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STRUCTURAL AND OPTICAL PROPERTIES OF ZnO:Ga THIN FILMS DEPOSITED ON ITO/GLASS SUBSTRATES FOR OPTOELECTRONIC APPLICATIONS

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Abstract

Doped (with $GaCl_3$), undoped ZnO and ITO/ZnO:Ga nanostructured thin films are synthesized using the spray pyrolysis method. The doped ZnO thin films are synthesized at the atomic ratio of Ga/Zn added in the starting solution fixed at 1, 2, 3, and 5. Gallium-doped ZnO films synthesized on glass/ITO substrates are annealed at 450°C in different environments: vacuum, oxygen, and hydrogen. X-ray diffraction (XRD), Energy-dispersive X-ray spectroscopy (EDX), atomic force microscopy (AFM), and current–voltage (I–V) measurements are applied to characterize the structural properties, composition, surface morphology, and electrical properties of ZnO:Ga nanostructured thin films. X-ray diffraction analysis shows that ZnO:Ga films deposited on glass substrates have a dense and homogeneous surface with a hexagonal structure. The ZnO:Ga films deposited on glass/ITO substrates are composed of two phases, namely, hexagonal ZnO and cubic ITO. The I–V characteristics show the presence of good ohmic contacts between Al and In metals and ZnO:Ga thin films regardless of the nature of the substrate and the annealing atmosphere.

Keywords: zinc oxide, gallium, annealing, structural properties, film morphology.

Rezumat

Au fost sintetizate straturi subțiri nanostructurate ZnO atât dopate cu ($GaCl_3$), cât și nedopate, precum și straturi de ITO/ZnO:Ga, folosind metoda prin pulverizare cu piroliză. Straturile subțiri de ZnO dopate au fost sintetizate la raportul atomic Ga/Zn adăugat în soluția inițială fixă la 1, 2, 3 și 5 Straturile nanostructurate de ZnO dopate cu Ga obținute pe substraturi de sticlă/ITO au fost tratate termic la 450℃ în diferite medii: vid, oxigen și hidrogen. S-au realizat măsurătorile de difracție cu raze X (XRD), spectroscopie cu raze X cu dispersie energetică (EDX), microscopie cu forță atomică (AFM), curent-tensiune (I-V) pentru a caracteriza proprietățile structurale, compoziția, morfologia suprafeței și proprietățile electrice ale straturilor subțiri de ZnO:Ga. Analiza XRD arată că stratul de ZnO:Ga depus pe substratul de sticlă are o suprafață densă și omogenă cu structura hexagonală. Stratul de ZnO:Ga depus pe substraturi de sticlă/ITO indică două faze, acestea fiind ZnO hexagonal și ITO cubic.

Caracteristica I-V prezintă contacte ohmice bune între metalele Al, In și straturile subțiri de ZnO:Ga, indiferent de natura substratului și de atmosfera de tratare termică.

Cuvinte-cheie: oxid de zinc, galiu, tratare termică, proprietăți structurale, morfologia straturilor subțiri.

1. Introduction

Zinc oxide has attracted great attention due to its versatile nature. Zinc oxide has a hexagonal wurtzite structure (*P63mc*) with lattice constants of a = 3.252 Å and c = 5.313 Å [1]. Zinc oxide is a wide bandgap semiconductor (3.37 eV at room temperature) that can be used in numerous applications, such as solar cells [2], flat displays, heat mirrors, thin-film transistors, and chemical sensors [3]. In particular, it is a promising alternative to indium tin oxide (ITO) in transparent conducting oxide applications due to its low cost, non-toxicity, and stability under hydrogen plasma [4, 5]. Zinc oxide thin films were synthesized by a wide variety of techniques, in particular, by chemical and physical routes, such as pulsed laser deposition [6], thermal evaporation [7], chemical vapor deposition [8, 9], electron beam evaporation [10], spray pyrolysis [11], sol–gel method [12], and magnetron sputtering on a variety of substrates [11]. The spray pyrolysis technique is one of these techniques to prepare large-scale production for technological applications. Recently, gallium (Ga) has engrossed great interest as a dopant due to enhanced structural, optical, electrical, and magnetic properties upon incorporation into a ZnO material. Gomez et al. [12] prepared gallium-doped zinc oxide (Ga:ZnO) thin films on glass substrates by the spray pyrolysis technique and found that ZnO:Ga exhibits the *n*-type conductivity with an electrical resistivity on the order of 8×10^{-3} Ω cm and an optical transmittance higher than 80% in the visible region. These results make chemically sprayed Ga:ZnO potentially applicable as transparent electrode in photovoltaic devices. According to Ramakrishna Reddy et el. [13], for higher [Ga]/[Zn] rates in solution, the Ga ions do not occupy more zinc sites, and a segregation of Ga in an oxide form takes place in the grain boundaries or interstices, which causes a decrease in the mobility and a consequent increase in the electrical resistivity. For low [Ga]/[Zn] ratios, the decrease in resistivity is attributed to an increase in the number of Ga atoms incorporated into the ZnO lattice in the Zn sites supplying one electron to the conduction band for each Ga atom until the maximum solubility of Ga into the ZnO lattice (minimum resistivity value) is reached [13]. Recently, many studies have been focused on the improvement of photoactivity by combining with other semiconductors, such as WO_3, ZnO, SnO_2, CdS, CuO, and Fe_2O_3 [14, 15]. In this study, bilayer ZnO films were grown under the same conditions on ITO layers with the same crystal structure. After deposition, the Ga-doped ZnO films were annealed in different environments: oxygen (O_2), hydrogen (H_2), and vacuum. To the best of the authors' knowledge, a similar study has not been carried out. The aim of this study is to optimize the preparation of Ga-doped ZnO deposited on ITO/glass substrate to explore their optoelectronic properties.

2. Experimental

Zinc oxide nanostructured thin films were synthesized using the spray pyrolysis method. Doped and undoped ZnO thin films were synthesized. The initial solution was prepared by dissolving zinc acetate [$Zn(CH_3COO)_2 \cdot 2(H_2O)$] in a methanol–water solution in a ratio of 25 : 65

to obtain a concentration of 0.2 M. The solution was stirred at 50°C for 1 h. In addition, to prevent the aggregation process, a few drops of concentrated acetic acid were added to the starting solution. For doping of ZnO thin films, gallium trichloride ($GaCl_3$) was used. Glass substrates were treated ultrasonically in soapy water, acetone, ethanol, and finally in distilled water for 60 min and then dried at ~110°C for ~20 min in a hydrogen atmosphere after cleaning. The solution was sprayed at a flow rate of 12 mL/min onto cleaned soda-lime glass substrates and onto ITO substrates. Argon gas at a flow rate of 10 mL/min was used as the carrier gas. The substrate temperature was 450°C. The ZnO thin films were synthesized at an atomic ratio of Ga/Zn added in the starting solution fixed at 1, 2, 3, and 5. The vacuum thermal annealing of Ga-doped ZnO thin films deposited on a commercial ITO/glass substrate was performed at 450°C for 90 min in different environments, namely, vacuum, oxygen, and hydrogen. The structural properties of nanostructured thin films were characterized by X-ray diffraction measurements. Atomic force microscopy (AFM) experiments were performed using a Digital Instruments Dimension 3100 AFM instrument (Veeco Company) equipped with a Nanoscope IV controller. Standard silicon cantilevers with a spring constant between 4.0–4.4 mN were used in the tapping mode. Current–voltage characteristics of the device were measured using a Keithley 2400 power supply under dark conditions.

3. Results and Discussion

The XRD studies of Ga-doped ZnO thin films deposited on a glass substrate (not shown here) at the Ga/Zn fixed atomic ratio of 1, 2, 3, and 5 revealed a polycrystalline nature with the (0002) plane as the dominant orientation. The XRD studies of Ga-doped ZnO thin films suggest that all the characteristic peaks correspond to zinc oxide. The crystal-lattice parameters were determined on the basis of the most intensive (0002) crystallographic plane. The structural parameters are listed in Table 1. With a decrease in Ga concentration, the intensity of the preferred (0002) plane decreases disorderly. The highest intensity of the preferred (0002) diffraction plane is revealed for 5% Ga. In addition, it is observed that the full width at half maximum (FWHM) of the peak corresponding to the (0002) diffraction varied only slightly with an increase in the Ga doping concentration from 1 to 5 at %. The mean grain size values obtained from the Scherrer formula applied on the (0002) XRD peak of Ga-doped ZnO thin films are shown in Fig. 1. The grain sizes reached about 29.0 nm.

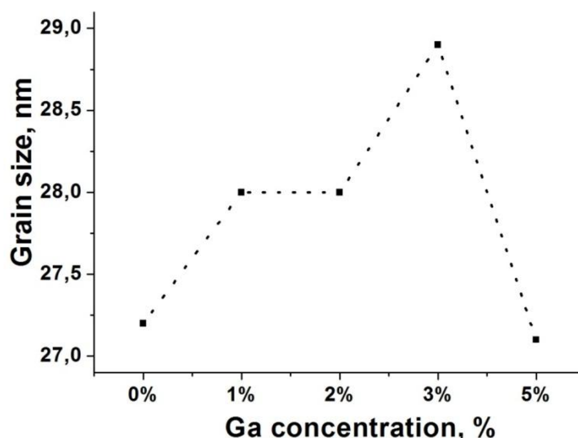

Fig. 1. Mean grain size value obtained from the Scherrer formula applied on the (0002) XRD peak of Ga-doped ZnO thin films.

The grain size of the 5%Ga-doped sample is found to be lower than that of the other doped samples, because the strain is inversely related to the grain size. According to Table 1, the internal strain values of the Ga-doped ZnO thin films do not change with an increase in the Ga concentration to 5%. The higher strain value of the 5%Ga-doped ZnO film shows that the crystallinity of the films is deteriorated. The peak broadening is a result of micro strains that appear due to the displaced atoms that are rearranged relative to their referenced lattice-points and due to the lattice defects occurring in the Ga-doped ZnO thin films. Probably, with an increase in the Ga concentration in the films, a contraction and decrease in the ZnO unit cell volume take place.

Table 1. Structural parameters of Ga-doped ZnO thin films

Samples	**Gallium concentration , %**	**2θ (deg)**	***d*, Å**	**FWHM, rad**	**ε (lattice strain) $\times 10^{-3}$**
as-deposited ZnO	0	34.47	2.6010	0.0052	4.2
Gallium-doped ZnO thin films synthesized in an Ar atmosphere	1	34.51	2.5981	0.0054	4.3
	2	34.49	2.5996	0.0052	4.2
	3	34.50	2.5988	0.0052	4.2
	5	34.48	2.6003	0.0055	4.5

Energy-dispersive X-ray spectroscopy (EDX) measurements were performed to study the elemental composition of the Ga-doped ZnO thin films. The compositional analysis of the ZnO thin films doped with 5% Ga that were synthesized in an Ar atmosphere is shown in Fig. 2. Table 2 lists the weight and atomic percent compositions (wt % and at %) of the components of ZnO thin films. The respective patterns confirm that the average atomic percentage of Zn and oxygen deviates from the stoichiometry. The elemental analysis also proved the presence of the Ga dopant in the structure of the 5%Ga-doped ZnO thin film. Some impurities (Si, Ca) are found in the spectra; they originated from the glass substrate [16]. The presence of the Ga dopant is available for all the ZnO thin films, except for that doped with 1%.

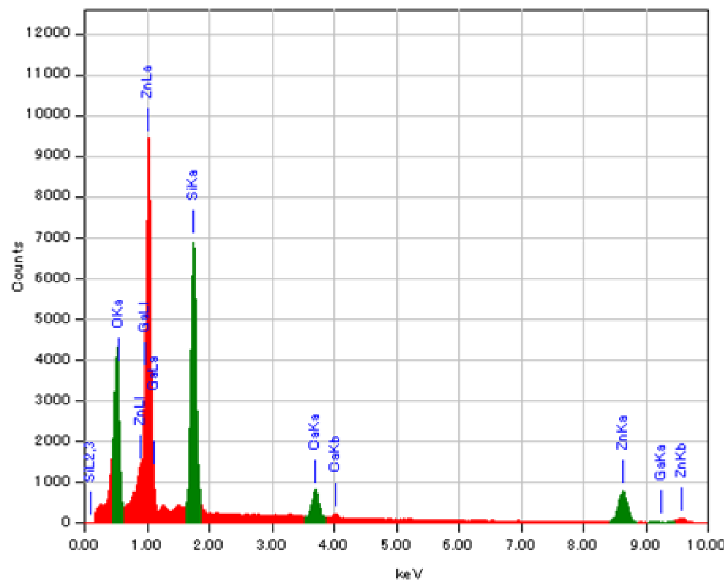

Fig. 2. Energy-dispersive X-ray spectra of the 5%Ga-doped ZnO thin film.

Table 2. Weight and atomic percent compositions (wt % and at %) of the 5% Ga-doped ZnO thin film

Element	Weight %	Atomic %
O K	23.73	47.18
Si K	22.37	25.34
Ca K	4.05	3.22
Zn K	49.85	24.26
Ga K	0.16	0.08
Total	100.00	100.00

As described in the Introduction of this paper, ZnO is considered to be an *n*-type semiconductor, where the most of the defects are zinc interstitials (Zn_i) and oxygen vacancy (V_O). Excess zinc and oxygen deficiency in the synthesized ZnO thin films that were observed in this study can possibly be assigned to Zn_i in ZnO thin films.

Figure 3 shows XRD patterns of the ZnO thin films with a 3% Ga doping concentration that are deposited on commercial ITO/glass substrates, glass substrates, and commercial ITO deposited on a glass substrate. According to Fig.3, the XRD pattern of the ITO thin film revealed a polycrystalline nature with the preferred (400) plane. Other ITO peaks are observed at 2θ of 21.27°, 30.26°, 45.25°, 47.39°, 48.21°, 50.68°, 55.61°, and 60.25°. The ITO thin film crystallizes in a cubic structure. For the Ga-doped ZnO thin film deposited on a glass substrate, the most intense maximum is revealed at 2θ ≈ 35.2° with regard to the (0002) plane. The d_{hkl} value of 2.6129 Å for Ga-doped ZnO thin films deposited on a glass substrate is higher than that of a standard ZnO powder (2.603 Å); this fact suggests that the crystalline plane distance of the Ga-doped ZnO film lengthens due to imperfections, such as lattice strains and interstitial defects. The crystal structures of the Ga-doped ZnO thin films deposited on commercial ITO/glass substrates are similar to each other and revealed weak diffraction maxima at 2θ = 47.39° and 62.71° for all the films deposited on ITO substrates, regardless of the annealing environment type, corresponding to the (1002) and (1003) diffraction planes. The XRD results revealed the polycrystalline nature of the films with a hexagonal wurtzite structure. The XRD peaks of the Ga-doped ZnO thin films deposited on commercial ITO/glass substrates are shifted toward the larger θ values; this shift leads to a decrease in the lattice parameter: $c = 5.1345$ Å compared with $c = 5.2331$ Å in the case of deposition on glass substrates. This decrease is directly related to the incorporation of Ga^{3+} ions in the Zn^{2+} substitutional sites. Then, the incorporation of the dopant into the ZnO matrix leads to a network contraction.

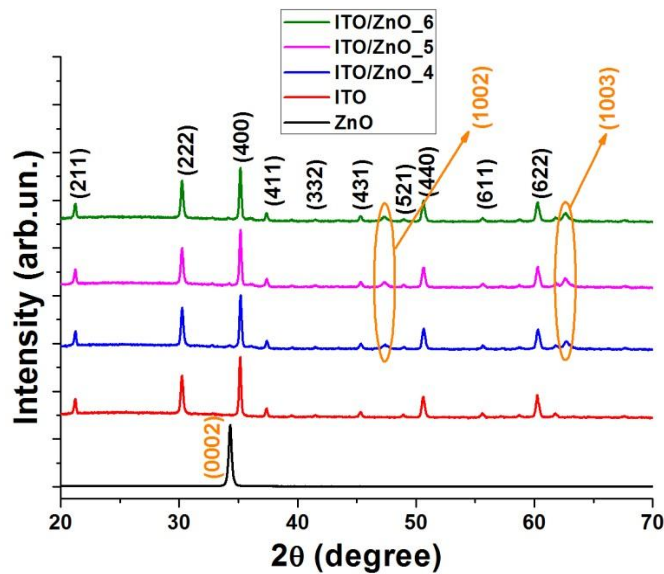

Fig. 3. X-ray diffraction patterns of the 3% Ga-doped ZnO thin films deposited on a commercial ITO/glass substrate annealed in different environments ((*4*) O_2, (*5*) H_2, (*6*) vacuum), 3% Ga-doped ZnO deposited on a glass substrate, and commercial ITO on a glass substrate.

The shift of Bragg's angles is attributed to changes in the interplanar spacing upon deposition on an ITO/glass substrate. The strain value for the 3% Ga-doped ZnO thin films deposited on a commercial ITO/glass substrate annealed in an oxygen atmosphere reached 5.4×10^{-3}. The lowest strain value (3.1×10^{-3}) was obtained for the Ga-doped ZnO thin films deposited on a commercial ITO/glass substrate annealed in a vacuum. The defects, impurities, and lattice strain lead to the presence of an intrinsic stress, whereas lattice mismatch and the thermal expansion coefficient mismatch give way to an extrinsic stress, which is developed between the film and the substrate [17].

The AFM images from Fig. 4 (left) show a columnar nanostructure and the occurrence of grain growth along the *c* axis, which is in good agreement with XRD analysis. It is observed that the grains grow uniformly with a homogenous distribution. The evolution feature can be more easily observed from the respective surface profiles of these films. The root mean square (RMS) roughness profiles of AFM images are compared in Fig. 4 (right). They indicate the formation of prominent wrinkles on the film surface. The height distribution over the surface of the Ga-doped ZnO thin films deposited on a commercial ITO/glass substrate annealed in an O_2 and H_2 atmosphere is sharp and wider compared with that in the case of the surface annealed in a vacuum.

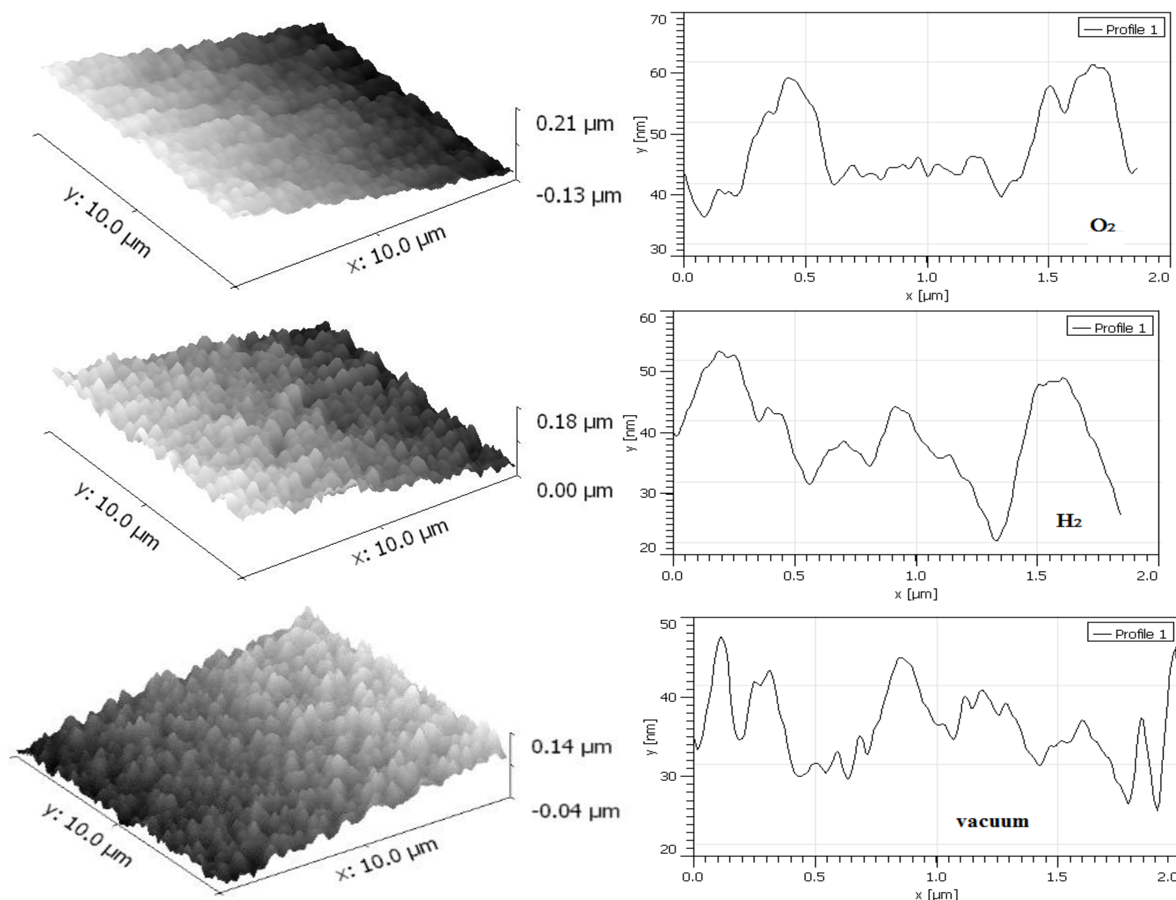

Fig. 4. Atomic force microscopy image of the 3%Ga-doped ZnO thin films deposited on a commercial ITO/glass substrate annealed in different environments and the relationship between (RMS) and profile scan.

Thus, it is evident from Fig. 4 that the interface width (RMS) values are slightly decreased for the Ga-doped ZnO thin film annealed in a vacuum.

Electrical properties play a key role in optoelectronic applications; it is well known that electrical characteristics are strongly affected by the doping content. As a result, the devices composed of glass/ITO/ZnO/metal contacts are manufactured to determine the effect of different metals on the electrical properties of the deposited ZnO thin films. Indium (In) and aluminum (Al) contacts were deposited by thermal evaporation through a mask having 2×2 mm^2 openings. Figure 5 shows the schematic representation of the fabricated glass/ITO/Ga:ZnO/Al and glass/ITO/Ga:ZnO/In samples (a) and dark current–voltage (I–V) characteristics of these devices (b).

Experimental results show good ohmic contacts between Al and In metals and ZnO thin films and the proportional increase in the current intensity to the supplied voltage for the films under both forward and reverse bias conditions. The current–voltage characteristics indicate also the increase in the slope of the I–V curves of the glass/ITO/Ga:ZnO contacts due to an increase in the Ga doping concentration in the ZnO lattice. This behavior can be attributed to the occupancy of a Ga ion on the Zn site acting as a donor, which can enhance the density of free charge carriers and the electrical conductivity of the ZnO films.

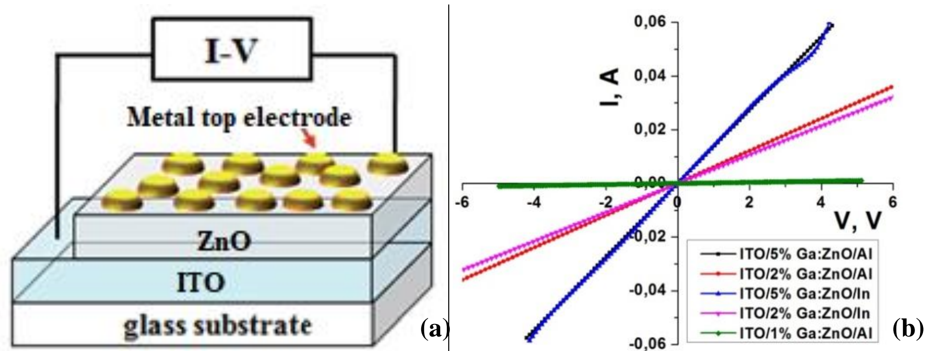

Fig. 5. Schematic representation of the fabricated glass/ITO/Ga:ZnO/Al and glass/ITO/GaZnO/In devices (a) and the dark current–voltage (I–V) characteristics of these devices (b).

The Al/ZnO and In/ZnO contacts exhibit a linear I–V variation over the voltage region ranging from −6 to 6 V, which indicates the ohmic nature of the contact. Resistivity values of the 2%Ga-doped ZnO and 5%Ga-doped ZnO thin films were determined to be 29.4 and 40.0 Ω cm, respectively. The resistivity of the 5%Ga-doped ZnO thin films is higher than that of the 2%Ga-doped films. The 1%Ga-doped film has the lowest resistivity value of all the studied films. The measured dark and illuminated I–V characteristics for the vacuum-annealed 1%Ga-doped ZnO films obtained in an Ar atmosphere are shown in Fig. 6. The wavelength of 365 nm was used for the illuminated I–V measurements. The dark current at 5 V bias voltages was 816 μA. The photocurrent under 365-nm UV light illumination was 44 mA at 5 V biases, which is obviously higher than the dark current. The UV detector operates in the photoconductive mode.

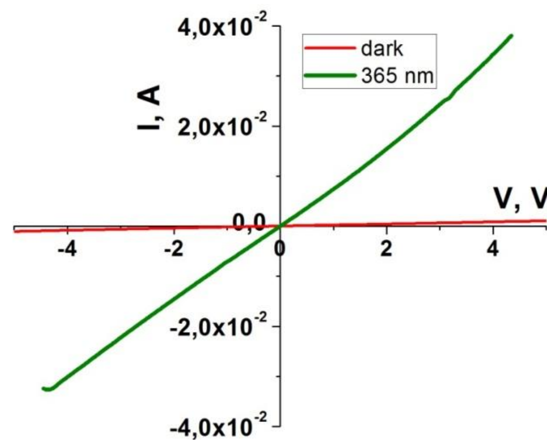

Fig. 6. Dark and illuminated I–V characteristics under 365-nm light excitation at room temperature for the vacuum-annealed ITO/Ga:ZnO/Al structure.

4. Conclusions

Nanostructured Ga-doped ZnO thin films were deposited on glass and ITO/glass substrates by spray pyrolysis in an Ar atmosphere at a substrate temperature of 450°C and then annealed at 450°C in different environments: vacuum, oxygen, and hydrogen. The key results are outlined as follows:

(1) X-ray diffraction analysis has revealed that the Ga-doped ZnO thin films have a hexagonal wurtzite phase with the preferred [0002] orientation in the case of deposition on glass substrates.

(2) X-ray diffraction analysis of Ga-doped ZnO deposited on ITO/glass substrates has shown the appearance of weak diffraction peaks corresponding to the (1002) and (1003) planes, regardless of the annealing environment type, which leads to a decrease in lattice parameter *c*.

(3) The elemental analysis has proven the presence of the Ga dopant in the structure of the 5%Ga-doped ZnO thin film. Moreover, the presence of the Ga dopant is available for all the ZnO thin films, except only for the one doped with 1%.

(4) Atomic force microscopy images of Ga-doped films deposited on ITO/glass substrates have shown a rough granular structure. The surface of the layers is affected by the nature of the annealing environment.

(5) Current–voltage characteristics have shown that the In and Al metals are good ohmic contacts for Ga-doped ZnO thin films.

(6) The UV-detection capability under 365-nm light excitation has been studied.

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