ZnO as a conductive layer prepared by ALD for solar cells based on n-CdS/n-CdTe/p-Cu$_{1.8}$S heterostructure

T.V. Semikina[1], S.V. Mamykin[1], M. Godlewski[2], G. Luka[2], R. Pietruszka[2], K. Kopalko[2], T.A. Krajewski[2], S. Gierałtowska[2], Ł. Wachnicki[2], L.N. Shmyryeva[3]

[1]*V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine,*
41, prospect Nauky, 03028 Kyiv, Ukraine; e-mail: tanyasemikina@gmail.com
[2]*Institute of Physics, Polish Academy of Sciences,*
Al. Lotnikow 32/46, 02-668 Warsaw, Poland; e-mail: godlew@ifpan.edu.pl
[3]*National Technical University of Ukraine "KPI", 33, prospect Peremogy 03056 Kiev, Ukraine*

Abstract. ZnO films with high conductivity are obtained by atomic layer deposition for application in solar cells based on $n-\mathrm{CdS}/n-\mathrm{CdTe}/p-\mathrm{Cu}_{1.8}\mathrm{S}$ heterostructure. The parameters of solar cells with ZnO electrode are calculated from light and dark current-voltage characteristics and compared with those obtained for structures with Mo contact. The advantages of ZnO electrode are discussed.

Keywords: solar cells on n-CdS/n-CdTe/p-Cu$_{1.8}$S heterostructure, conductive ZnO films, atomic layer deposition.

1. Introduction

ZnO is an intensively studied wide band gap semiconductor material for applications in electronics and photovoltaics, generally for use as a transparent conductive material (see [1, 2] and the references given there). Among numerous technological methods used to deposit ZnO (pulse laser deposition (PLD) [3, 4], radio-frequency and dc -magnetron sputtering [5, 6], reactive sputtering [7], metal-organic chemical vapor deposition (MOCVD) [8], sol-gel method [9], *etc.*), the atomic layer deposition method (ALD) demonstrates several sufficient advantages (see e.g. [1, 10-11]). For example, the ALD allows deposition of very homogeneous in thickness, completely conformal and pin-hole free ZnO films on very big substrates (e.g. 1.2×1.2 m^2) with the required structural properties without any plasma-related damage and atmosphere-related contaminations [12]. The ALD-grown ZnO films are highly transparent (85-90%) and conductive (order of 10^{-3} Ohm·cm) [10]. Moreover, ALD allows to load into the reaction chamber tens of substrates in one run, reducing the process costs considerably. Moreover, by using the ALD technique,

we can deposit the ZnO films at low temperature (100-200 °C) using various (often cheap) precursors, which results in costs reduction, a crucial factor for a further spread of solar cell panels.

Comparing the mentioned ALD advantages with possibilities of other technological methods, we should note that the sol-gel method [9], one of the main competitors from our view point, apart from simplicity and cheapness of the process itself and the equipment used in it, also allows to deposit films on large substrates. The main disadvantage of the sol-gel method is a necessity to carry out the high temperature (500 °C) post-deposition treatment (for 30 min and more) to improve the crystalline structure of deposited films. Concerning the ZnO deposition on a glass substrate, such a high temperature is unacceptable. In turn, MOCVD is too expensive and a rather sophisticated one, dc-magnetron sputtering demands the substrate temperature 500 °C [6] to get a structurally perfect ZnO layer, the high growth temperature 450…700 °C is also used for PLD [3]. Moreover, all the methods based on sputtering, including rf- and dc-magnetron, or on reactive processes (PLD) result in defects generation in the grown films [6].

In this work, we use ALD to prepare ZnO films for their application as conductive electrodes in solar cells of the second generation based on heterojunctions of selected II-VI materials. ZnO film replaces the molybdenum contact, often considered as the best electrode for structures based on II-VI materials [13, 14]. Mo is usually deposited by either magnetron sputtering or ion beam deposition. The main disadvantage of these methods is low productivity. It is impossible to deposit a film on a large substrate, that is why we test an alternative approach in the present study. We compare the photoelectrical characteristics of solar cell structures $n-\text{CdS}/n-\text{CdTe}/p-\text{Cu}_{1.8}\text{S}$ deposited on a pyroceram glass/Mo with those deposited on a silica substrate covered with ZnO.

2. Technology and properties of ZnO films

Formally, ALD is a variant of chemical vapor deposition (CVD), but contrary to CVD, reaction precursors are introduced sequentially into the growth chamber, and their pulses are separated by purging the chamber with an inert gas (nitrogen). Therefore, precursors meet only at the surface of a growing film, where they react forming the required compound. In the ideal case, one cycle of precursors builds a monolayer on the substrate, since the ALD process is a self-limiting growth process. The ALD cycle includes the pulse of the first precursor, followed by purging a growth chamber with a neutral gas (purging occurs after each precursor pulse), and the pulse of the second precursor. The ALD cycles are repeated until the desired layer thickness is obtained.

The studied ZnO films were grown using de-ionized water and diethyl zinc $[\text{Zn}(\text{C}_2\text{H}_5)_2]$ in a commercial ALD reactor (Cambridge Nanotech Savannah 100, USA). Diethylzinc (DEZn) and de-ionized water served as zinc and oxygen precursors, respectively. Each step of precursor's doze inlet into a chamber is separated by purging a chamber with nitrogen. The process was optimized by performing different series of ZnO-ALD processes, in which we applied very short pulsing and long purging times or long pulsing and short purging times. The details of these investigations are given elsewhere [11]. From these investigations we determined that the growth window of the ALD process ranges from 100 to 240 ºC (substrate temperature). Inside the growth window, we achieved the growth rate 1.7…2.1 Å per cycle.

3. Influence of technological regimes on ZnO film properties

The different applications require suitable and reproducible properties of materials like surface roughness, optical and electrical properties, suitable crystallographic orientation. For example, to apply transparent conductive electrodes in solar cells, it is necessary to get ZnO films with high conductivity (order of 10^4 Ohm·cm). Our previous investigations proved that ALD technology allows to control the films properties in a wide range via altering process parameters, in particular substrate temperature [1, 10-11]. We have determined the technological regimes for depositing the films with good structural properties [15]. The X-ray diffraction (XRD) measurements showed that the growth mode of ZnO films (e.g. the *c*-axis perpendicular or parallel to the surface) and grain diameters depends on a purging time [15]. In the case of the samples deposited with short purging times, the main diffraction peak corresponds to the [10.0] direction, which indicates the growth mode with *c*-axis parallel to the substrate. In turn, for the layers prepared with an increased purging time, the *c*-axis is perpendicular to the surface and the XRD peak [00.2] dominates the patterns, especially at higher growth temperature (200 ºC). The lattice parameters (*c* and *a*) approach the value of the lattice parameters of the bulk ZnO crystal with an increase of the growth temperature [15].

A good structural quality of our ZnO films is a unique feature. It was generally assumed that the films grown at low temperature should be rather amorphous. In contrast, we found that ZnO films grown at low temperatures (within the growth window) are ordered and polycrystalline. The good structural quality of the films is additionally confirmed by the results of photoluminescence (PL) measurements at room temperature [16]. We observed a bright edge excitonic PL at room temperature. Furthermore, we did not observe defect related bands in the PL spectra. The surface morphology was studied by atomic force microscopy (AFM) [10]. We have found that roughness clearly depends on such parameters as growth temperature (100 to 200 ºC), thickness of the film and purging time. The root mean square (RMS) of the surface roughness values could be changed from 0.9 to 3.9 nm.

The electrical measurements (Hall effect studies) showed that higher growth temperature leads to the increase of free electron concentration (*n*) [11]. The results discussed in details in [11] are presented in Table. The electron concentration varied between $10^{20}\,\text{cm}^{-3}$ (for the samples grown at 200 ºC and above) down to $10^{16}\,\text{cm}^{-3}$ (for the films obtained at 100 ºC). We noticed that not only the substrate temperature influences on the value of carrier concentration. A lower electron concentration was obtained for the films grown with longer purging times applied after introducing the H_2O precursor into the growth chamber [11]. The effect was tentatively explained as follows – under longer purging process, the growing layer is better protected from the build-up of hydroxyl groups, which are responsible for the increase of electron concentration, as they contain hydrogen atoms [11]. The values of electron mobility were usually between 10 and 50 cm²/V·s, though in the case of ZnO layers grown on crystalline substrates (GaN), mobility exceeds 100 cm²/V·s [11].

Table. Results of Hall effect measurements for the films deposited on a glass substrate with following growth parameters: time (H$_2$O) = 15 ms, purging time = 20 s, time (DEZn) = 60 ms and purging time = 8 s (after the reference [11]).

As-grown layer	Growth temperature (ºC)	Thick-ness (nm)	Concentration (cm^{-3})	Mobility (cm^2/V·s)	Conductivity Ohm^{-1}·cm^{-1}
ZnO/glass	200	66.5	1.67×10^{20}	16.1	431.03
ZnO/glass	140	93.0	7.00×10^{18}	38.0	42.60
ZnO/glass	130	110.0	1.10×10^{18}	2.25	0.39
ZnO/glass	100	188.0	4.50×10^{17}	8.0	0.58

The obtained values of mobility correlate with the results of other authors [17], where mobility of ZnO films deposited by different methods varies from 1 to 100 cm^2/V·s with electron concentration in the range of $10^{14}...10^{20}$ cm^{-3}. It should be noted that obtained by us the value of electron concentration 10^{20} cm^{-3} was reached without any intentional film doping, which is a unique result. For example, the maximal carrier concentration for undoped ZnO prepared by low-pressure MOCVD and pulse laser deposition was $10^{18}...10^{19}$ cm^{-3} [4, 18]. We also observed the new type of dependence between the carrier concentration and mobility (Fig. 1). In our case, we get the increase of carrier concentration accompanied by the increase of carrier mobility. The data shown in Fig. 1 were obtained for the ALD process with the increased growth temperature, and other technological parameters were kept the same. Generally, for thin films the dependence between concentration and mobility is another one. The increase in carrier concentration leads to a mobility drop [19]. The nonmonotonic dependence of these transport parameters (with a peak at some parameters) was observed in the work [20] for ZnO films deposited by reactive sputtering on sapphire. In this work, the main technological factor influencing the free electron concentration and mobility was the oxygen flow rate. The authors explained the nonmonotonic character of the dependence by structural variation of ZnO generated by different oxygen flow rates.

In our case, such explanation cannot be used. The alternative explanation can relate to the fact that hydrogen (present e.g. in hydroxyl groups) is often the main source of electrons in ZnO. We observed that the sample conductivity decreases under the condition of longer purging times, which may be related to a decrease in amount of hydroxyl groups on a surface. In turn, the

dependence on the process temperature can be explained as follows. Hydrogen can faster penetrate/diffuse into the volume of ZnO films at higher substrate temperature. This can explain the increasing electron concentration. On the other hand, the higher growth temperature stimulates the growth of larger crystallites, and the more ordered crystal lattice is observed by us in the XRD investigations. The lattice parameters determined from the XRD examinations are then close to those of bulk ZnO. Then, the electron scattering by grain boundaries and dislocations is reduced. Despite the fact that the growth of the scattering by ionized impurities should increase, since the density of donor impurities is increased in the samples grown at higher temperature (free electron concentration is increased), the overall result is an increase in the carrier mobility. Thus, our dependence between the concentration and mobility indicates that the process of scattering by ionized impurities is weaker in comparison to the scattering by grain boundaries and dislocations.

4. Properties of ZnO films for electrode applications

Based on the results of the investigations mentioned above, we selected the technological parameters for deposition of ZnO films used in the present study. To get highly conductive layers of ZnO for solar cell electrodes, we selected the following parameters: the substrate temperature 200 ºC, pulse duration for DEZn 0.06 s, purging time after DEZn 8 s, pulse time for H$_2$O 0.016 s, purging time after de-ionized water 22 s. The number of cycles was 1500. ZnO films were deposited with the thickness 200 nm.

The selected parameters allow to get ZnO films with atomically flat surfaces, the RMS is below 2 nm. ZnO films have a polycrystalline structure with the dominant (00.2) crystallographic orientation, i.e., the situation when the *c*-axis is perpendicular to the layers surface.
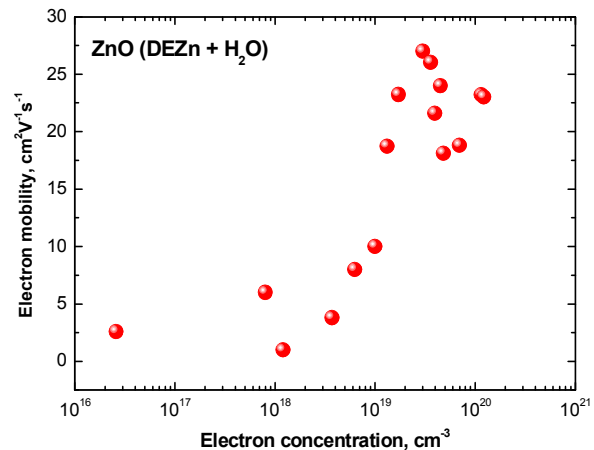

Fig. 1. Dependence between carriers concentration and electron mobility.

Electrical properties were obtained from the Hall measurements performed at room temperature in a magnetic field of 0.426 T by the dc four-probe method (system produced by PhysTech GmbH). The Hall effect measurements of the prepared ZnO films show the high concentration of carriers $(1.3 \cdot 10^{20} \, cm^{-3})$, mobility $24.8 \, cm^2/V \cdot s$ and a low value of the specific resistance $(1.94 \cdot 10^{-3} \, Ohm \cdot cm)$.

5. Solar cells on ZnO and Mo

CdS/CdTe structures were deposited under the same process conditions on two different types of substrates (pyroceram covered by Mo or silica substrate covered with ZnO acting as bottom electrodes) mounted on the same holder in a growth chamber. Polycrystalline films CdS and CdTe were prepared by a quasi-closed sublimation method from CdS and CdTe powders during one technological cycle. The temperature of sublimation for CdS powder is 750 ºC and the durability of the process varied from 10 s to 1 min. The chamber temperature was 550 ºC that was kept constant during the whole technological procedure. After finishing CdS deposition, heating of CdTe powder started. The powder of CdTe was sublimated at the temperature 500 ºC.

The n-CdS layer in our case formed the ohmic contact with a bottom electrode (Mo or ZnO). The thickness of the CdS layer was varied from 60 to 800 nm. CdS also served as a template for the following growth of CdTe that is an absorbing layer of the so-obtained solar cell. We deposited a relatively thick film of a lightly doped n-type CdTe (resistive film). Time of deposition varied from 3 to 6 min, to get the layers with the thickness 1…3 μm. Since both CdS and CdTe layers have the n-type conductivity, it was necessary to deposit the layer of p-type for $p-n$ junction formation. For this purpose we used a layer of p-$Cu_{1.8}S$. Degenerated semiconductor $Cu_{1.8}S$ is also used as a top electrode for CdTe. The square shape working area of the solar cell was $0.196 \, cm^2$. Construction of the solar cells allows illumination of cells from the both sides (through the top and bottom electrodes). From the viewpoint of practical applications, this construction results in the increased efficiency of the cells.

The measurements of solar cells characteristics were performed in the dark and under two illumination intensities of 0.013 and 0.136 W/cm^2 (tungsten lamp). We illuminated the solar cells from the bottom electrode side and from the top electrode side for the comparison. The results show that the efficiency of the cells is higher in the case of illumination from the side of $Cu_{1.8}S$. Thus, in further discussion we present the results for illumination from the top electrode ($Cu_{1.8}S$).

The dark and illuminated current-voltage (*I-V*) characteristics of solar cells are presented in Fig. 2. It is evidently seen that better results are obtained for the structures deposited on ZnO films in comparison with the ones on Mo. The calculated efficiency of the best-

prepared solar cells is 1.89% for the samples on ZnO (short circuit current j_{sc} = 2.49 mA/cm^2, open circuit voltage U_{oc} = 0.3695 V, fill factor FF = 2.67%). It should be noted that we do not observe any clear correlation between the device performance and the thickness of CdS and CdTe layers. This is because of stronger influence of other technological factors that are under investigation now.

In Fig. 3, we present the energy band gap diagrams of the examined structures. The working barrier in our solar cells is formed between n-type CdTe and p-$Cu_{1.8}S$. In the energy band diagram, we assume that Fermi level in CdTe is approximately in the middle of a band gap. We assumed this, having in mind that this layer is of high resistivity. The open circuit voltage (U_{oc}) is determined by the value of band bending. The experimentally obtained small value of U_{oc} relates likely to high resistivity of CdTe layer. This value can be increased theoretically to U_{oc} = 0.7…0.8 eV by electron doping of CdTe.

The short circuit current I_{sc} depends on recombination losses in heterojunction, at the interface, and in the volume of each layer. The density of surface states is crucial here. Seemingly, the interface between CdS and ZnO has a lower density of surface states as a contact of CdS and Mo because of ZnO film properties. Additionally the relatively good polycrystalline structure of ZnO promotes the more ordered growth of CdS layer than in the case of growth on Mo. Therefore, the recombination current in the case of ZnO is lower, and the value of I_{sc} increases. Moreover, in the case of the contact with ZnO, the diagram indicates formation of a higher barrier for the holes and consequently a higher value of the built-in electric field. Due to this field, the holes move away from the ZnO/CdS contact and take part in photocurrent generation. It can be the reason of the better characteristics of the solar cells made on ZnO.
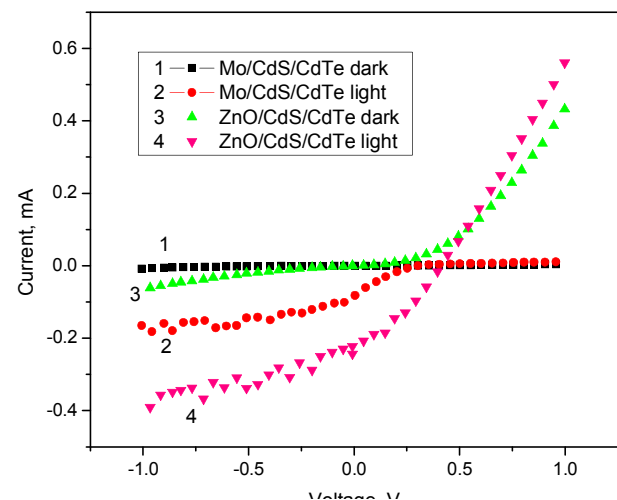

Fig. 2. *I-V* characteristics of CdS/CdTe solar cells made on metallized with Mo pyroceram substrate and on silica substrate covered with ZnO.
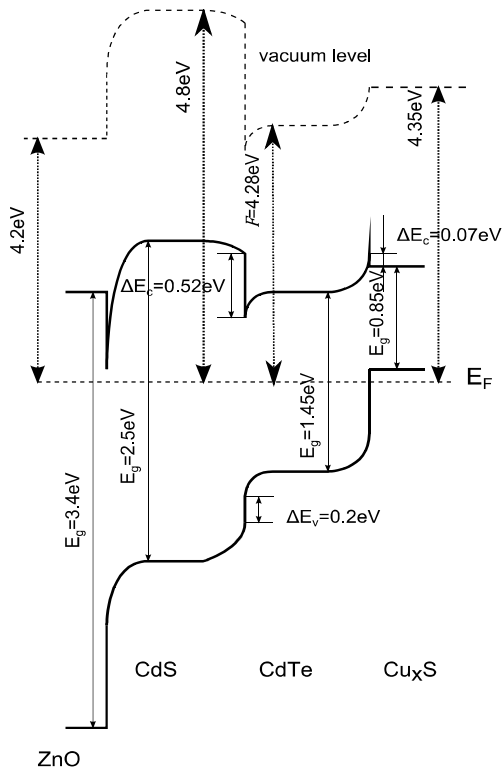
Fig. 3. Energy band diagram of solar cell CdS/CdTe/Cu$_{1.8}$S on ZnO.

6. Conclusion

The ALD growth allows deposition of ZnO films with suitable properties for solar cells applications. Varying the growth parameters, we can modify the structural and electrical properties of ZnO in a wide range. In particular, we determined the technological parameters for ZnO deposition with the required structural properties and high conductivity. We have demonstrated the possibilities to apply ZnO film as an electrode in CdTe-based solar cells. The solar cells $n - \text{CdS} / n - \text{CdTe} / p - \text{Cu}_{1.8}\text{S}$ made on ZnO show the improved photoelectrical characteristics as compared to those made on Mo.

Acknowledgment

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