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Energy Procedia 60 (2014) 135 – 142

Energy Procedia

E-MRS Spring Meeting 2014 Symposium Y "Advanced materials and characterization techniques for solar cells II", 26-30 May 2014, Lille, France

Effect of Hydrogen gas dilution on sputtered Al:ZnO film

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Abstract

Al doped zinc oxide (ZnO:Al) is a transparent and conductive oxide used as contact and antireflection layer in solar cell based on Si or chalcogenide. Generally it is grown by magnetron sputtering but the resistivity of our films grown with this technique are still in the order of 10^{-3} Ωcm for layers grown at the temperatures used to produce the solar cells. The doping property of Hydrogen for Al:ZnO grown with two different sputtering techniques, DC magnetron sputtering and Pulsed magnetron sputtering at different growth parameters have been studied and the sample characterized optically, electrically and structurally. The best resistivity is $6.7*10^{-4}$ Ωcm was obtained using Pulsed magnetron sputtering.

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Keywords: Al:ZnO; solar cell; pulsed magnetron sputtering; hydrogen dilution

1. Introduction

The ZnO doped with Al (Al:ZnO) is gaining more importance between transparent conductive oxide (TCO) for its good electro-optical properties, no toxicity, high chemical and thermic stability and low cost. The most commonly used growth technique is the magnetron sputtering due to its low cost, high deposition rate at low temperature, uniformity of the film on large scale and good adhesion. Theoretical calculation and experiments demonstrated that the electrical properties of Al:ZnO improve by H_2 doping. Different hypothesis have been formulated on hydrogen role: interstitial position of the hydrogen with positive charge, substitutional position of the hydrogen in the oxygen position (donor H_O^+) and reduction of the adsorption of O^- "on grain surface" and bulk [1–6]. Furthermore hydrogen doping is claimed to improve UV transmittance and emission and to reduce absorption losses in the near infrared [7-8].

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Peer-review under responsibility of The European Materials Research Society (E-MRS)
doi:10.1016/j.egypro.2014.12.355

The scope of this paper is the study of hydrogen doping effects on electrical and optical properties of Al:ZnO in order to obtain a good contact and antireflection layer in solar cell based on Si or chalcogenide. To this end the Al:ZnO has to have a very low resistivity and a low work function.

2. Experimental

Our Al:ZnO films are deposited with a Kenosistec KS-300 in line sputtering system on glass at a pressure of $8*10^{-4}$ mbar at different temperatures (100-250 °C) with magnetron DC or magnetron pulsed sputtering. The 8x3 inches target is Al:ZnO with 2% Al_2O_3. The hydrogen is introduced directly in the sputtering atmosphere during the growth [9]. The effects of the $H_2/(Ar+H_2)$ ratio on Al:ZnO electrical, optical and structural properties are studied as a function of the growth parameters. The thickness of the samples were measured using a Tencor Alpha Step 300 profiler. The optical properties were investigated by transmittance and reflectance measurements in the 250–2500 nm wavelength range, using a spectrophotometer Perkin Elmer Lambda9, equipped with an integrating sphere. XRD data were collected using a Rigaku MiniFlex diffractometer, with CuKα radiation and Bragg Brentano geometry. The Hall effect and the resistivity data were obtained using a Biorad Hall profiler.

3. Results

Before the introduction of the hydrogen in the growth process some parameters have been optimized. By varying the target power in the range 350-600 W at 250° C the resistivity decreases as can be seen in Fig. 1. The best result was obtained at 600 W at a power density of 4 W/cm^2, higher power densities are normally not recommended as dangerous for the target and the solar cells.

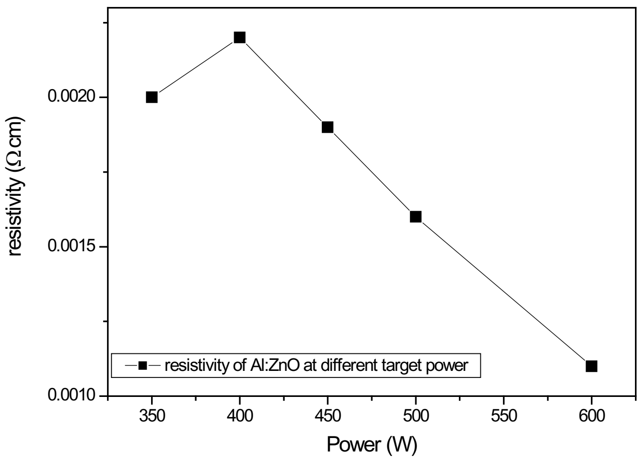

Fig. 1 Target power dependence of the resistivity of Al:ZnO grown without hydrogen dilution

In table 1 are listed the characteristic parameters of the Al:ZnO grown with different $H_2/[Ar+H_2]$ ratio and substrate temperature. As the temperature increases the resistivity decreases independently from the hydrogen content [10].

Table 1 Electrical and structural chracteristics of Al:ZnO grown at different hydrogen dilution and temperatures

sample	$H_2/(Ar+H_2)$(%)	T(°C)	Thickness(nm)	Resistivity (ohm cm)
AZO_150_0	0	150	460	$1.3 \cdot 10^{-3}$
AZO_150_2	2	150	460	$1.1 \cdot 10^{-3}$
AZO_150_4	4	150	460	$8.5 \cdot 10^{-4}$
AZO_250_0	0	250	420	$1.1 \cdot 10^{-3}$
AZO_200_2	2	200	420	$8.5 \cdot 10^{-4}$
AZO_200_4	4	200	410	$7.2 \cdot 10^{-4}$

Unfortunately temperatures higher than 200 °C can be destructive for solar cells based on chalcogenides and a:Si-H. The lowest resistivities have been obtained at high ratio of $H_2/[Ar+H_2]$ (4%) . It has to be noted that the samples grown at T< 200°C and a ratio of 4% are brownish probably for a reduction process of Al:ZnO at high hydrogen concentration and consequent excess of atoms of Zn at the grain boundary. The mobility of our films is rather low (≤ 15 cm^2/Vs) and improve increasing the temperature and the thickness of the films. This is probably due to the grain size increase with the thickness [11-12].

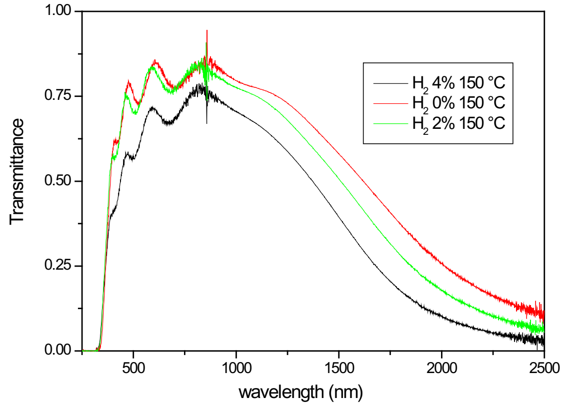

Fig. 2 Transmittance curves of Al:ZnO at different hydrogen dilution at T= 150°C

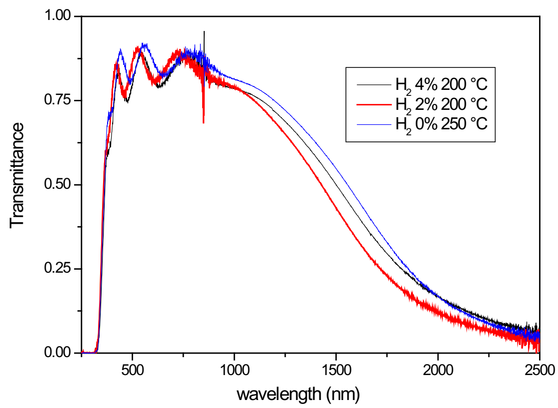

Fig. 3 Transmittance curves of Al:ZnO at different hydrogen dilution at T= 200°C

In Fig. 2 and 3 are shown the transmittance curves of the samples with different hydrogen concentration. It can be seen that the samples grown at 200 °C have a maximum transmittance of about 90 % similar to the best results reported in the literature while at 150 °C the transmittance is slightly lower. The sample grown at 150 °C and $H_2/[Ar+H_2]$= 4% has a low resistivity value of $8*10^{-4}$ Ωcm, but the sample is brownish, as confirmed from its lower transmittance in the entire range of measurement (see Fig. 2). In the infrared region the absorption due to free carrier reduces the transmittance.

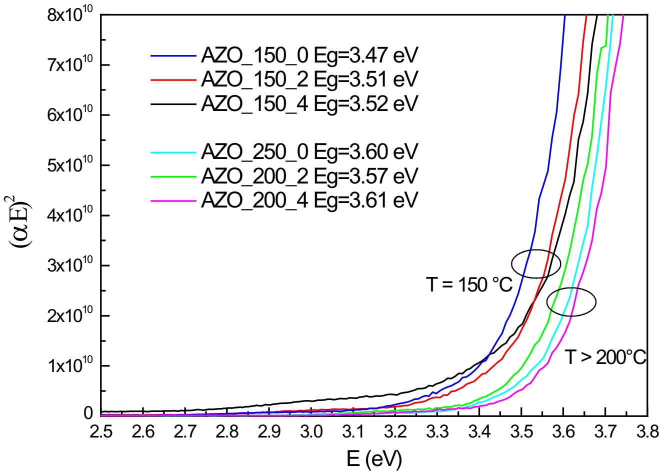

Fig. 4 Tauc plot of αE^2 as a function of E

The absorption coefficient was deduced from transmittance and reflectance curves and $(\alpha E)^2$ as a function of E has been plotted to extrapolate the E_g of the samples deposited at different $H_2/[Ar+H_2]$ ratio and at different T (Fig 4). It can be seen that the bandgap increases with increasing substrate temperatures and with increasing $H_2/[Ar+H_2]$ ratio too. The uncertainty on the absolute gap values is a few percent and therefore larger than the reported differences but the figure shows that the trend is quite clear. As can be seen from table 2 the bandgap variations are due to the change of the free carrier concentration (Burstein-Moss effect): the samples grown at high T have a higher free electron concentration and an higher Eg. The only exception to the trend with hydrogen concentration is the sample AZO12 deposited at 250 °C instead of 200°C.

Table 2 Carrier concentration and bandgap of Al:ZnO films at different hydrogen dilution

sample	n (10^{20} cm^{-3})	Eg(eV)
AZO_150_0	3.9	3.47
AZO_150_2	3.97	3.51
AZO_150_4	4.28	3.52
AZO_250_0	5.82	3.60
AZO_200_2	5.16	3.57
AZO_200_4	6.1	3.61

The XRD curves represented in Fig. 5 show a preferred orientation along c-axis with a single peak (002). From Fig. 6 worsening of the crystal structure can be observed with increasing $H_2/[Ar+H_2]$ ratio. At a given temperature the (002) peak decreases with increasing $H_2/Ar+H_2$ ratio. This behavior has already been noted in other articles where they assumed that the excess of H_2 is adsorbed at the surface hampering a crystal growth with preferred c-axis orientation [10]. Another hypothesis is that the excess of H atoms incorporated in the Zn-O bond produce a relaxation of the neighboring atoms by increasing the number of defects at the grain boundaries.

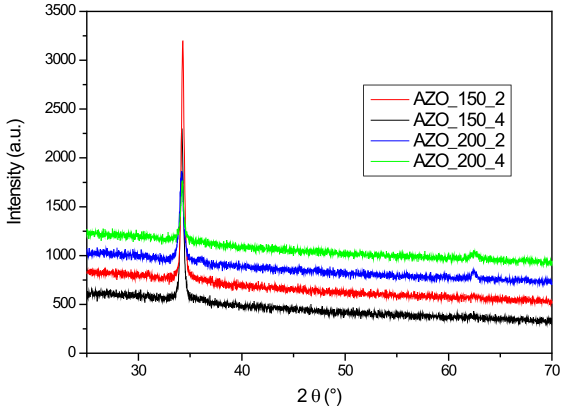

Fig. 5 XRD curves of films of Al:ZnO deposited at different dilution of hydrogen and at different temperatures

In order to improve the structural quality of our samples pulsed magnetron sputtering has been utilized. Indeed the DC sputter deposition causes the inside surfaces of the system to accumulate electric charges from the plasma. These charges create mini- or macro-arcs which result in very uneven removal of material from the target electrode and particulate formation [13] and deeply influence the energy and type of ions impinging on the growing film.

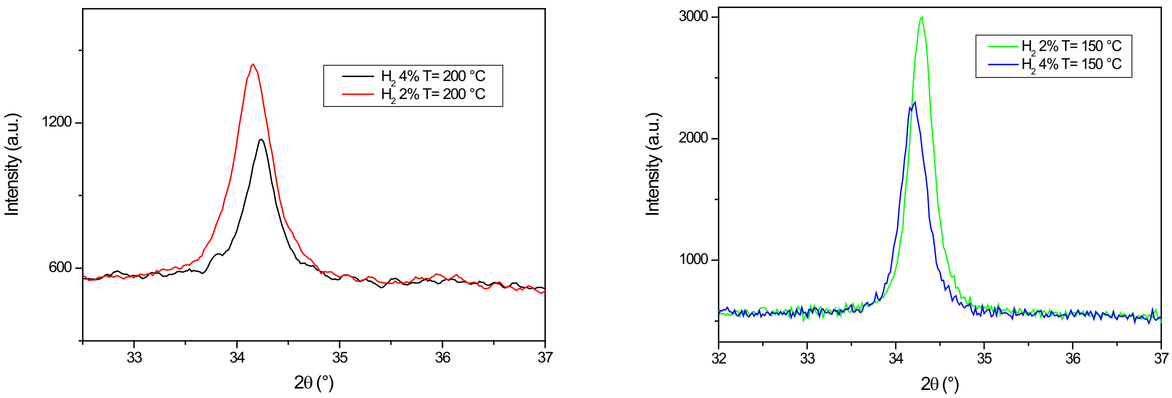

Fig. 6 XRD spectra of two pair of films deposited with different hydrogen dilution. Decrease of XRD (002) peak of Al:ZnO with increasing hydrogen dilution can be noted.

The use of pulsed dc plasmas should avoid these problems. A voltage sequence of pulsed magnetron sputtering is schematically shown in Fig.7.

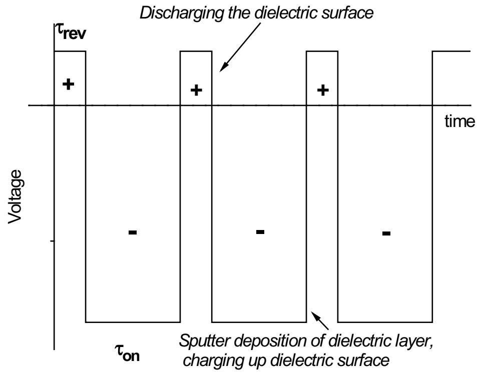

Fig. 7 Voltage sequence of pulsed magnetron sputtering

During τ_{on}, the 'on-time' a negative voltage pulse of a few hundred volts is applied to the target. Then the power is switched off for a period of time τ_{off} , the 'off-time', or, switched to a small positive voltage. Typically, the 'reverse' time is about 1/10 of the 'on-time' [14]. Pulsed dc reactive sputtering has been widely used to deposit thin films of dielectric materials such as alumina, Al_2O_3 [15] and titania, TiO_2 [15], which have a smooth structure due to the absence of particulates created by micro-arcs [16, 17]. In our case the optimized parameters for the Pulsed DC magnetron sputtering deposition were found to be T_{on}= 42 ms and T_{off} =8 ms. In Fig. 8 the difference between the XRD curves of Al:ZnO films grown at a H_2/[Ar+H_2] ratio of 4% in DC magnetron sputtering and Al:ZnO films grown at a H_2/[Ar+H_2] ratio of 4% but in pulsed DC magnetron sputtering are plotted: the (002) peak higher intensity for the sample grown in pulsed DC magnetron sputtering indicates better structural characteristics. The resistivity obtained with samples grown by pulsed magnetron sputtering is 6.7 10^{-4} Ωcm.

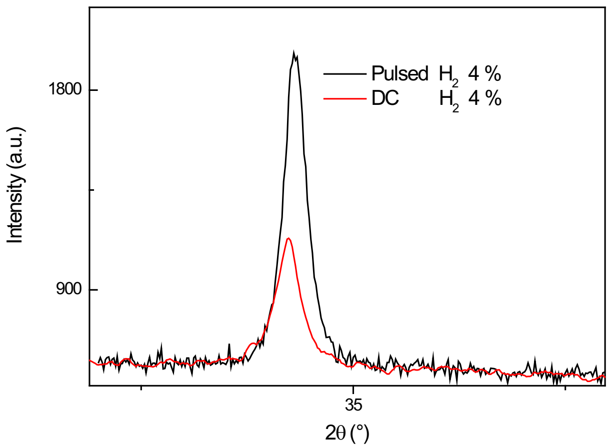

Fig. 8 XRD curves of Al:ZnO grown at 200 °C with DC magnetron sputtering and pulsed magnetron sputtering at the same hydrogen dilution

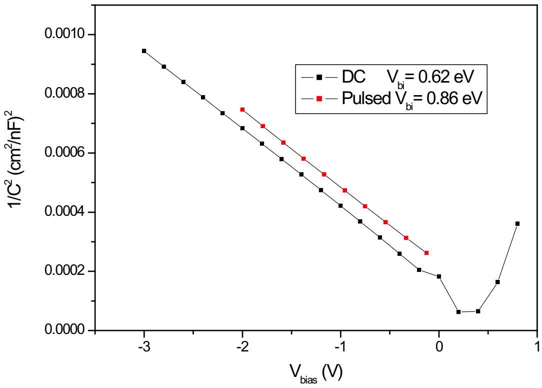

Fig. 9 Plot of $1/C^2$ as a function of the Voltage

As already said another important parameter that our Al:ZnO has to possess is a low work function. In a first approximation the work function of a metal can be obtained from C-V measurement of a semiconductor/metal junction (Fig.9) using the simplified Anderson model**:** $W = \chi_{Si} + Eg_{Si} - (V_{bi} + Ea)$, where χ is the electron affinity of the Si (4.05 eV), V_{bi} the built-in potential and E_a the activation energy of p-type Si (0.158 eV for our substrate). In Fig. 9 the plot of $1/C^2$ vs V of two Al:ZnO/p-type Si junction are plotted. From this plot the V_{bi} is obtained as intercept of the linear fit. The work function for a Al:ZnO films grown at a $H_2/[Ar+H_2]$ ratio of 4% in DC magnetron sputtering has resulted to be 4.39 eV, whereas the work function of a Al:ZnO films grown at a $H_2/[Ar+H_2]$ ratio of 4% in pulsed DC magnetron sputtering has resulted to be 4.15 eV. Further studies are necessary to better understand why the Pulsed magnetron sputtering has this beneficial effect on the work function of Al:ZnO. A possible hypothesis is a better interface due to a lower incorporation of particulates.

4. Conclusion

In conclusion the electrical properties of Al:ZnO grown by DC magnetron sputtering have been improved by using H_2 doping. A further improvement has been obtained by using Pulsed magnetron sputtering. This technique is supposed to improve the structural quality of dielectric films with respect to the simple DC magnetron sputtering. The Pulsed magnetron sputtering has improved the electrical and structural characteristics of our samples and lowered the work function of the Al:ZnO.

Acknowledgments

The authors would like to thank Dr. Luca Serenelli for the help with the C-V measurements. The activity is supported by the Italian Ministry of Economic Development in the framework of the Operating Agreement with ENEA for the Research on the Electric System.

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