JOURNAL OF NANO- AND ELECTRONIC PHYSICS
Vol. **11** No 2, 02003(4pp) (2019)

ЖУРНАЛ НАНО- ТА ЕЛЕКТРОННОЇ ФІЗИКИ
Том **11** № 2, 02003(4cc) (2019)

Effect of Au Dopant on the Structural and Optical Properties of ZnO Thin Films Prepared by CVD

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(Received 08 January 2019; revised manuscript received 07 April 2019; published online 15 April 2019)

Thin zinc oxide films doped with Au have been synthesized by CVD technique. Increase in the dopant from 0 to 15 wt. % Au in ZnO thin films led to pronounced changes in the film morphology. It follows from the optical properties that the band gap of pure ZnO thin film is 3.28 eV, and with increasing Au dopant from 5 to 15 wt. % it does not change. X-ray diffraction has shown that the peak of the maximum intensity corresponds to the preferred orientation (101) for ZnO films at 15 wt. % Au. SEM images show that crystal growth is due to an increase in the dopant concentration. EDX analysis showed that the undoped ZnO film contains Zn and O elements, and the film doped with 15 wt. % Au in addition to the Zn and O elements contains Au and Cu elements. All diffraction peaks can be attributed to crystalline ZnO with a hexagonal structure. In addition to these peaks, two new peaks (111) and (200) appear due to gold. Study of the morphology of ZnO films indicates the presence of homogeneous grains, while when Au atoms are added, the grains are not homogeneous and have different sizes. EDX analysis for pure ZnO shows two strong peaks corresponding to Zn and O, which confirm the high purity of ZnO thin films. And in doped thin films (15 wt. % Au), the appearance of high-intensity Au element, as well as the two strong peaks corresponding to the Cu and Zn elements, and the presence of low-intensity peaks due to the Au, Cu and Zn elements, are observed.

Keywords: II-VI compounds, Transparent oxide compound, Semiconductor thin films.

DOI: 10.21272/jnep.11(2).02003 PACS numbers: 78.66.Hf, 78.66.Bz

1. INTRODUCTION

ZnO, a wurtzite compound semiconductor of the II-VI family, which has direct band gap energy of 3.37 eV at room temperature with large binding energy of 60 meV, is a remarkable material with a broad range of optical, electrical, and piezoelectric prospective applications. Due to its unique properties, it is used in making solar cells [1], optical coatings, photo catalysts, electrical devices, and as a gain medium in UV semiconductor lasers, gas sensing [2]. Also, it is a promising material for exciton-related optoelectronic applications, allowing in principle efficient excitonic lasting operation at room temperature [3]. As ZnO films exhibit preferential growth along (002) plane, which favor the piezoelectric effect, they can also be used for manufacturing surface acoustic wave transducers [4], acousto-optic and acousto-electronic devices [5]. It is used as transparent electrodes for thin-film solar cells, light emitting diodes and it is expected to be a material for blue or UV emitting devices [6]. Doping is an effective way to improve the properties of ZnO thin films. Therefore, addition of selective elements to ZnO offers an important route to enhance and control its optical and electrical properties, which is crucial to its practical applications. Some elements have been added to ZnO for improving its photoelectrochemical performance [7, 8]. The Au-coated ZnO nanostructures showed a good selectivity in biosensors and detection [9, 10] and have been applied to optoelectronic and energy harvesting devices [11, 12]. Although Au is the most inert of all metallic elements, it has interesting properties as a heterogeneous catalyst. There are a number of interesting aspects of catalysis by gold which are currently attracting academic investigation, while the observation that gold-based catalysts are active at room temperature and below is driving considerable industrial interest [9]. Different deposition techniques have been employed to deposit the ZnO thin films. Among the various methods, CVD has the advantages of low cost, easy-to-use, safe and can be implemented in a standard laboratory. Due to the simplicity of the apparatus and good productivity of this technique on a large scale, it offered a most attractive way for the formation of thin films [11]. By introducing Au particles on the ZnO surface to form Schottky junctions, the screening effect was dramatically suppressed, resulting in greatly enhanced piezoelectric conversion efficiency. Reduction of the screening effect was confirmed by the lowered Fermi level of the Au@ZnO (ZnO nanoarrays decorated with Au nanoparticles (Au@ZnO NAs) were synthesized) NAs (nanoarray based), the increased internal resistance, and RC time constant in the Au@ZnO NA-based PNG (piezoelectric nanogenerator). In addition, a smaller capacitance value was obtained for the Au@ZnO.

NA based PNG is also responsible for the enhanced output after Au-particle modification. These results represent a simple and effective method to optimize the performance of PNGs, which could be applied to piezotronics and piezophototronics [12].

So this encouraged us to study how the presence of Au affects the structure of ZnO and also affects the optical properties, as well as with using 5 %, 10 % and 15 % as maximum percentage. It follows from the results that the diffusion of Au atoms through different directions was non-isotropic.

2. EXPERIMENTAL METHOD

Pure and ZnO:Au thin films have been deposited on cleaned glass substrates by CVD using zinc acetate $Zn(CH_3COO)2{\cdot}2H2O$ (99.99 % pure) and gold chloride

acid (Sinopharm Reagent Co). Glass substrates were first rinsed in ethanol for 5 min. Then they were rinsed thoroughly in distilled water and dried in acetone just before they were loaded into the system for film deposition. After preparing the substrates, they were placed and adjusted in the deposition unit while the temperature adjusted to 500 °C in order to ensure optimum film properties. The pressurized air flow was also adjusted to the best flow rate, which was found to be 0.5 L/min to produce the best samples. The deposition time was kept constant at 10 minutes for both the pure and doped samples in order to determine the combination of optimal duration with temperature that produces the best results of zinc oxide deposition, and the samples were left afterwards to cool. The deposition temperature was kept constant at 500 °C for all the samples. The temperature was controlled with an electronic temperature controller. The films were investigated by using field-emission scanning electron microscopy (FESEM, HITACHI S7900, Japan), energy dispersive X-ray spectrometer (EDS, HORIBA EMAX Energy EX-950, Japan) and X-ray diffraction (XRD, Bruker/D8-advance with Cu Kα radiation ($\lambda = 1.54178$ Å), Germany). The UV-Vis Systronics-119 spectrophotometer was used for investigation of the optical properties from 300 to 800 nm.

3. RESULTS AND DISCUSSION

Fig. 1 shows the optical transmittance spectra of ZnO:Au thin films in the wavelength range between 300 and 800 nm. The transparency properties of all thin films are more than 95 % at a visible wavelength of 400-800 nm. For Au doped ZnO, the surface absorption of gold in the visible light overlaps with the tail of ZnO film. So, the doped material absorbs light strongly in the visible region [14] compared to pure ZnO. The optical transmittance of the doped ZnO films was measured by using a UV-vis spectrophotometer, as shown in Fig. 1. It is observed that the transmittance has a tendency to decrease with Au doping. Reduction in the transmittance percentage is due to the progression of Au in the thin film that enlarges the particle size, and it slightly contributes to this phenomenon. And the reason to observe such low transmittance is not only due to high Au concentration, the thin film quality plays a major role because of light scattering by grain boundaries.

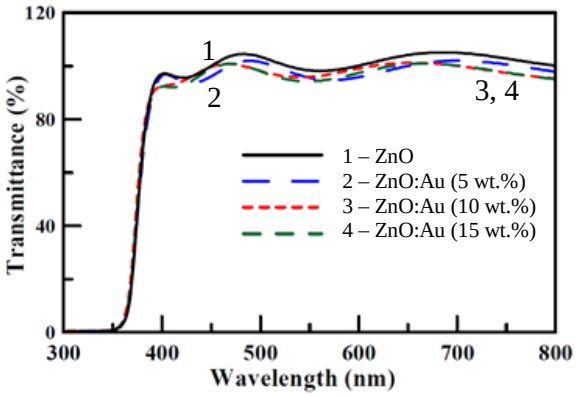

Fig. 1 – Optical transmittance spectra of ZnO:Au films with 5, 10, and 15 wt. % Au

The relation between absorption coefficient (α) and photon energy for direct transitions is given by [15]:

$$\alpha h\nu = A(h\nu - Eg)^{1/2},$$

where h is the Plank constant, ν is the frequency of the incident photon, A is a constant depending on the electron-hole mobility and Eg is the optical band gap energy. Fig. 2 shows the measured optical band gap energy versus Au doped and it also shows a blue shift in the thin film. By extrapolating the linear part of the curve that intersects the x axis, it will give the optical band gap energy value. For pure ZnO thin film, the optical bandgap energy was estimated as 3.28 eV and this value is a little bit smaller than the band gap value of 3.34 eV for bulk ZnO as reported in the literature [16, 17]. With an increment in the Au content to 5 wt. %, the band gap obtained increases to 3.35 eV. This was followed by 3.37 and 3.36 eV for 10 and 15 wt. % of Au content, respectively. An increase in the Eg for Au/ZnO films indicates an increase in free charge carriers within the films, as explained by the Burstein-Moss effect [18-21]. Moreover, the increase in the Eg with increasing Au concentration is also due to the fact that Au ions tend to occupy ZnO lattice planes, which leads to an increase in the number of transport paths of charge carriers into ZnO lattice. A band gap narrowing was observed from 5-15 wt. % Au doped films that is seen in Fig. 2. This narrowing is not expected according to the reasons mentioned above or for larger grain sizes. A detailed investigation is needed to explain this observed property [22].

Fig. 3 shows the XRD patterns of pure and Au-doped ZnO films, which demonstrate that all the ZnO films are crystallized in the wurtzite structure.

Fig. 3a shows the XRD pattern of pure ZnO films recorded in the range of 30-100°. All diffraction peaks (100), (002), (101), (102), (110), (103) and (112) can be attributed to crystalline ZnO with a hexagonal structure.

The data are in agreement with the Joint Committee on Powder Diffraction Standards (JCPDS) card for

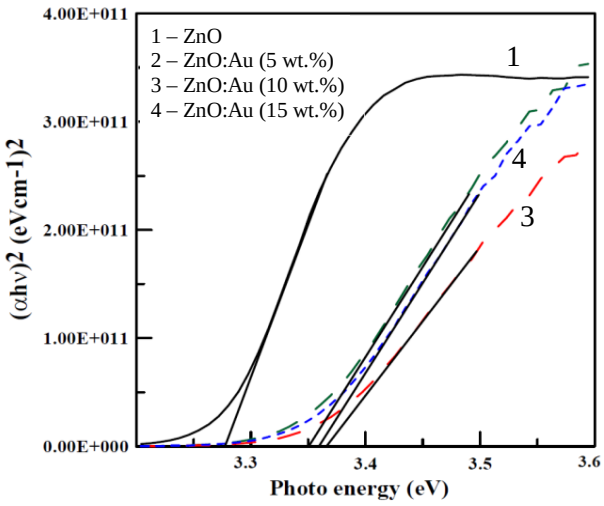

Fig. 2 – Dependence of the optical band gap versus the photon energy of ZnO (pure and doped with 5, 10, 15 wt. % Au)

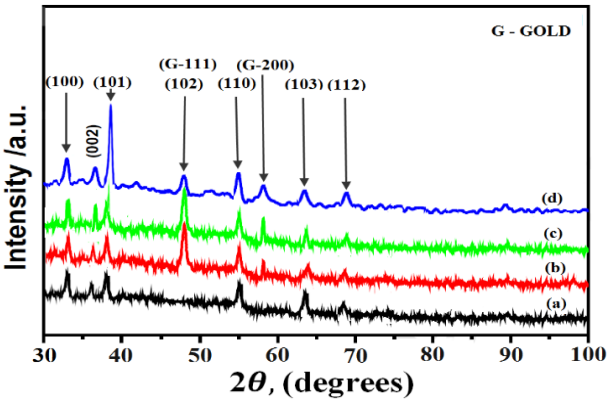

Fig. 3 – XRD patterns of ZnO:Au with various concentrations: 0 (a), 5 (b), 10 (c), and 15 (d) wt. % Au

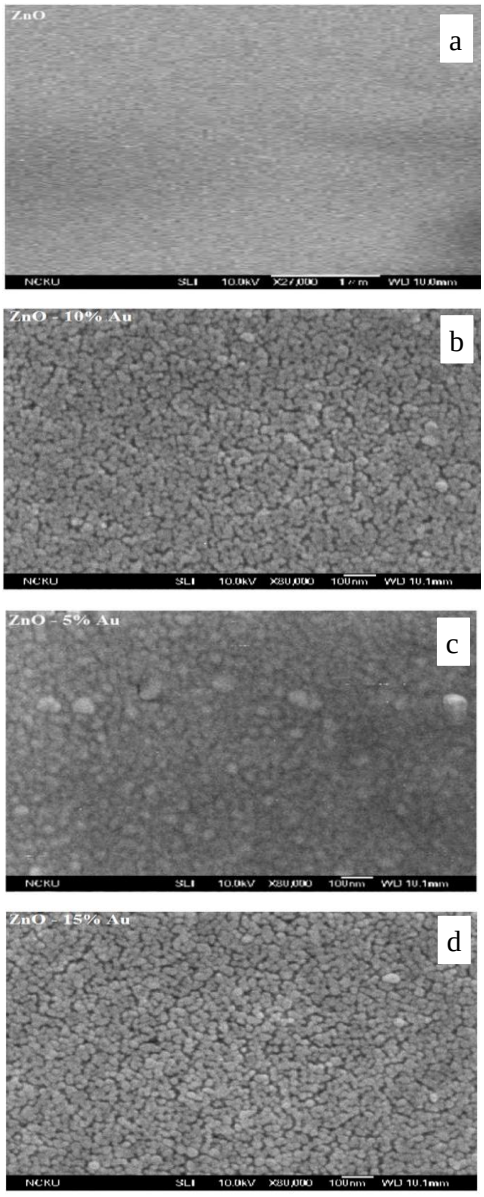

Fig. 4 – SEM of ZnO films: pure (a) and doped with 5 (b), 10 (c), and 15 (d) wt. % Au

ZnO (JCPDS 036-1451) [23]. It is shown in Fig. 3b, c that appearance of another peak in the plane (102) with high intensity is due to ZnO films in addition to the other peaks, and appeared two new peaks (111) and (200) are due to the gold.

Fig. 3d shows that improvement in the crystallinity and increase in intensity of (101) plane are expected due to an increase in diffusion of Au atoms in this direction and decrease in intensity of (102) plane is due to ZnO films and of (111) and (200) planes – is due to gold, respectively, by increase in Au doping with 15 wt. % due to the increasing gold content.

To examine the surface morphology, SEM has been used. Typical SEM images of the pure and doped ZnO films are shown in Fig. 4. The overall morphology of the pure ZnO films on the substrate is presented in Fig.4, which shows the presence of homogeneous grains and well covers the glass substrate. Whereas the films doped with 5 wt. % Au show the presence of simple distortions in the pattern and the grains are non-homogeneous having different sizes. We observed the sample doped with 10 wt. % Au that shows more homogeneous structure than that from the films doped with 5 wt. % Au. In the case of the sample doped with 15 wt. % Au, the film shows more crystalline behavior and the grains are densely packed, well defined and quasi-spherical.

EDX analysis for pure and doped ZnO thin films as shown in Fig. 5a, b, respectively, shows that the dominant composition of ZnO and the details of the relative analysis are given in Table 1. Fig. 5a shows two strong peaks corresponding to Zn and O, which confirm the high purity of the ZnO thin films. In Fig. 5b we observe

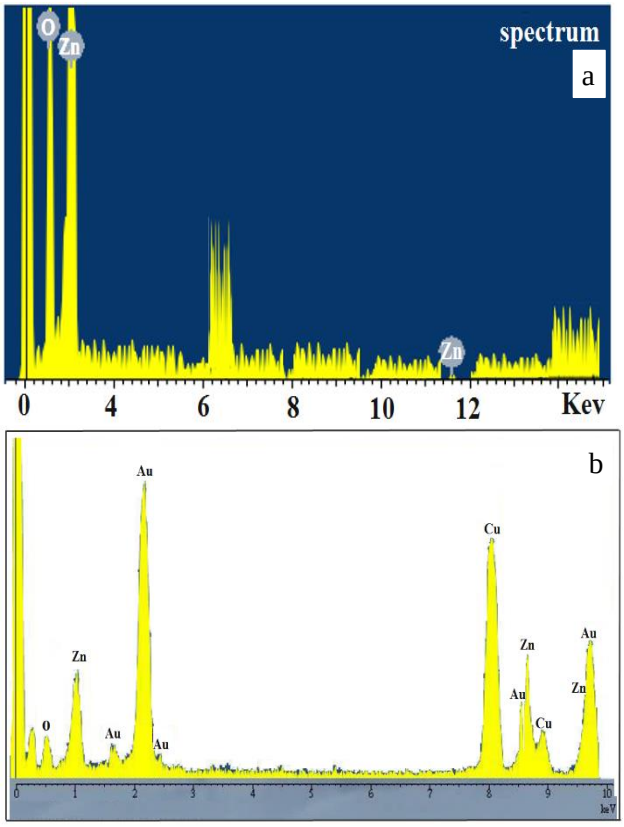

Fig. 5 – EDXA of the pure ZnO thin films (a) and doped with 15 wt. % Au (b)

Table 1 – Elemental analysis of ZnO doped with 15 wt. % Au

Element	Weight %	Atomic %
O	20.34	54.18
Zn	63.20	41.20
Au	16.46	4.62

in the doping state the appearance of Au element with high intensity due to high concentration (15 wt. % Au), as well as two strong peaks corresponding to Cu and Zn elements and the presence of peaks with low intensity due to Au, Cu and Zn elements.

4. CONCLUSIONS

In summary, pure and Au doped ZnO thin films were successfully synthesized by CVD technique. The influence of Au doping on the structural and optical properties of the samples is studied. XRD measurements indicate that the synthesized ZnO and ZnO:Au films are in the hexagonal phase with preferred orientation (101). SEM images show that the grains are non-homogeneous having different sizes. EDX analysis shows the chemical composition of pure and films doped with 15 wt. % Au. A direct optical band gap was found from the transmittance spectra. With an increment in the Au content, the bandgap increases.

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Вплив домішки Au на структурні та оптичні властивості тонких плівок ZnO, отриманих методом CVD

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Тонкі плівки оксиду цинку, леговані Au, синтезували методом CVD. Збільшення легуючої домішки від 0 до 15 мас. % Au в тонких плівках ZnO призводить до виражених змін морфології плівок. З оптичних властивостей витікає, що ширина забороненої зони чистої тонкої плівки ZnO становить 3.28 еВ, і при збільшенні легуючої домішки Au від 5 до 15 мас. % вона не змінюється. Рентгенівська дифракція показала, що пік максимальної інтенсивності відповідає переважній орієнтації (101) для плівок ZnO при 15 мас. % Au. Зображення SEM показують, що збільшення кристалів відбувається за рахунок збільшення концентрації легуючої домішки. Аналіз EDX показав, що нелегована плівка ZnO містить елементи Zn і O, а плівка, легована 15 мас. % Au, додатково до елементів Zn і O містить елементи Au і Cu. Усі дифракційні піки можна віднести до кристалічного ZnO з гексагональною структурою. Крім цих піків, з'явилися два нових піки (111) і (200), які обумовлені золотом. Вивчення морфології плівок ZnO вказує на наявність однорідних зерен, тоді як при додаванні атомів Au зерна не однорідні і мають різні розміри. Аналіз EDX для чистого ZnO демонструє два сильних піки, які відповідають Zn і O, що підтверджує високу чистоту тонких плівок ZnO. А в легованих тонких плівках (15 мас. % Au) спостерігається поява елемента Au з високою інтенсивністю, також два сильні піки, що відповідають елементам Cu і Zn, і наявність піків з низькою інтенсивністю за рахунок елементів Au, Cu і Zn.

Ключові слова: Сполуки II-VI; Прозоре оксидне з'єднання; Напівпровідникові тонкі плівки.