Synthesis of Ag-Doped ZnO Nanostructured Films for UV Photodetectors

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***Abstract*— In this work, the Ag-doped ZnO nanostructured films were successfully synthesized via a simple chemical solution based method (SCS). The influence of post-growth thermal annealing, namely rapid thermal annealing (RTA) and conventional thermal annealing (TA) in electrical furnace on the UV sensing properties were investigated. The increase in UV sensing properties by doping with Ag, as well as by applying post-growth annealing was observed. The optimal Ag content was found to be ~ 0.95 wt%, while the optimal RTA regime is 725 °C for 60 s.**

***Keywords*—Ag-doped ZnO, SEM, nanostructured films, UV photodetector.**

I. Introduction

Zinc oxide (ZnO) micro- and nanostructures have been attracted a major interest for many researchers due to their unique and superior optical, chemical and physical properties [1]. A rich family of ZnO morphologies were used for a wide range of applications, including optoelectronics, photocatalysis, gas sensing, biosensing, UV photodetectors (blind to visible light), etc. [2-4].

In the case of sensing properties, the diameter of particles is the critical parameter [5,6]. It was demonstrated that sensitivity of metal oxide particles is drastically promoted when diameter (D) is comparable or less than $2L_D$, where L_D is the width of surface space-charge layer [6,7]. In this context, the doping of ZnO micro- and nanostructures with acceptor elements from group-I, especially with silver ions (Ag^{+1}) is highly efficient in order to decrease the Debye length (λ_D), i.e. L_D and respectively of sensing properties [8]:

$$L_D = \lambda_D \left(\frac{qV_S}{kT} \right)^{1/2} \quad (1)$$

Recently, Lupan *et al.* fabricated UV nanophotodetector based on individual ZnO:Ag NW with highly improved sensing properties [8].

In this work, ZnO:Ag nanostructured films were deposited on glass substrates by chemical solution synthesis (SCS) method on glass substrate. The two types of post-growth thermal annealing was used in order to tune the UV sensing properties of ZnO:Ag. Such parameters as temperature and duration of annealing were investigated in detail.

II. Experimental Part

The synthesis of ZnO:Ag nanostructured films with thickness of ~ 1.5 μm was already reported in previous works [9, 10]. The content of Ag in the studied samples is 0.5 wt%, 0.95 wt% and 1.3 wt%. These contents were achieved by adding 1.8 mM, 5.3 mM and 12.3 mM of silver nitrate ($AgNO_3$) to complex solution, respectively. The content of Ag was measured using energy-dispersive X-ray spectroscopy (EDX), in combination with SEM. After growth of films, the RTA and TA were applied at different temperatures and durations. In the case of RTA, the 475, 575 and 725 °C temperatures were applied for 30, 60 and 120 s, while for TA the 400, 500 and 650 °C were applied.

The UV sensing properties of ZnO:Ag nanostructured films were performed as was reported previously [8]. The intensity of UV light (λ = 365 nm) was set to 10 mW/cm^2. The UV response (S) was defined as ratio of current under UV illumination (I_{UV}) and current in the dark (I_{dark}), i.e. $S = I_{UV}/I_{dark}$. The structure of photodetector based on ZnO nanostructured films was reported previously [11].

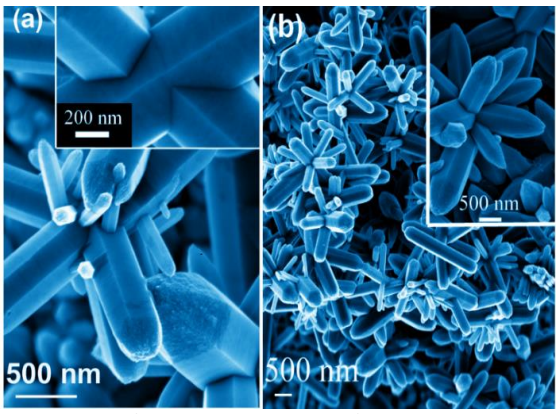

Fig. 1. SEM images of ZnO:Ag nanostructured films with 0.95wt%Ag: (a) as-grown. In inset is presented the penetration of the crystals; (b) after RTA at 650 °C for 30 s. In inset is presented SEM image of the sample with 1.3 wt% Ag treated at the same temperature and during the same time.

III. Results and Discussions

Figure 1 shows the SEM images of Ag-doped ZnO nanostructured films. The samples are composed of grains that grown directly on the glass substrate with different diameters (250 – 450 nm, not shown), on top of this layer were growth different forms of chaotic interpenetrated crystals with the hexagonal configuration and different sizes (see Fig. 1). Similar crystals of ZnO:Sn were reported by Chow *et al.* [12], but in current case shape of microcrystals are well-defined with clear grains. In Fig. 1a is presented as-grown sample of ZnO:Ag nanostructured film with 0.95 wt% Ag content, while in inset is demonstrated the penetration of the crystals. For samples subjected to RTA at 650 °C for 30 s and with the same content of Ag it can be observed that diameter of crystals was decreased in size after treatment (Fig. 1b). For comparison, in inset is presented the sample with 1.3 wt% Ag, where crystals are bigger in size, and it can be concluded that diameter of crystallites are decrease after RTA in air, and with increase in Ag content the crystallites are increased in diameter.

Figure 2a shows the current – voltage characteristic of ZnO:Ag nanostructured films with 0.95 wt% Ag treated RTA at different temperatures during 60 s. The measurements were performed at room temperature using two-probe station connected to Keithley 2400 SourceMeter [13]. All samples showed linear behavior, i.e. formation of Ohmic contacts. It can be observed that electrical resistivity of the ZnO:Ag nanostructured films is increasing by rise in RTA temperature. Increasing in the electrical resistivity of ZnO:Ag nanostructured films by the rise in RTA temperature can be attributed to the decrease in the Zn interstitials by Zn evaporation [14], which decreases the carrier concentration.

Figure 2b shows the current – voltage characteristic of ZnO:Ag nanostructured film with 0.95 wt% Ag and treated RTA at 575 °C. The measurements were performed in the dark and under UV illumination. As can be observed, the difference in current value in the dark and under UV illumination is relatively high, which is very suitable for UV photodetectors.

Figure 3a shows the UV response of ZnO:Ag samples versus content of Ag and temperature of RTA (during 60 s). It can be observed that optimal Ag content for all temperatures of RTA is 0.95 wt%, even for as-grown films. For example, in the case of samples treated RTA at 725 °C the UV response for 0.0, 0.5, 0.95 and 1.3 wt% Ag is 5.4, 29, 184 and 40, respectively. Also, it can be observed that the highest response demonstrated sample treated at highest temperature, i.e. RTA at 725 °C. The UV response for samples with 0.95 wt% treated as-grown, RTA at 475, 575 and 725 °C is 6.3, 50, 124 and 184, respectively. Thus, it can be concluded that optimal content of Ag is 0.95 wt% and 725 °C for RTA. Figure 3b shows the dependence of UV response on time of RTA treatment for ZnO:Ag nanostructured samples with 1.3 wt%, i.e. 30, 60 and 120 s, showing that optimal duration of RTA is 60 s, in order to obtain the highest UV response (UV response of 13.2). In the case of TA treatment for ZnO:Ag samples with 0.95 wt% Ag, the optimal annealing temperature is 450 °C (see Fig. 3c). The UV response for 400, 450, 500 and 650 °C is 34, 45, 8.7 and 6.3, respectively.

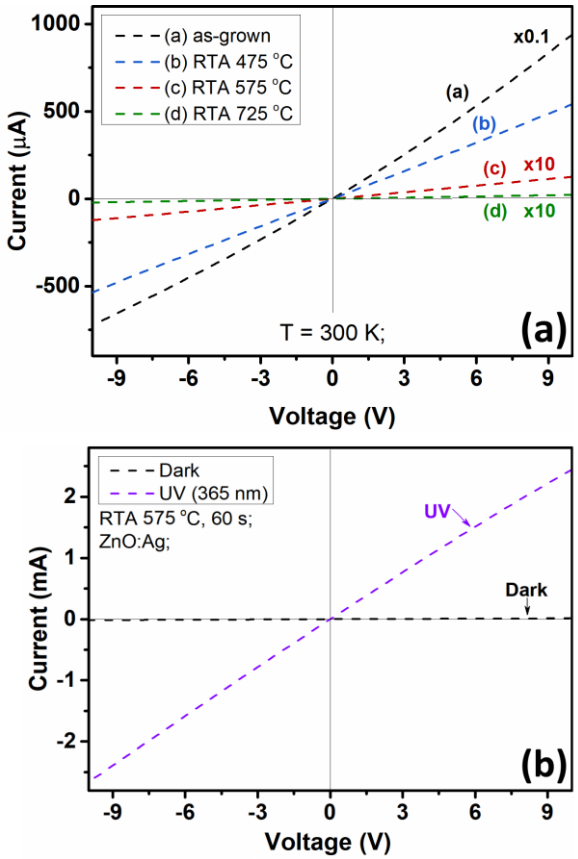

Fig. 2. (a) The current-voltage characteristics of UV photodetectors based on Ag-doped ZnO (0.95 wt% Ag) nanostructured films treated RTA at different temperatures for 60 s. (b) The current-voltage characteristics at room temperature in the dark and under UV illumination, sample was treated RTA at 575 °C during 60 s.

The highest UV response for samples with 0.95 wt% Ag can be explained based on higher electrical resistivity, i.e. lower dark current value (I_{dark}). Even for Fe-doped ZnO nanostructured films was demonstrated that lower I_{dark} leads to higher UV response [15]. A lower value of I_{dark} can be found for specimens with weaker crystallinity and higher concentration of defects which lead to a larger amount of adsorbed oxygen molecules onto the nanocrystallites surface, and as a result to a higher UV response [16]. In our case, the increase in resistivity by rise in Ag content up to 0.95 wt% can be explained based on substitution of Ag^{1+} ions at the Zn^{2+} sites, which could act as acceptors [17]. By further increase in Ag content, more Ag^{1+} ions occupy the Zn^{2+} sites, and more acceptors are formed [17]:

$$Ag_2O \rightarrow 2Ag'_{Zn} + V_O^{\bullet\bullet} + 2ZnO \qquad (2)$$

The detailed UV sensing mechanism of individual Ag-doped ZnO nanowire was reported in previous work [8]. The enhanced UV sensing properties after doping with Ag was explained on increased surface electron depletion layer due to acceptor effect of silver ions [8].

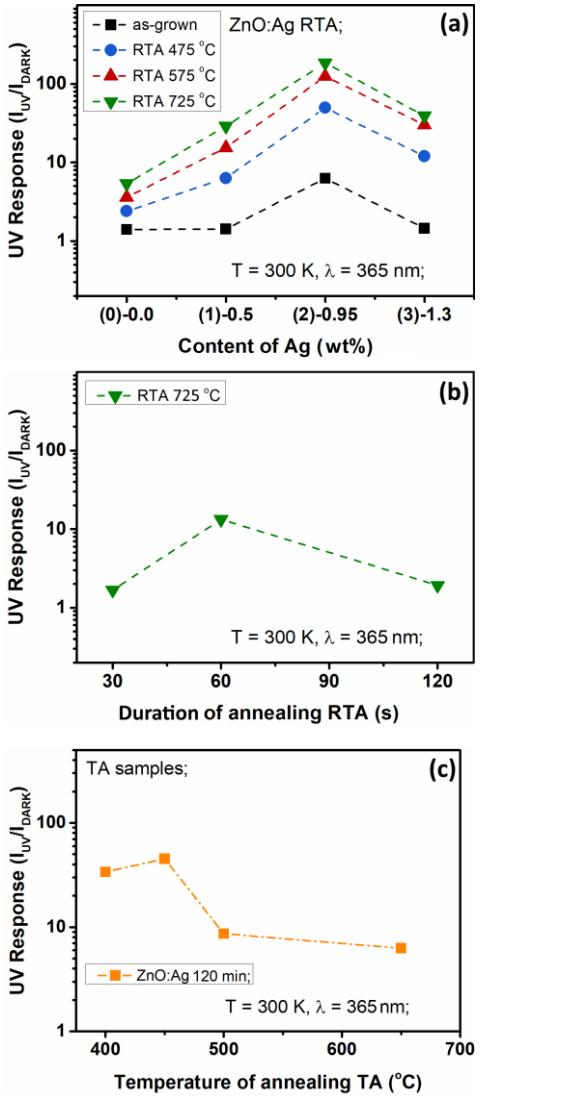

Fig. 3. (a) The dependence of UV response on content of Ag in ZnO:Ag nanostructured films and temperature of RTA treatment. (b) The dependence of UV response on duration of RTA treatment at 725 °C for ZnO:Ag samples with 1.3 wt% Ag. (c) The dependence of UV response on temperature of TA annealing during 2h (samples with 0.95 wt% Ag).

The dynamic UV response of undoped ZnO and Ag-doped ZnO (0.95 wt% Ag) nanostructured films treated RTA at 575 °C during 60 s is presented in Figure 4a and 4b for comparison reasons. It is obviously that by doping with Ag the response and recovery times of photodetectors was highly improved. The multiple pulses of UV light were applied in order to check the repeatability. As can be observed, due to incomplete recovery of current after switching off the UV light source, the poor repeatability for undoped ZnO nanostructured films is obtained. In the case of Ag-doped ZnO samples the recovery of current is faster, which leads to better repeatability. However, in the case of doped samples the recovery to initial electrical baseline is complete (see Fig. 4b,c). In order to compare the response and recovery times, the bi-exponential fitting of rising and decaying photocurrent was performed [18]:

$$I(t) = I_{dark} + A_1\left(1 - e^{-\frac{t}{\tau_{r1}}}\right) + A_2\left(1 - e^{-\frac{t}{\tau_{r2}}}\right) \quad (3)$$

$$I(t) = I_{dark} + A_3 e^{-\frac{t}{\tau_{d1}}} + A_4 e^{-\frac{t}{\tau_{d2}}} \quad (4)$$

where A_1 , A_2, A_3 and A_4 are positive constants, τ_{r1} , τ_{r2} and τ_{d1}, τ_{d2} are time constants for rising and decaying photocurrent, respectively [18]. On the basis of the curve fittings, the rise time constants for ZnO nanostructured films were τ_{r1} = 12 s and τ_{r2} = 138 s, and decay time was τ_{d1} = 15.5 s and τ_{d1} = 226 s. In the case of Ag-doped ZnO nanostructured films the rise time constants were τ_{r1} = 9.3 s and τ_{r2} = 97 s, and decay time was τ_{d1} = 8.6 s and τ_{d1} = 103 s. It can be clearly observed that the slow component of decaying photocurrent (i.e. τ_{d1}) was considerably reduced from 226 s for ZnO to 103 s for ZnO:Ag nanostructured films. The other time constants of rising and decaying photocurrent were also reduced by doping with Ag.

The increase in UV sensing properties for ZnO micro- and nanostructures by modifying with Ag was also observed by Lin *et al.*, showing that optimal content of Ag nanoparticles is 7.5 at.% [19]. Rajan et al. also reported on enhanced response of Ag-doped ZnO thin films synthesized by sol-gel method [20].

The fabricated UV photodetectors based on ZnO:Ag nanostructured films were also tested to white light. However, no response was observed (not shown), demonstrating that fabricated photodetectors are visible-blind and can selectively detect the UV light with λ = 365 nm. UV radiation has been regarded by many as an important component of the solar radiation since its discovery by Johann Ritter in 1801. Thus, the detection of UV light is very important for such applications like advanced communications, flame detection, air purification, ozone sensing and leak detection [8].

IV. Conclusions

In this work, the Ag-doped ZnO nanostructured films with thickness of ~ 1.5 µm were successfully deposited on glass substrates via a simple chemical solution based method (SCS) at relatively low temperatures (> 95 °). SEM images showed that films are composed of partially interconnected grains with diameter of 250 – 450 nm. The influence of post-growth thermal annealing on the room temperature UV sensing properties of ZnO:Ag nanostructured films was investigated. It was demonstrated that rise in Ag content up to 0.95 wt% can lead to increase in the UV sensing properties, as well as by applying RTA annealing at 725 °C for 60 s.

Acknowledgements

This research was in part supported by the Project Institutional (Project No. 45inst-15.817.02.29A) funded by the Government of the Republic of Moldova. Author would like to express sincere gratitude to prof. univ., dr. hab. Lupan Oleg, Ph.D. Thesis supervisor, for support and guidance during PhD studies at the Technical University of Moldova and Professor Dr. Adelung Rainer from Kiel University for his kind support.

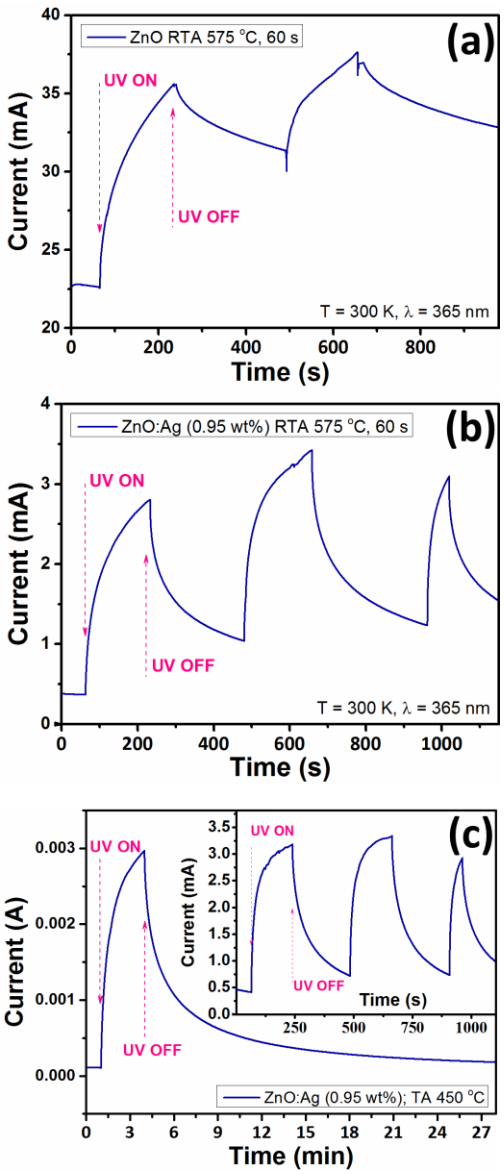

Fig. 4. The dynamic UV response: (a) of ZnO sample treated RTA at 575 °C during 60 s; (b) of ZnO:Ag (0.95 wt%) treated RTA at 575 °C during 60 s; (c) of ZnO:Ag (0.95 wt%) treated TA at 450 °C during 2 h. In inset is presented the dynamic UV response to multiple pulses of UV light.

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