УДК: 537. 221:537.221

# ZnO:Al WIDE ZONE «WINDOWS» DEPOSITED BY MAGNETRON SPUTTERING ON UNHEATED SUBSTRATE

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Electrical and optical properties of ZnO:Al films deposited on unheated glass substrate by non-reactive RF magnetron sputtering of target ZnO:$Al_2O_3$ (98/2 wt.%) were studied. It was shown that Zno:Al films with the thickness of 0.75 μm deposited at the magnetron power 130 W and 4 μbar argon pressure with adding of $4\cdot10^{-3}$ μ bar oxygen pressure during the first minute of condensation has the following electrical and optical characteristics: surface, resistance 6 Ω/ and transmittance in visible spectral range about 88%. The ZnO:Al films with such optical and electrical parameters are suitable for substrate configuration highly efficiency thin film solar cells on $CuInSe_2$ base.

## 1. INTRODUCTION

One of the most perspective materials for wide-zone «windows» for the solar cell are ZnO:Al films , obtained by magnetron sputtering method [1]. Up to now [1…3] the optimal electrical and optical properties of ZnO:Al layers were prepared by magnetron sputtering at the substrate temperature only in the range 200-450°C.

In process of preparation of Cu-In-Se thin film solar cells in substrate configuration and with CdS buffer layer it is desirable to deposit ZnO:Al layers at possible low temperature to minimise mutual diffusion of atoms Zn, Al, Cd, In, Cu in conjunction layers of solar cells [2].

So, the definition of optimal conditions of magnetron sputtering for formation high quality ZnO:Al films without special heating of substrate is the important problem for further increase of efficiency of thin film solar cells on the base Cu-In-Se system compounds.

## 2. EXPERIMENT

The ZnO:Al films were deposited on soda lime glass substrates by non-reactive RF magnetron sputtering of ZnO:$Al_2O_3$ (98/2 wt.%) target in atmosphere of clean argon (99,999 %) . The initial pressure in the vacuum chamber was $3\cdot10^{-7}$ mbar. The ZnO:Al film have been prepared without substrate heating . The distance between the target and substrate was 35 mm. The thickness of films t were determined by Dektat 3030 profilometer. Surface resistance $R_s$ and electrical resistivity ρ of ZnO:Al films were measured by four-probe method. The value of charge carriers concentration n and mobility μ were determined in constant magnetic field 0,2 Tesla at room temperature using van der Pauw method [4]. Optical transmittance T measurements have been carried out in the visible spectral range (300…900 nm) on the double beam spectrophotometer (type Perkin) by two-channel method [5].

## 3.RESULTS AND DISCUSSION

### 3.1 THE INFLUENCE OF THE MAGNETRON POWER AND ARGON PARTIAL PRESSURE ON THE ELECTRICAL AND OPTICAL PROPERTIES OF ZNO:AL FILMS

The ZnO:Al films were prepared at the following magnetron powers P: 80W, 100W, 130 W, 150W, 200W and argon partial pressures $p_{Ar}$: 4 , 8 and 12 μbars. The results of the ZnO:Al films optical and electrical properties are shown in the table 1.

Table 1

The influence of magnetron power and argon partial pressure on the ZnO:Al films optical and electrical properties

| P, W | 200 | 200 | 200 | 150 | 130 | 100 | 80 |
|---|---|---|---|---|---|---|---|
| $p_{ar}$,μbar | 12 | 8 | 4 | 4 | 4 | 4 | 4 |
| t, μm | 0,80 | 0,55 | 0,55 | 0,68 | 0,24 | 0,25 | 0,15 |
| ρ,$10^{-4}$, Ω cm | 7,8 | 8,9 | 11,4 | 9,5 | 5,2 | 5,3 | 148 |
| μ, $cm^2/V*s$ | 8 | 10 | 11 | 11 | 12 | 13 | 6 |
| n, $10^{20}cm^{-3}$ | 10 | 7 | 5 | 6 | 10 | 9 | 0,7 |
| T, % | 30 | 60 | 90 | 80 | 60 | 65 | 90 |

As it is seen from the table 1 the increase of argon partial pressure from 4 μbar up to 12 μbar at the constant 200W magnetron power results in decrease electrical resistivity from $\rho=1{,}14\cdot10^{-3}$ Ωcm up to $\rho=7{,}8\cdot10^{-4}$ Ωcm as the result of substantial increase of charge carriers concentration from $n=5\cdot10^{20}$ $cm^{-3}$ up to $n=1\cdot10^{21}$ $см^{-3}$ with the small decrease of the mobility. At the same time the optical transmittance of ZnO:Al films decreases from T=90 % up to T=30 %. As we can see from the table 1 the films which were prepared at the 200W magnetron power and 4 μbar argon partial pressure have the maximum transparent. Therefore in our experiments (samples 5…8) we did not change the argon partial pressure ($p_{ar}$ =4μbar).

At constant partial argon pressure 4 μbar - the reduction of magnetron power from 200 up to 130W

results in decrease of electrical resistivity (ρ) from $1{,}14\cdot10^{-3}$ up to $5{,}2\cdot10^{-4}$ Ωcm . In this case the charge carriers concentration (n) in the ZnO:Al films increases from $5\cdot10^{20}$ up to $10\cdot10^{20}$ см$^{-3}$ at minor increase of the mobility. The transmission of ZnO:Al films in visible spectral range (T) decreases from 90 up to 60 %. The further reduction of magnetron power up to 80W was accompanied by increase of ρ as the result of the decrease of charge carriers concentration (n) from $10\cdot10^{20}$ up to $7\cdot10^{19}$ см$^{-3}$ with increase of the transmission up to 90 %.

Thus, minimum electrical resistivity ρ =(5,2… 5,3)$\cdot10^{-4}$ Ωcm was observed in ZnO:Al films prepared at magnetron power of P=(130…100)W and argon partial pressure $p_{ar}$=4μbar. The transmittance of these films was 60…65%. In the solar cells ZnO:Al films usually have the thicknesses 0,5… 0,7 μm. At such thickness and above ρ the surface resistance $R_s$ are 8…10 Ω/ . It is well known [6], that at $R_s$ = 12 Ω/ the surface resistance of ZnO:Al does not influence on the characteristics of solar cells. Therefore the ZnO:Al films prepared in our experiments at magnetron power 100W and 130W and argon partial pressure 4 μbar have electrical parameters which permit to use it for creation of highly effective film solar cells . However their optical transmission should be increased up to 90 % [1].

### 3.2 INFLUENCE OF THE OXYGEN ADDITIVE TO ARGON SPUTTER GAS ON ELECTRICAL AND OPTICAL PROPERTIES OF ZNO:AL FILMS

For the increase of the optical transmission of ZnO:Al films prepared by non-reactive magnetron sputtering, but without the change their electrical properties it is necessary to add small quantity of oxygen to argon sputter gas [1]. As it is known [7], the presence of oxygen vacancies in grains reduces the transmission of ZnO:Al polycrystalline films . The additive of oxygen in the argon sputter gas allows to reduce nonstoichiometry and thus to increase the transmission of ZnO:Al films. However, the excess of oxygen atoms in ZnO:Al film results in formation $Al_2O_3$ on the grain boundaries [8]. In this case the concentration of aluminium atoms in volume of the grain decreases and therefore the charge carriers concentration reduces .

Thus, from our point of view, the quantity of oxygen additive to argon sputter gas is the critical value for non-reactive RF magnetron sputtering method of preparation ZnO:Al films with good optical and electrical properties. Therefore we started to add to argon sputter gas the possible minimum value of oxygen (on the level 0.1% from argon partial pressure). The magnetron power were 100 and 130W, argon partial pressure was 4 μbar and the partial oxygen pressure in our case was $4\cdot10^{-3}$ μbar. The results of optical and electrical properties of ZnO:Al films prepared in such conditions are presented in the table 2, where τ - admission time of oxygen additive to argon sputter gas.

As one can see from the table 2, under magnetron power 100 W and argon partial pressure 4 μbar the addition of oxygen to argon sputter gas during the all process of film condensation (i.e. 35 min) results in increase of transmission ZnO:Al film in a visible spectrum range from 65 up to 92 % (compare sample 7 in table1 and sample 9 in table 2). However, the electrical resistivity of sample 9 in comparison with the sample 5 was increased on five orders. It testifies that in such ZnO:Al film there is an excess of oxygen, which formats oxides $Al_2O_3$ on the grain boundaries. To decrease the amount of oxygen in argon sputter gas during ZnO:Al film preparation we reduced admission time τ of oxygen additive. So, under admission time of oxygen to argon during 3 minutes in the beginning and during the last 3 minutes ( 3/3 ) of 35 minute process of ZnO:Al film condensation we prepared sample No.10. In this case the decrease τ did not reduce the transmission of film, but results in decrease of electrical resistivity up to ρ=$1{,}7\cdot10^{-2}$ Ωcm.

Table2

Influence of the oxygen additive to argon sputter gas on electrical and optical properties of ZnO:Al films

| Samples | 9 | 10 | 11 | 12 | 15 |
|---|---|---|---|---|---|
| P, W | 100 | 100 | 100 | 130 | 130 |
| $P_{ar}$, μbar | 4 | 4 | 4 | 4 | 4 |
| τ , min | 35 | 3/3 | 1 | 1 | 1 |
| t, μm | 0,13 | 0,15 | 0,15 | 0,30 | 0,75 |
| $R_s$, Ω/ | $1{,}8\cdot10^{6}$ | $1{,}2\cdot10^{3}$ | 470 | 22 | 6 |
| ρ,$10^{-4}$ Ωсм | $2{,}3\cdot10^{5}$ | $1{,}7\cdot10^{2}$ | 65 | 7,0 | 4,2 |
| n,$10^{20}$ cm$^{-3}$ | --- | 0,3 | 0,8 | 7 | 10 |
| μ, cm$^2$/V*s | --- | 12 | 13 | 13 | 15 |
| T, % | 92 | 92 | 92 | 92 | 88 |

The minimization of τ up to 1 minute in the beginning of process of condensation was stipulated the further decrease of resistivity up to $6{,}5\cdot10^{-3}$ Ωсм (sample No.11, table 2) The transmission of such films did not change (T=92%) . The increase of magnetron power up to 130W (sample No.12, table 2) results in reduction of electrical resistivity up to ρ=$7{,}0\cdot10^{-4}$ Ωcm. The charge carriers concentration in such layers was increased up to n=$7\cdot10^{20}$ см$^{-3}$, the charge carriers mobility was μ=13 cm$^2$/V·s. From our point of view, the optimization of optical and electrical properties was stipulated by increasing the film speed deposition due to the increasing of magnetron power from 100 up to 130W. The increasing of film speed deposition under minimum τ =1 min, results in reduction of relative quantity of oxygen, that stipulated only doping process of ZnO by Al. Besides, the increasing of speed deposition under the constants time condensation was resulted in essential increasing of film thickness (compare samples 11 and samples 12, table 2).

According to [9] the grain sizes are increased with the increase of ZnO:Al film thickness. The increase of the grain sizes reduces the quantity of aluminium atoms located on the grain boundaries in electrical non-active condition (as $Al_2O_3$), that also increases charge carriers concentration [9]. Under above condition we prepared

ZnO:Al film with thickness t=0,3μm, the transmission T= 92 % and the surface resistance $R_s$ =22 Ω/ . In order to decrease the surface resistance of ZnO:Al film up to a best value ($R_s$ = 12 Ω/ ) it is necessary to increase the film thickness. By increasing the time of condensation up to 80 minutes we prepared ZnO:Al film with thickness t=0,75μm (sample 15, table2). The surface resistance of such film was decreased up to $R_s$ =6 Ω/ . The transmission of ZnO:Al film was acceptable (T= 88 %). It was shown that the surface resistance was decreased not only due to the geometric increase of film thickness, but also as a result of decreasing the resistivity (ρ) from $7{,}0\cdot10^{-4}$ Ωсм up to $4{,}2\cdot10^{-4}$ Ωсм. The decrease of electrical resistivity is stipulated by further increase of charge carriers concentration (n) from $7\cdot10^{20}$ up to $1\cdot10^{21}$ $см^{-3}$ and due to the growth of their mobility (μ) from 13 $cm^2/V\cdot s$ up to 15 $cm^2/V\cdot s$.

## 4. CONCLUSION

The optical and electrical properties of ZnO:Al films prepared by non-reactive RF magnetron sputtering without special heating of the substrate were investigated. It was shown, that the film ZnO:Al obtained at the magnetron power 130W, partial pressure of argon 4 μbar with adding of $4\cdot10^{-3}$ μbar oxygen pressure during the first minute of condensation has transmission in visible spectral range 88 % and surface resistance 6 Ω/ . The ZnO:Al films with such optical and electrical parameters are suitable for substrate configuration of thin film solar cells on $CuInSe_2$/OVC/CdS base.

## ACKNOWLEGMENT

This work has been supported by the INTAS-96-0206 Project of European Commission and 7IP 050129 Project of Swiss National Science Foundation.

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