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Effect of Alumina-Doping on Structural and Optical Properties of Zno Thin Films by Pulsed Laser Deposition

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Abstract

Alumina-doped Zinc Oxide (AZO) thin films on quarts glass substrates have been deposited by pulsed laser deposition technique using a pulsed Nd-YAG laser with the wavelength of (λ= 532 nm) and duration (7ns).

The structural and optical properties of these films were characterized as a function of Al_2O_3 content (0-5w.t%)in the target at substrate temperatures (400°C) and energy fluence (0.4 J/cm^2). The X-ray diffraction patterns of the films showed that the undoped and Al_2O_3 -doped ZnO films exhibit wurtzite crystal structure and high crystalline quality. The optical properties were characterized by transmittance, absorption spectroscopy measurements. For all films the average transmission in the wavelength range (330-900) nm was over 90% and the absorption edge shifted toward a shorter wavelength as Al_2O_3 concentration increased. The optical energy gap of Al_2O_3 doped ZnO thin films, measured from transmittance spectra could be controlled between (3.32eV and 3.59eV) by adjusting alumina concentration. AFM results show that the samples with increasing concentration of Al_2O_3, the surface roughness increases.

تاثير الالمنيوم المشوب على الخصائص التركيبية والبصرية للغشاء الرقيق ZnO بواسطة الترسيب بالليزر (PLD)

الخلاصة :

جرى ترسيب اغشية اوكسيد الخارصين المطعمة بالالومينا على قواعد الكوارتز بتقنية الترسيب بالليزر باستخدام ليزر النيدميوم-ياك النبضي العامل بالطول الموجي (532nm) و امد نبضة (7ns).

تم دراسة الخصائص البصرية و التركيبية للاغشية المحضرة كدالة لنسبة تطعيم (0-5%wt)و بدرجة حرارة 400 درجة مئوية وكثافة طاقة (0.4J/cm). اظهرت انماط حيود اشعة اكس التركيب السداسي لاوكسيد في حبيباته للاهداف المطعمة و الغير مطعمة و تبلور عالي .

اما بالنسبة للخصائص البصرية و التي تبينت من خلال اخذ طيف النفاذية,فكانت معدل النفاذية للاغشية كلها ضمن ا لمدى الطيفي (330-900nm) اعلى من 90% و زحزحة حافة الامتصاص باتجاه الاطوال الموجية القصيرة بزيادة تركيز الالومينا . وحسب فجوة الطاقة من خلال طيف النفاذية وكانت تتراوح بين (3.32-3.59eV) من خلال تغير تركيز الالومينا.وقد اظهرت نتائج مجهر القوى الذري زيادة الخشونة بزيادة تركيزنسبة الالومينا الى اوكسيد الخارصين .

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Key words: Al_2O_3 doped ZnO, Pulsed Laser Deposition (PLD), U.V emission, XRD.

1-Introduction

In recent years, there has been a great deal of interest in wide band gap semiconductors for use in optical devices near-ultraviolet (UV) region. ZnO is one of the most attractive materials because of its good optical, electrical, and piezoelectric properties. Also it is a II-VI compound semiconductor with a wide direct band gap of 3.3 eV at room temperature [1]. It has been used for several applications, such as transparent conductive oxide (TCO) films, solar cell windows, bulk acoustic wave devices and gas sensor [2-6]. ZnO is promising candidate for such application due to its high transparency in the visible wavelength range and low electric resistance [7, 8].The similarity of the properties between ZnO and GaN makes ZnO one of the most promising materials for the photonic devices in the ultraviolet range. Also the binding energy of the exciton of ZnO (60 meV) is larger than that of GaN (25 meV) at room temperature, giving it an advantage over GaN for exciton-related device applications [9]. Among them alumina-doped ZnO films is a wide band gap semiconductor, which shows good optical transmission in the visible wavelength region (330-900 nm) [7]. Furthermore there were various methods produce ZnO film, such as the metal-organic chemical vapor deposition (MOCVD) [8] and pulsed laser deposition (PLD) [10-15]. In comparison with other techniques, PLD provides several advantages. For example, PLD films can crystallize at relatively low substrate temperatures due to the higher energy of the ablated particles in the laser-produced plume and relatively high deposition rates [16].In some reports [17],ceramic targets prepared by sintering the mixture ZnO powder and Al_2O_3 powder was used. However, the expensive ceramic targets are usually brittle and would cause the cracking during deposition [18]. The aim of this work is to produce high-quality Al_2O_3 -doped ZnO thin films for optical gas sensor application by PLD. Special attention was paid to the influence of the processing parameters, such as dopant concentration into the targets on the structure, morphology, and optical properties of the films during the deposition.

2. Experimental procedure

2.1 Preparation of material powder and thin films.

Al_2O_3-doped ZnO thin films were synthesized by pulsed laser deposition system using a second harmonic Nd:YAG laser. Thin films were grown in a vacuum chamber generally in (10^{-3} Torr) vacuum conditions. The Nd:YAG laser was operated at the wavelength of (λ=532 nm) with the repetition rate of (10Hz) and pulse duration of (7 ns). The target to substrate distance was (3cm). Targets of pure ZnO and Al_2O_3 -doped ZnO films (0-5wt.%) porcelain materials were prepared by sintering at the temperature of 10°C. Amorphous fused silica (commercial available from Alfa Aesar) was used as substrates thin films were grown in Oxygen environment with O_2 partial pressure of 10^{-1} mbar at substrate temperature of 400^0C and

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of laser fluence focused on the target was about (0.4 J/cm^2). The deposition thin films were grown typically 10 min after the deposition thin films were cooled to room temperature.

2.2 Characterization of thin films

The absorption spectra of undoped and Al_2O_3-doped ZnO thin films were studied by UV-visible (Perkin Elemer Company) spectrophotometer in spectral range of (330-900) nm. The data from transmission spectrum could use in the calculation of the absorption coefficient (α) by using the following equation [19]:

$$a = \frac{1}{d}\ln\frac{1}{T} \quad \dots (1)$$

Where d: is the thickness of thin film, and T is the transmission.

The absorption coefficient (α) and optical energy gap (Eg) are related by [20]:

$$\alpha h\nu = A(h\nu - Eg)^n \quad \dots (2)$$

Where A: is constant depending on transmission probability, h: is Plank's constant , ν: is the frequency of the incident photon, Eg: is the energy gap of the material and n has different values depending on the nature of absorption process.

The microstructures of the films were analyzed using Atomic Force Microscopy (AFM-Digital Instruments Nan Scope) working in tapping mode. Thickness measurements were carried out using a He-Ne laser at λ=362nm .The thicknesses of the films were calculate in the range from (X=330-900) nm. The polycrystalline structure of the films was analyzed with X-Ray Diffraction (XRD, Rigakn DMAX 2800), power diffraction system with Cu-Kα x-ray tube (λ = 1.54056 Å) was used. The x-ray scans were performed between 2θ values of 30° and 38°.

3- Results and discussion

The XRD spectra of Al_2O_3-doped ZnO films obtained from 2θ between 30° and 38° indicated that the deposited films were polycrystalline as shown in Fig. (1). A reflection corresponding to the (100), (002) and (101) planes of wurtzite ZnO at $2\theta = 31.6^o, 34.44^o, 36.3^o$ is observed, respectively. The FWHM of the all peaks decrease with Al_2O_3 content indicating smaller polycrystalline size. It was suggested that Al_2O_3 concentrations on ZnO grains. A careful comparison of the (100) diffraction peaks shows that the peak position of ZnO with different Al_2O_3 contents shifts slightly towards high 2θ value. The average grain size, in the films is calculated to an accuracy of 10% Appling Scherrer equation to the FWHM of the all peaks. The data obtained from the XRD spectra are given in table (1).

Fig.(2) shows the optical transmittance spectra (330-900) nm as function of wavelength for pure ZnO and Al_2O_3-doped ZnO films grown at various Al_2O_3 concentration in the targets (0-5wt.%) . The transmission spectra of the films indicate that the ZnO films have a high average transmittance of approximately 70% to 95% in the wavelength range (330-900) nm.

The average transmittance of ZnO films is increased by Al_2O_3 doping increasing (0-5 wt. %) and a sharp absorption edge for all as-

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grown pure ZnO and Al_2O_3-doped ZnO films. The low value of transmittance may be because of excessive zinc ion is exiting at interstitial sites that probably absorb light [19]. Light transmittance above 90% was exhibited by films prepared at previous above conditions. Fig.(3) exhibits the variation of the absorption coefficient as afunction of wavelength for Alumina doped Zinc oxide thin films in different concentration of alumina.

The energy gap values depends in general on the film crystal structure, the arrangement and distribution of atoms in the crystal lattice, also it is affected by crystal regularity. The energy gap (Eg) value is calculated by extrapolation of the straight line of the plot of $(\alpha h\nu)^2$ versus photon energy for different Al_2O_3 concentration in the target (0-5 wt.%) as shown in Fig.(4). The linear dependence of $(\alpha h\upsilon)^2$ with $(h\nu)$ indicates direct band gap. ZnO is naturally an n-type marital and the Fermi level will fall in the conduction band when it is heavily doped. Since the states below are filled, the optical band gap should be increased to the higher energies .This means that the absorption edge of the Al_2O_3 doped films will be shifted to the shorter wavelengths compared to that of pure ZnO films [7].

Figures (5) shows the AFM analyses show that the use of doped targets leads to deposition of the ZnO (undoped and Al_2O_3 doped) films deposited at 400 ºC substrate temperature thin films with droplets. 3D AFM images of the films prepared from different targets are presented in figures 4. The root mean square (RMS) surface roughness of Al_2O_3 doped ZnO films are found to be 50.95 nm, 57.09 nm, 136.03 nm and 188.53 nm for pure, 1%, 3% and 5% Al_2O_3 doping concentrations respectively (see table 4), i.e the root mean square (RMS) surface roughness exponentially increases with the dopant concentration. On the other, a droplet free smooth surface is necessary to ensure optical detection. The density and the size of the droplets increase with the dopant concentration into the targets. This result is probably due to the density of the sintered targets. [21] .The 3D AFM images taken from an area of (10 µm x 10 µm) were used for estimation of the grain size on the film surface. Concerning the morphology characteristics, the ZnO target with the highest dopant concentration (3 wt% Al_2O_3) and (5 wt% Al_2O_3) is suitable for preparation of thin films for optical sensor application. Our previous investigation of the influence of the processing parameters on the morphology of the undoped ZnO films have shown that the increase of the substrate temperature leads to deposition of smoother films which is associated with the mobility of the atoms on the surface [22]. The morphology of the sensing films is an important characteristic for optical gas detection. On the one hand, a porous surface with small grain size is recommended for better gas sensitivity [23].

4. Conclusions

Thin films of Al_2O_3 have been deposited on to the glass substrate by PLD in 10^{-3} mbar O^2 ambient at different alumina concentration with

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laser fluency energy 0.4 J/cm^2 .It was found that doped ZnO films with good structural and morphological properties can be deposited at x=0.05. The film deposited at an optimum alumina concentration 0.05 exhibited more intensity and FHWM with average grain size of (33-70) nm maintaining average RMS roughness of (51-189) nm.

The band gap was increased with increase of Al_2O_3 concentration from 3.32eV to 3.59eV as well as with the change of thickness. The absorption edge was found to shift toward lower wavelength with increase in Al_2O_3 (0-5wt. %) value. The increase of the doping concentration increase the roughness of the films.

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Table (1): XRD parameters of Al_2O_3 doped ZnO

Sample	2θ (deg.)	FWHM (deg.)	Grain size (nm)
ZnO-pure T= 400°C	31.748	0.254	32.7
ZnO- Al_2O_3 (1%)	31.74	0.138	60.3
ZnO- Al_2O_3 (3%)	31.78	0.119	69.7
ZnO- Al_2O_3 (5%)	31.76	0.135	61.55

Table 2. AFM characteristics of the ZnO (undoped and Al_2O_3 doped) films deposited at 400 °C substrate temperature 0.4 J/cm^2 leaser energy and 10^{-1} mbar Oxygen pressure.

Al_2O_3 dopant content in the target w.t.%	RMS [nm] taken from 10×10 µm
ZnO-pure	50.95
ZnO:Al_2O_3 (1%)	57.09
ZnO:Al_2O_3 (3%)	136.03
ZnO:Al_2O_3 (5%)	188.53

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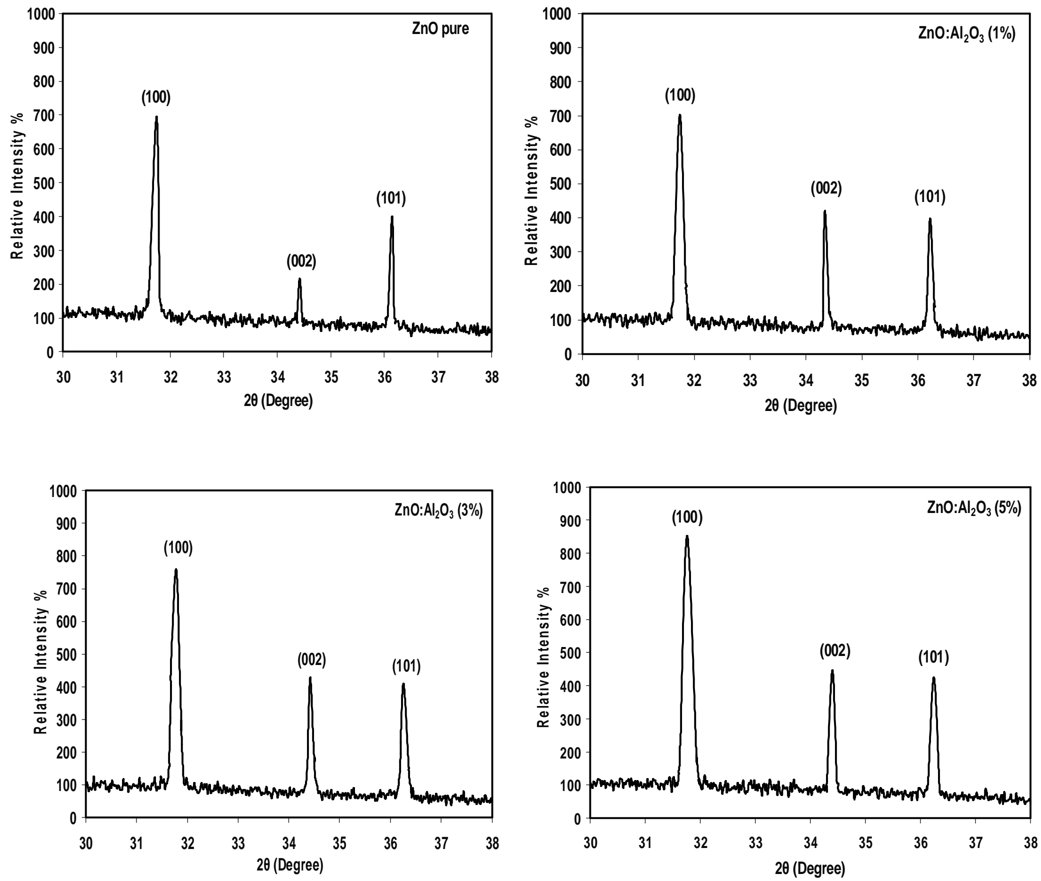

Figure(1): XRD spectrum of ZnO pure and alumina-doped ZnO thin films Deposited on glass substrate.

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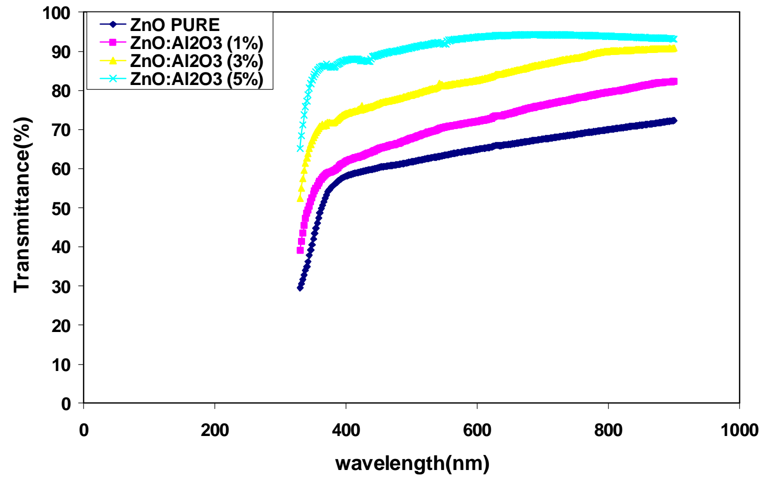
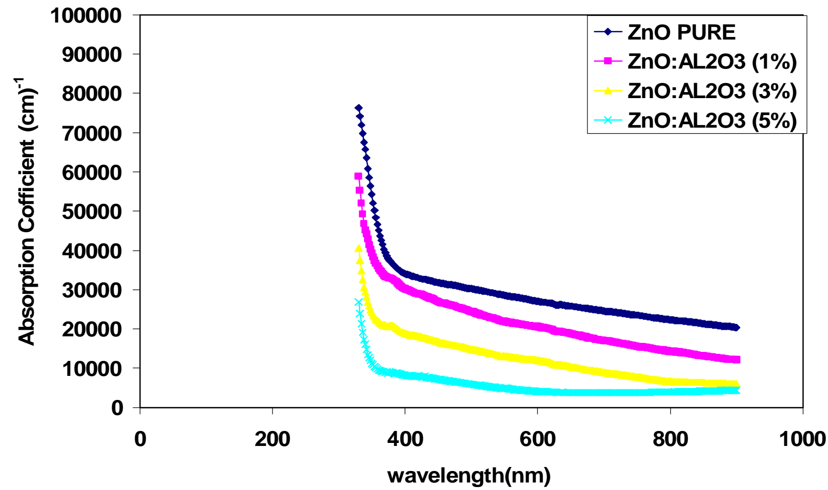


Figure (2).The optical transmission spectra of A_2O_3 doped ZnO thin films at different concentration with temperature substrate of 400°C and laser energy fluency 0.4J/cm^2.



Figure(3). The optical absorption coefficient spectra for the ZnO thin film with various Al_2O_3 doped concentrations indicated at temperature of 400°C and laser energy fluency 0.4J/cm^2.

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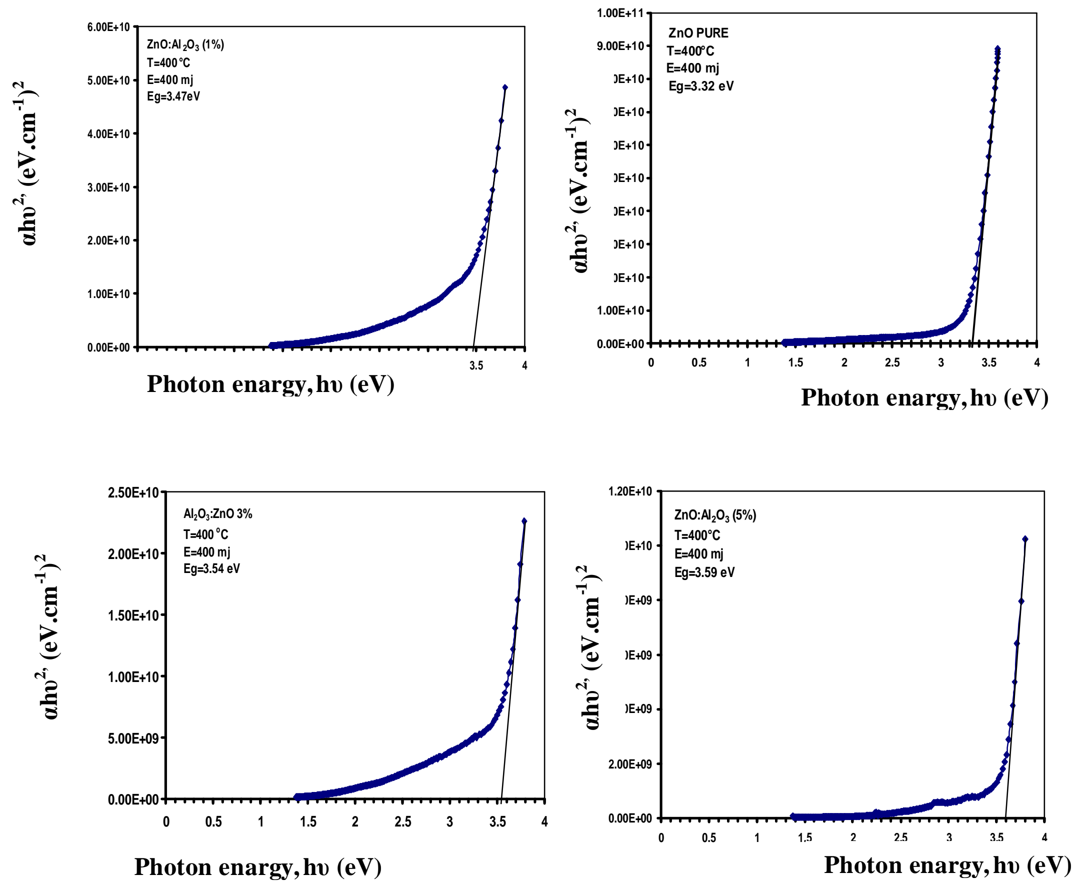

Figure(4) A plots of $(\alpha h\nu)^2$ verses photon energy ($h\nu$) of ZnO thin films with various Al_2O_3 doped concentrations indicated at temperature of 400°C and laser energy fluency $0.4J/cm^2$.

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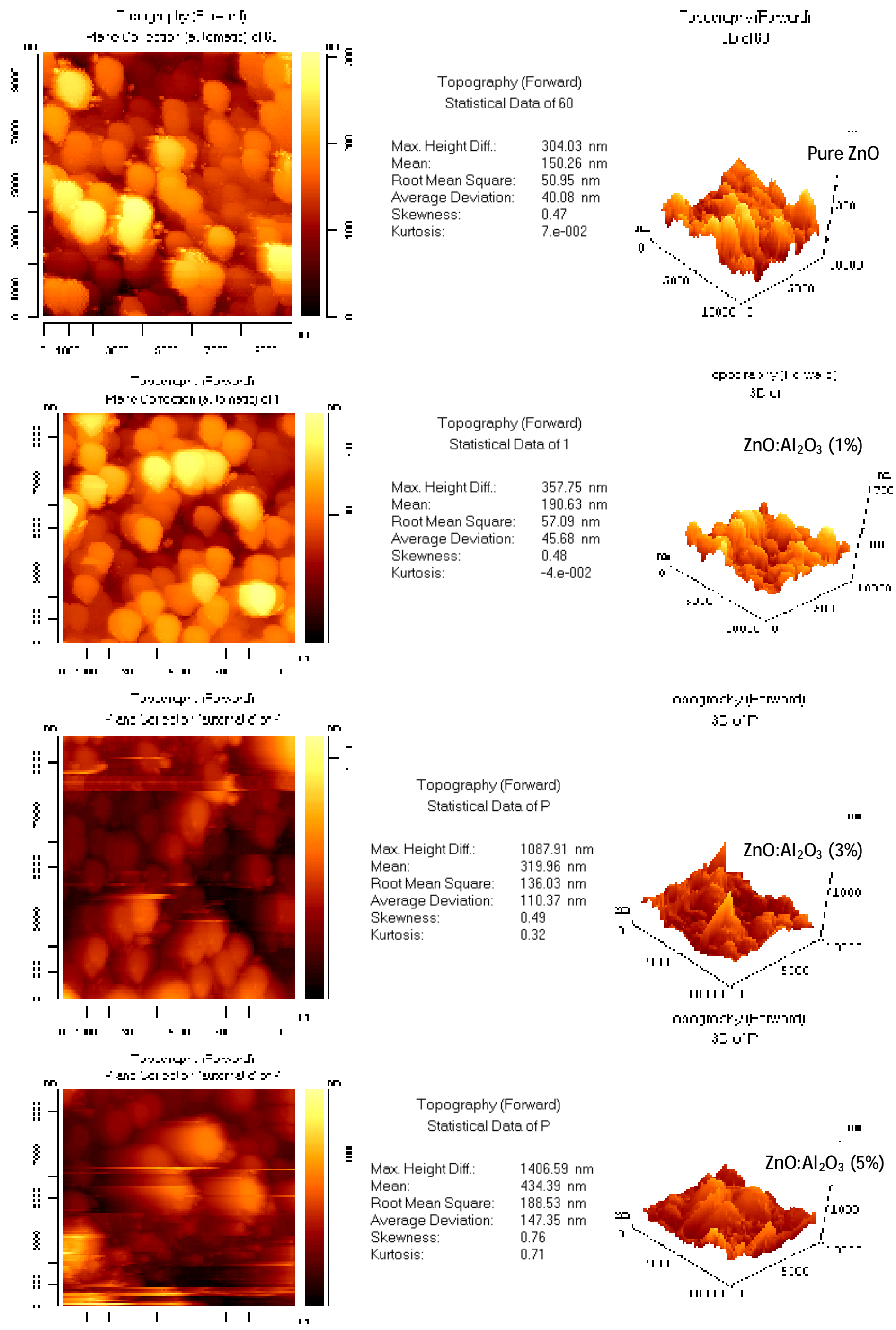

Figures 5. Atomic force microscopy (AFM) ofpure ZnO and Al_2O_3 doped ZnO films grown on a glass substrate.

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