Zinc aluminate spinel impurity phase in Al doped ZnO ceramic target and pulsed laser ablated films: curse or blessing?

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Abstract

Al doped ZnO films have been grown by pulsed laser deposition (PLD) technique using ceramic targets sintered at different temperatures in the range 800 °C to 1400 °C. The effect of target sintering temperature on the structural, optical and electrical properties of the AZO films has been investigated. The X-ray diffraction (XRD) patterns show that besides the major hexagonal wurtzite phase of ZnO, the zinc aluminate (ZnAl_2O_4) spinel impurity phase is present predominantly in the targets sintered at 900 °C onwards. The XRD peak intensity of the spinel phase increases as the sintering temperature increases. Although, no such impurity has been primarily appeared in the XRD pattern of the films deposited from these targets, the presence of a probable spinel phase has been sensed by the X-ray photoelectron spectroscopy (XPS) measurements. All the films show more than 90% transparency in the region 500 nm to 1400 nm. The electrical resistance of the target pellets also decreases with an increase in the sintering temperature up to 1100 °C and then increases. Similarly, the carrier concentration increases and the resistivity decreases with the sintering temperature attaining the values of $6.36 \times 10^{20} \text{ cm}^{-3}$ and $6.38 \times 10^{-4} \text{ ohm-cm}$ respectively for the films ablated from the targets sintered at temperatures 1000 °C (AZO1000) and 1100 °C (AZO1100) beyond which both the values deteriorate. An increase in the carrier concentration value is assigned to the modification of the grain boundaries by the spinel phase. Vacuum annealing of AZO1000 film at 350 °C results in a further increase in the carrier concentration to a value of $1 \times 10^{21} \text{ cm}^{-3}$. This film has been applied as a transparent electrode without texturing for a-Si:H solar cell which shows a conversion efficiency of ~3.93%. Our study for the first time shows that the presence of a ZnAl_2O_4 phase to a certain extent in AZO film rather helps to achieve higher carrier concentration.

Key words: Pulsed laser deposition; Transparent electrode; Impurity phase; Al doped ZnO.

1. Introduction

Transparent conductive oxide (TCO) is an important component of many transparent electronics such as flat panel displays, light-emitting-diodes, transparent thin film transistors, thin film solar cells etc (Levy et al., 2008; Ohta et al., 2001; Park et al., 2009). A carrier concentration in the order of 10^{20} cm^{-3} or higher and a transparency of >90 % in the visible region are the general requirements of a TCO material (Castañeda, 2011; Minami, 2005). Among the various TCO thin films, tin-doped indium-oxide (ITO) is the one which has been in practical use reliably for a long time (Li et al., 2005; Park et al., 2009). However, recently many efforts have been concentrated on developing a substitute of ITO as indium is a rare and expensive element, making the cost of ITO very high. Impurity-doped ZnO films have been actively studied as an alternate material to ITO because unlike ITO, ZnO is a non-toxic, inexpensive and abundant material, and is chemically (and thermally) stable under hydrogen plasma processes that are commonly used for the production of solar cells (Aktaruzzaman et al., 1991; Hu, Gordon, 1992). In the last decade, ZnO films doped with impurities, such as B, Al, Ga and In, have been actively studied as prospective TCO materials (Fortunato et al., 2008; Kim et al., 2002; Major et al., 1983; Yamamoto et al., 2001) among which Al-doped ZnO (AZO) film showed the lowest electrical resistivity ($8\text{-}9 \times 10^{-5} \text{ Ohm-cm}$), which is quite similar to that of ITO film (Ray et al., 1983). Besides, it has a more proper work function for the cathode electrodes of transparent organic light emitting diodes (Kim et al., 2000; Li et al., 2012; Zhao et al., 2000) and wider band gap ($E_g = 3.4\text{--}3.7 \text{ eV}$), which shows good optical transparency in the visible wavelength region (400 nm–800 nm). In general, the electrical resistivity of a material can be decreased by increasing either the carrier concentration or carrier mobility. Although, many studies have been carried out to increase the number of free carriers in polycrystalline ZnO thin films by doping with more and more Al^{+3} , Al concentration beyond a certain limit however deteriorates the number of carrier concentration due to ionized impurity scattering. Therefore, other techniques such as increasing the intrinsic defects, reducing the traps for free carriers (reducing the number of surface adsorbates) have been adopted to achieve higher carrier concentration (Asghar et al., 2013; Ghosh, Basak, 2013; Ghosh, Basak, 2012). However, there are several other parameters namely composition which may also control the electrical property of such oxide thin film. Especially for oxide and nitride materials, oxygen or nitrogen deficiency (besides intrinsic donor or

compensating acceptor defects) is a spontaneous phenomenon causing intrinsically n-type character in the materials (Boguslawski et al., 1995; Look et al., 2005; Tuomisto et al., 2003).

AZO films can be prepared using various techniques (Ghosh, Basak, 2012; Minami et al., 2006; Singh et al., 2001; Volintiru et al., 2007) among which pulsed laser deposition (PLD) can be mentioned having the major advantages of the ability to transfer material stoichiometrically from a multicomponent ablation target to a growing film (Chrissey, 1994). However, it is well known that stoichiometric transfer may not be favorable under all experimental conditions which might give rise to defects primarily affecting the electrical property. Therefore, the target sintering temperature becomes one of the very crucial criteria to obtain the proper target composition. Knowing the fact that the composition of an oxide film depends on the composition of ceramic target used for ablation, in this paper, we examine the influence of target sintering temperature on the properties of the AZO film grown by PLD and applied as a transparent electrode for a-Si:H solar cells. First of all, the Al content in ZnO has been optimized for the highest conductivity (not described here) (Kim et al., 2002; Pei et al., 2001; Singh et al., 2004; Singh et al., 2001) containing 2.5wt % Al_2O_3 impurity. Then, the properties of the films have been measured as a function of sintering temperature of the ceramic target. It has been observed for the first time that the presence of a probable zinc aluminate (ZnAl_2O_4) spinel impurity phase in the AZO film up to a certain extent rather helps to reduce the carrier trapping at the modified grain boundary of the films and thus improves the carrier concentration value.

2. Experiment

The PLD targets were prepared by conventional ceramic technique by mixing high purity commercial ZnO powder (MERCK, 99% purity) with 2.5 wt % Al_2O_3 powder (MERCK, purity 99.5%) in an agate mortar for several hours and pressing them in the form of pellet with diameter 1.5 cm under 5 ton pressure. Then the pellets were sintered for solid state reaction at various temperatures in the range of 800 °C to 1400 °C for 24 hours in a tubular furnace in ambient condition. AZO thin films were deposited on properly cleaned glass substrates by ablating these sintered targets in a PLD system (Neocera) fitted with a KrF excimer laser (Coherent) with an emission wavelength of 248 nm, repetition rate 10 Hz, and energy 275 mJ in oxygen partial pressure 2.5 mTorr. The number of laser pulse used were 60K, base pressure was 5×10^{-5} Torr and the target to substrate distance was 10 cm. The substrate was maintained at 300 °C. The

deposited films have been named as AZOX where X is the respective sintering temperature. A post growth annealing treatment of the AZO1000 films was carried out at different temperatures 350 °C, 450 °C, and 550 °C under vacuum condition (4×10^{-6} torr) and the films have been named as PGA350, PGA450 and PGA550 respectively.

X-ray diffractometry (XRD, model Seifert XDAL 3000) with Cu K_{α} ($\lambda = 1.5406$ nm) radiation was used to characterize the crystal structure of the pellets as well as the films. The optical transmission measurements were made using a UV-VIS-NIR spectrophotometer (model: Cary-5000, 200–3200 nm). The resistivity, carrier concentration, and mobility at room temperature were measured by the Hall measurements using four probe in Van der Pauw geometry with the help of ECOPIA Hall measurement system (model: HMS 3000). X-ray Photoelectron Spectroscopy (XPS, Omicron, serial no: 0571) was studied to know the elemental states.

The application of the AZO film as the front TCO contact without texturing has been tested in the superstrate configuration to deposit a-Si:H single junction solar cell. For this purpose, a multichamber plasma enhanced chemical vapor deposition system with ultrahigh vacuum capacity was used. The structure of the solar cell is as follows: glass/AZO/p-a-SiC:H/i-a-Si:H/n-a-Si:H/Al in which the deposition parameters for the p-type amorphous silicon carbide (p-a-SiC:H), intrinsic amorphous silicon (a-Si:H) and the n-type amorphous silicon (n-Si:H) were the same as our standard single junction solar cells (Chaudhuri et al., 2004). The conversion efficiency (η) of the solar cell was measured under AM1.5G illumination using a solar simulator. The series and shunt resistances of the solar cell were calculated using the single I-V curve method (El-Adawi, Al-Nuaim, 2001).

3. Results and Discussion

3.1 Structural Property

The inset in the Fig. 1 shows the digital image of the AZO target. Fig.1 shows the XRD patterns of the AZO targets sintered at different temperatures. Each target shows (100), (002), (101), (102), (110), (103), (200), (112), (004), (202) diffraction peaks corresponding to the hexagonal wurtzite structure of ZnO supported by JCPDS data (Fang et al., 2003). The presence of multiple peaks of ZnO hexagonal structure indicates that the target ZnO material is polycrystalline in nature. The (220), (311), (400), (331), (422), (511), (440), (620) diffraction peaks corresponding to the cubic ZnAl_2O_4 spinel phase also appear predominantly for the targets

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4 sintered from 900 °C (Chou et al., 2011). The inset in the Fig.1 clearly shows a gradual increase
5 in the intensity of the (422), (511), (440) peaks of ZnAl_2O_4 phase with an increase in the
6 sintering temperature. Therefore, the ceramic targets sintered at and above 900 °C, contain
7 ZnAl_2O_4 spinel phase in addition to the major ZnO phase. Chou et al. (Chou et al., 2011) have
8 synthesized Al-doped ZnO ceramic target by solid state reaction of ZnO and Al_2O_3 dopant
9 sintered at 1500 °C for 6 hours and the XRD patterns of their Al_2O_3 -doped ZnO samples also
10 showed the presence of a second ZnAl_2O_4 spinel phase. It has also been reported that when the
11 Al_2O_3 content has been raised from 1.5 to 2.5 wt%, the relative peak intensity of ZnAl_2O_4 spinel
12 phase has been increased (Fang et al., 2003). Fang et al. have also found 5 wt% ZnAl_2O_4 in the
13 ZnO target when RF sputtering target is prepared by sintering the mixture powder of ZnO and
14 Al_2O_3 at 1300 °C for 6 hours in an Ar atmosphere. Formation of ZnAl_2O_4 spinel phase in our
15 targets at much lower temperature is due to much longer sintering times.

16
17 Fig. 2 shows the XRD patterns of AZO thin films deposited at 300 °C in 2.5 mTorr of O_2
18 ambient by ablating the prepared ceramic AZO targets. The patterns of all the films show a sharp
19 peak corresponding to [0002] plane of wurtzite hexagonal structure of ZnO. This indicates that
20 the films have been grown preferably along the *c*-axis. The full width half maximum (FWHM)
21 values of the (002) peak for all the films have been shown in the inset in the Fig. 2 which shows
22 that the FWHM values vary only slightly with the sintering temperature. This is expected as the
23 substrate temperature remains unaltered. No diffraction peak due to ZnAl_2O_4 phase has been
24 primarily detected in the films similar to earlier report (Chou et al., 2011). The value of the
25 reaction enthalpy of ZnAl_2O_4 is only 0.83 eV (negative) which indicates that the formation of a
26 spinel structure is highly favored thermodynamically (Dixit et al., 2011). Therefore, if one
27 considers the very high energy of the excimer laser beam, in that case, all the phases present in
28 the ablating target should have been vaporized and condensed on the substrate (Kreutz,
29 Gottmann, 1998; Singh, Narayan, 1990). However, the absence of the diffraction peaks in the
30 XRD patterns due to the spinel phase indicates the fact that the amount of the impurity phase in
31 the film structure is either insufficient to produce XRD peaks with detectable intensity or the
32 phase is amorphous. However, considering the reaction enthalpy, one can rule out the possibility
33 of the latter.

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35 The representative XPS spectra of one of the AZO films (AZO1400) is shown in the Fig. 3
36 which shows the Zn $2\text{P}_{3/2}$, Zn $2\text{P}_{1/2}$, Zn $3\text{P}_{1/2}$, Zn $1\text{S}_{1/2}$, and O $1\text{S}_{1/2}$ peaks indicating the presence

of Zn and O in the films. The inset in the figure shows a peak at around 74.25 eV confirming the presence of Al in the doped film. The XPS spectrum in the Fig. 4(A) shows a peak signal for O 1S_{1/2} for the film AZO800. This peak can be well fitted with two Gaussian peak components centered at 530.54 ± 0.01 eV and 531.04 ± 0.01 eV respectively. The component on the lower binding energy side of the O 1S_{1/2} spectrum is attributed to O²⁻ ions within wurtzite structure of hexagonal Zn²⁺ ion array surrounded by Zn (or the substituted Al) atoms with their full complement of nearest neighbor O²⁻ ions (Mass et al., 2003). The higher binding energy component located at 531.04 ± 0.01 eV is generally attributed to either the presence of loosely bound O on the surface of the films (Mass et al., 2003) or belongs to a specific species like – CO₃, adsorbed H₂O and O₂ hydrated oxides (Chen et al., 2001). It may also be associated to O²⁻ ions in the oxygen deficient regions within the ZnO matrix (Mass et al., 2003). O 1S_{1/2} peak for AZO1400 in Fig. 4(B) shows a similar nature to that of AZO800. Here the two Gaussian components are centered at 530.61 ± 0.01 eV and 531.14 ± 0.01 eV respectively. However, the relative peak intensity of the O 1S_{1/2} due to loosely bound O on the surface is less as compared to the lattice O indicating that the surface adsorbed O is less in the films ablated from the high temperature sintered pellet. The Figs. 4(C) and 4(D) show that the Al 2P_{3/2} peaks for AZO800 and AZO1400 respectively. While the peak for AZO800 can be well fitted with single Gaussian peak at around 74.41 ± 0.01 eV, the peak for AZO1400 can be well fitted with two Gaussian peaks at 74.26 ± 0.04 eV and 74.37 ± 0.03 eV. It indicates that there is an additional peak at lower binding energy in AZO1400 which is due to Al 2P_{3/2} in ZnAl₂O₄ spinel phase (Strohmeier, Hercules, 1983).

3.2 Optical Property

The Fig.5 shows the transmission spectra of the AZO films as a function of wavelength. All the films exhibit sharp band-edge absorption below 380 nm. A very high transparency (>90 %) in the visible solar spectrum region i.e from 400 nm to 800 nm is evident from the Fig 5. Above 1400 nm, the value of transmittance shows a steady fall for all the AZO films and reaches to 40% - 50% at ~3000 nm. This fall in the transmittance value beyond 1400 nm is due to an increase in the free carrier absorption (Minami et al., 1985; Singh et al., 2001). However, more than 80% transmittance up to ~1700 nm in the AZO films indicates the potential of the films for applications as a NIR transmitted TCO material for solar cells. The transmittance values at 2500 nm show that the lowest and highest free carrier absorption occur in the AZO800 and AZO1100

film respectively. While the AZO1400 film again shows a higher transmittance value indicating slightly lower free carrier absorption. It has been found that transmission is strongly affected by Al doping in 800-2000 nm range of spectra (Singh et al., 2004). The inset in the figure shows a digital photograph revealing the high transparency of the film AZO1000 similar to glass as it is evident from the appearance of the colored letters through the film. As the sintering temperature increases, the absorption edge shifted to higher wavelength value. In degenerate semiconductor, the absorption edge shift in the shorter wavelength direction with increasing electron concentration is known as Burstein-Moss effect. Since ZnO is heavily doped with Al, optical band gap increases as the lower conduction band states become occupied and unavailable for excitation. However, as the Al concentration is kept constant in our study, the shift towards lower energy side indicates different stoichiometry of the AZO phase as the band gap depends on the stoichiometry also (Mahanty et al. 1999). As more and more ZnAl_2O_4 is formed in AZO, it is expected that the stoichiometry of AZO phase (cation and anion vacancy) would deviate more and more from the original one. This is in conformity with the structural results.

3.3 Electrical property

The electrical resistance of the pellets measured between two lateral contacts on the top of the pellet target noted in the Table-1 shows that the resistance gradually decreases as the sintering temperature increases attaining the minimum value of 200 ohm for 1100 °C sintered one. However, the resistance increases to a value of 1750 Ohm when the temperature is increased to 1400 °C. Similarly, the variations in the values of carrier concentration, resistivity and mobility (inset) for the AZO thin films in the Fig.6 show that as the sintering temperature increases, the resistivity value decreases attaining a minimum value of 6.38×10^{-4} Ohm-cm for AZO1100 and then again increases to 1.89×10^{-3} Ohm-cm for AZO1400. The carrier concentration initially increases attaining the maximum value of $6.36 \times 10^{20} \text{ cm}^{-3}$ for AZO1000 and then decreases to $3.34 \times 10^{20} \text{ cm}^{-3}$ for AZO1400. As more and more spinel phase is formed in the target, it is expected that more and more spinel impurity would also be there in the films. Generally, the impurities segregate at the grain boundary; hence we expect that the ZnAl_2O_4 would remain at the grain boundary (Chou et al., 2011; Wei et al., 2013). Therefore, similar change in the electrical properties of both the target and film may be due to the fact that segregation of the spinel impurities at the grain boundaries modifies the properties of the AZO films probably by reducing the number of adsorbates on the surface which act as the trap levels.

Thus, as the target sintering temperature increases, more and more spinel impurities accumulate at the grain boundaries causing reduced number of traps and thus increased free carriers. The inset (Fig.6) shows that the mobility value slightly increases as the sintering temperature increases. Normally, when the carrier concentration increases, mobility value decreases due to ionized impurity scattering in single crystals. The transport in polycrystalline materials and especially in semiconductors is much more complex as compared to that in single crystals since in addition to ionized impurity scattering, grain boundary scattering becomes very significant in case of polycrystalline materials. For doped ZnO wherein for sufficiently higher carrier concentrations, the grain barrier scattering is found to be inactive due to the narrow width of the barriers between grains which can be tunneled by the electrons (Ellmer, Mientus, 2008). However, when the impurity phase increases further for sintering temperature 1400 °C, accumulation of highly resistive spinel phase at the grain boundary probably hinders carrier transport from grain to grain.

3.4 Post-growth annealing effect

When the films were subjected to post-growth annealing treatment, structural aspects of the thin films remain unaltered i.e the films show only (002) and (004) peaks owing to the hexagonal wurtzite structure (Fig.7). No impurity phase is apparent from the patterns. The FWHM values noted in the Fig.7 show that the film PGA550 has a lower FWHM value. A narrow peak means large coherence length or smaller strain in the film. The transmittance spectra of the annealed thin films are >90 % in the visible region as shown in Fig.8. In contrast to the untreated films, the annealed films, PGA350 and PGA450 show much lower transmittance values beyond 1300 nm which clearly indicates higher free carrier absorption in these annealed films due to higher carrier concentrations. The Hall measurement on the annealed films (Fig.9) confirms that the film PGA350 has the highest carrier concentration of $1.0 \times 10^{21} \text{ cm}^{-3}$ and the lowest resistivity of $4.26 \times 10^{-4} \text{ ohm-cm}$ respectively. Kim et al. (Kim et al., 2002) have shown similar resistivity value of $4 \times 10^{-4} \text{ ohm-cm}$ for Al doped ZnO (3 wt % Al_2O_3) film on glass substrate. In undoped as well as doped ZnO, the n-type carrier concentration depends on many factors including presence of donor defects and thus, the interpretation of broader XRD peak width in PGA350 with lower resistivity is not straightforward. The resistivity further increases with an increase in the annealing temperature. O_2 molecules are readily adsorbed on the surface of ZnO. Adsorbed

O₂ traps the free carriers causing a depleted region on the surface. Therefore when the films are annealed under vacuum, the adsorbed O₂ molecules are desorbed from the surface, thereby increasing the carrier concentration. The figure further shows that the carrier concentration goes down with the annealing temperature which may be due to decrease in the intrinsic donor defects (Ghosh, Basak, 2013). Similar result has been obtained by Chen et al. (Chen et al., 2001). Fang et al. (Fang et al., 2003) also have shown that the electrical resistivity of AZO films deposited at 320 °C is 2.67×10^{-4} Ohm-cm and can further be reduced to as low as 1.5×10^{-4} Ohm-cm by annealing at 400 °C for 2 hrs in a vacuum pressure of 10^{-5} Torr. The change in the mobility values with annealing is not significant and the maximum mobility value obtained at 350 °C is 14.61 cm²/Vs. This is at par with the report of Ellmer et al. wherein it was shown that even at sufficiently high carrier concentration, the grain barrier scattering is not active (Ellmer, Mientus, 2008). The transmittance spectra of the annealed films in Fig.8 show that the average transmittance of the films is above 90% in the wavelength region 400-1300 nm indicating that the vacuum annealing does not degrade the transmittance properties. This is similar to the reports of Fang et al. (Fang et al., 2003) wherein the average transmission of the AZO films in the visible range is around 90%.

4. Application of AZO film in solar cell:

The current (I) vs. Voltage (V) characteristics of a single junction amorphous silicon solar cell having structure glass/AZO/p-a-SiC:H/i-a-Si:H/n-a-Si:H/Al under AM1.5G illumination has been shown in the Fig.10. Since AZO350 shows the lowest resistivity after post-growth treatment, it has been used as the front transparent electrode. However, it is worth to mention here that unlike most commercial TCOs, AZO350 has been applied for solar cell growth without texturing. The effective area of the solar cell is 1 cm². A high open circuit voltage of 0.84 V indicates formation of a good junction. The value of the short circuit current density (J_{sc}) of 9.6 mA/cm² and conversion efficiency (η) of 3.93% which are however lower compared to the standard solar cells on commercially available textured SnO₂ coated films (Das et al., 2000). This may be explained by the absence of any texture on the surface of the AZO films.

Conclusions

In summary, we have investigated the effect of PLD target sintering temperature on the properties of AZO film. It is observed that the highly transparent AZO film obtained from the target sintered in the temperature range 800 °C to 1400 °C. The film obtained from the target sintered at 1000 °C has the best electrical characteristics showing resistivity and carrier concentration values of 6.91×10^{-4} ohm-cm and $6.36 \times 10^{20} \text{ cm}^{-3}$ respectively. Therefore presence of a spinel impurity phase to some extent in the film is rather makes a blessing that it improves the carrier concentration value by improving the grain boundary properties. The vacuum annealed film having much lower resistivity value of 4.26×10^{-4} Ohm-cm has been applied as transparent electrode in a-Si:H solar cell which shows a conversion efficiency of 3.93% which is expected to be improved by further optimization and/or texturing of the AZO layer. The results reported in this study will be useful in formulating optimum doping process to enhance the desired carrier concentration in AZO TCO films for solar energy application but also useful for fundamental studies on the effect of an impurity phase in a conducting matrix.

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Figure Caption

Fig.1. X-ray diffraction patterns of AZO pellets sintered at different temperatures. The inset shows the digital image of the sintered AZO target (left). The inset in the figure (right) shows the magnified view of the XRD patterns showing clearly the peaks of both ZnO and ZnAl_2O_4 phases.

Fig.2. X-ray diffraction patterns of AZO thin films ablated from different targets. The FWHM values of the (002) peak of the films are noted in the figure.

Fig.3. A representative XPS spectrum of AZO1400 film. Inset shows the XPS peak corresponding to Al $2\text{S}_{1/2}$.

Fig.4. Representative XPS spectrum of O $1\text{S}_{1/2}$ peak for (A) AZO800 and (B) AZO1400. Representative XPS spectrum of Al $2\text{P}_{3/2}$ for (C) AZO800 and (D) AZO1400 films.

Fig.5. NIR Transmission spectra of the AZO films obtained from pellets sintered at different temperatures. The inset shows the digital images of the transparency of the glass substrate and a representative film.

Fig.6. Variation in the carrier concentration and resistivity values with sintering temperature. The inset shows the variation in the mobility values with sintering temperature and its theoretical fitting.

Fig.7. X-Ray diffraction patterns of different AZO thin films annealed in vacuum. The FWHM values of the (002) peak of the films are noted in the figure.

Fig.8. NIR transmission spectra of annealed AZO thin films.

Fig.9. Variation in the carrier concentration and resistivity values of the annealed AZO films. The inset shows the variation in the mobility values of the annealed films.

Fig.10. I-V characteristics under AM1.5G illumination of a single junction amorphous silicon solar cell deposited on PGA350 substrate.

Fig.1

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Fig.2
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Fig.3
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Fig.8
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Fig.9
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Fig. 10
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Sample name	Resistance (ohm)
AZO800	15,000
AZO900	1,500
AZO1000	700
AZO1100	200
AZO1400	1,750

Table – 1: Resistance of the pellets sintered at different temperatures