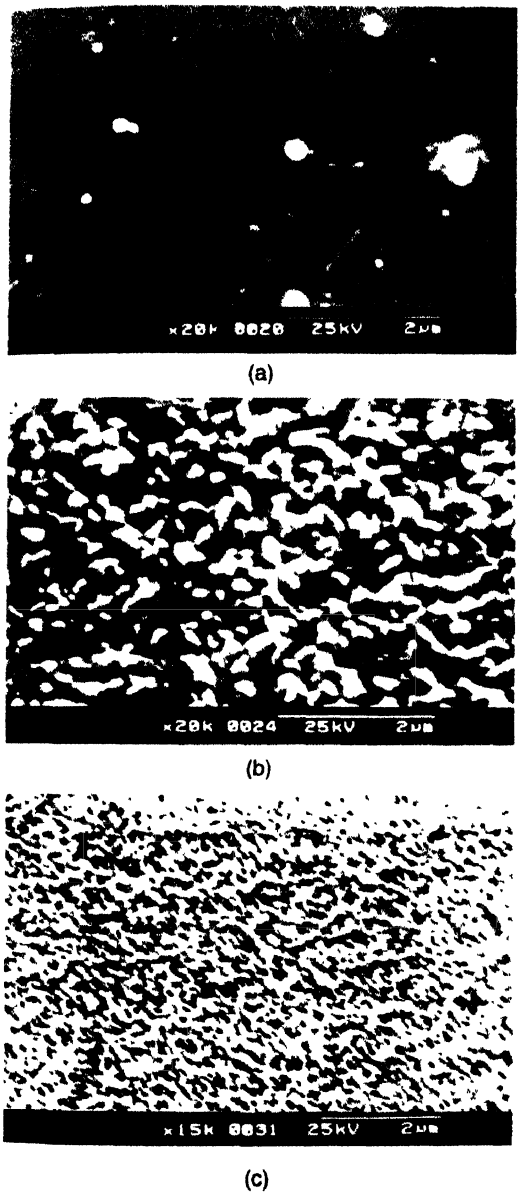

Figure 6. Scanning electron micrograph of ZnO film with film thickness (a) 85 nm (b) 340 nm and (c) 1175nm.

from 85nm to 340nm. Again, with further increase of film thickness, variation of carrier concentration is not significant. For the ZnO film with thickness = 1000nm, there is no further increase of carrier concentration. The film resistivity depends on both carrier concentration as well as mobility. Mobility depends on grain boundary scattering, impurity scattering and surface roughness scattering. For the combined effect of them, the carrier mobility in 1175nm thick film decreases which causes a slight decrease of resistivity.

This ZnO:Al films with different thicknesses have been used as back reflector of a-Si:H single and double junction solar cells. The cell performances have been investigated in details. The I-V characteristics of these solar cells have been shown in Figure-7a. In Figure-7a, curve-1 shows the current-voltage characteristic of a single junction a-Si solar cell with Al as back contact. Here, Open circuit voltage (V_{0c}), Short circuit current (I_{sc}), Fill factor (F.F) and efficiency of the cell are 0.87 V, 14.85 mA, 0.667 and 8.62% respectively which are shown in Table-3. Then the ZnO layers of different thicknesses have been applied before Al as

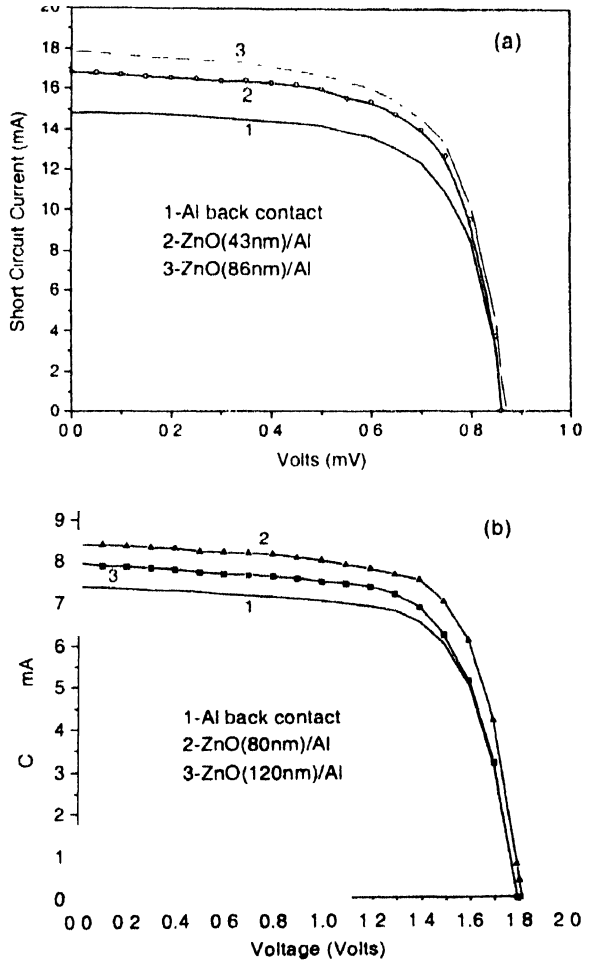

Figure 7. IV characteristics of (a) single junction and (b) double junction a-Si:H solar cell.

back reflector of solar cell. These films are deposited under Ar-ambience. For 43 nm thick ZnO interface layer, I_{sc} increases by 12.7% which further increases by 20% when 86 nm ZnO layer was used between n/Al interface. But, % increase of I_{sc} is much lower for 120nm thick ZnO layer (not shown in the graph) as back reflector at n/Al interface. The improvements of performance of solar cell using ZnO as back contact are shown in the Table 3.

The I-V characteristics of double junction a-Si:H solar cells are depicted in Figure-7b. The double junction solar cell with Al as back contact (shown in Figure-7b, curve-1) shows open circuit