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# Ellipsometric studies of optical properties of copper doped zinc oxide films on glass substrates

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ABSTRACT

Copper-doped ZnO films with thickness about 1200 nm were prepared by radio-frequency (RF)-magnetron sputtering on glass substrates. The influence of dopant on the optical properties was investigated using ellipsometry technique. It has been found that only three layer model of surface can be satisfactory fitted with experimental data of ellipsometric measurements obtained in wide range of incident angles. Presence of additional layers within the model can be explained by the interface roughness. The atomic force microscopy (AFM) analysis indicates that thickness of additional layers and value of interface roughness are commensurable. The optical parameters of copper-doped ZnO structures with different concentration of copper dopant were obtained using the fitting procedure within the three-layer model. Absence of copper clusters in the ZnO:Cu layer microstructure was confirmed using X-ray diffraction and the effective media approximation (EMA) analysis. Refractive indices of doped ZnO:Cu layers ($n = 2.002\ldots2.04$) are very close to the index of ZnO film ($n = 1.98$) at 632.8 nm. Extinction coefficient increase gradually to ($k = 0.002$) with the dopant concentration increasing.



## 1. Introduction

Zinc oxide (ZnO) is a wide-band-gap semiconductor and is also a piezoelectric material which has a reasonably large piezoelectric coefficient. Such unique property has been widely studied for its practical applications [1]. A rich family of ZnO nanostructures provides numerous opportunities for researchers to explore their properties and find potential applications.

For semiconductors, doping is a powerful tool to tailor the electrical and optical properties, facilitating the construction of many electronic and optoelectronic devices. Cu doping modifies the photoluminescent transitions in ZnO by creating localized impurity levels [2,3]. Additionally, Cu behaves as an acceptor in ZnO with its energy level locating at 0.17 eV below the bottom of the conduction band, making itself a good candidate for creating *p*-type ZnO [4]. More interestingly, previous studies, both theoretical and experimental, showed that ZnO doped with appropriate transition metals are diluted magnetic semiconductors [5] which attracted a lot of interest due to their potential applications in spintronics. Coexistence of the ZnO and Au nanoparticles gives a substantially enhancement of photoinduced second harmonic generation [6] that can be explained by the contribution of the electron–phonon interactions [7].

Therefore, optical properties of ZnO thin film tailored by Cu doping can be informative to predict the structural, electrical and other characteristics of material.

Ellipsometry is a powerful and attractive technique that recently has found much favor in the non-destructive and in situ characterization of solids, thin surface films, structure of interfaces at nanometer scale [8]. Structural changes and optical constants modification of solid induced by doping procedure can be estimated using ellipsometric method too [9].

## 2. Materials and experiment

Optical characteristics of ZnO:Cu thin films with different atomic amount of Cu dopant were explored using multiple angle of incidence (MAI) ellipsometry at single wavelength ($\lambda = 632.8$ nm). The ZnO:Cu thin films were deposited on glass substrates by means of radio-frequency magnetron sputtering system using ZnO-powder targets together with oxide CuO in argon-oxygen atmosphere at the gas pressure of $10^{-3}$ Torr. In order to minimize the thermal stresses the substrate temperature was fixed at 300 °C. The target-to-substrate distance was 60 mm and RF-power – 100 W.

The atomic amount of Cu dopant in the film material (taken from energy dispersive X-ray (EDX) analysis using a REMMA-102-02 scanning electron microscope, working at 20 kV dc acceleration voltages in vacuum) changed from 0.5% to 5%. The thickness of ZnO:Cu thin films was estimated by the deposition time and was about 1200 nm for all the specimens.

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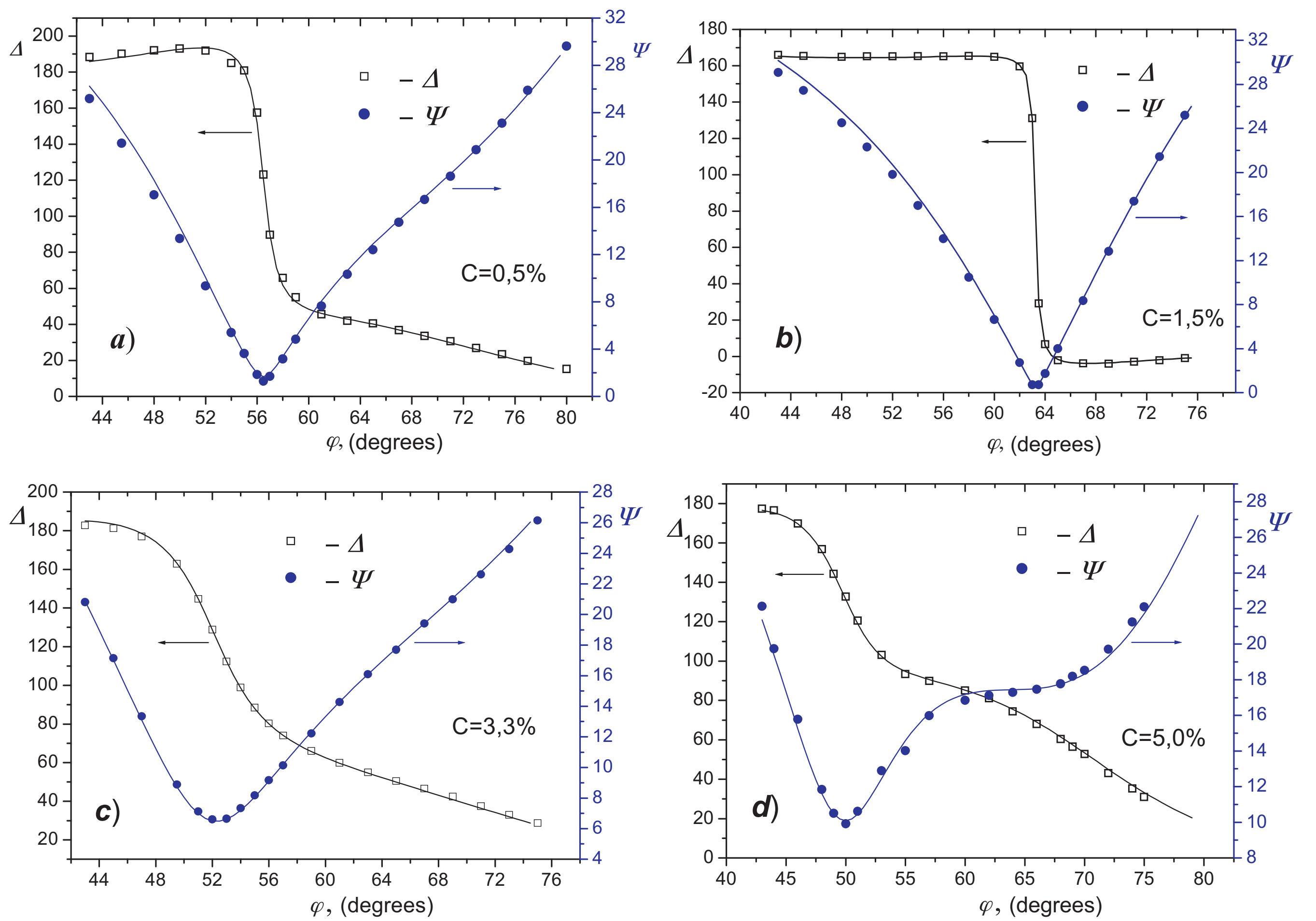


**Fig. 1.** Dependencies of ellipsometric parameters $\Delta$ and $\Psi$ on the incident angle of light for specimens of ZnO:Cu-layers with different atomic amount $C$ of Cu dopant: (a) $C = 0.5\%$; (b) $C = 1.5\%$; (c) $C = 3.3\%$; and (d) $C = 5.0\%$. Experimental data are presented by filled circles ($\Psi$) and empty squares ($\Delta$). Solid curves are results of fitting procedure using a three-layer surface model shown in Fig. 2.

The X-ray diffraction (XRD) measurements were carried out using STOE STADI P diffractometer with linear position sensitive detector in transmission Bragg-Brentano geometry (Cu K$\alpha_1$ radiation at $\lambda = 1.5406$ Å, Ge(1 1 1) monochromator, detector scanning step: 0.480° 2$\theta$, accumulation time: 320 s, 2$\theta$ angle resolution: 0.015°, 2$\theta$ range: 23–115°).

Ellipsometric parameters were determined in maximally wide range of the incidence angles, which is provided by a serial device LEF-3M. The incidence angle $\varphi$ was changed within the limits from 44 to 76 degrees with average step of increment about 2 degrees. In the region of principal angle of incidence (rapid change of phase ellipsometric parameter $\Delta$) the step was diminished to 0.5 degree.

The dependencies of experimental data on the angle of incidence are presented in Fig. 1(a–d) as discrete values by circles and squares. The filled circles and empty squares determine the value of amplitude $\Psi$ and phase $\Delta$ ellipsometric parameters as a function of incident angle $\varphi$.

Two circumstances, which arise at the solution of inverse ellipsometry problem, were the reason to collect such great volume of experimental data: (a) choose of model adequate to real state of surface and (b) correlation decreasing between the thickness and refractive index of ZnO:Cu film.

## 3. Results of data processing and discussion

The ellipsometry is one of the most sensible characterization techniques for detecting the structural and phase changes on a surface. But it is fundamentally indirect technique where the sought parameters are always obtained as result of the inverse problem solution.

The data was fitted using the iterative fitting algorithm, to minimize the value of $f^2$, the merit function which quantifies the difference between the measured and calculated ellipsometric values, defined here as

$$f^2 = \frac{1}{n-m-1}\sum_{i=1}^{n}\left[\frac{(\Delta^{\rm exp}-\Delta^{\rm calc})^2}{\sigma_\Delta^2}+\frac{(\Psi^{\rm exp}-\Psi^{\rm calc})^2}{\sigma_\Psi^2}\right], \qquad (1)$$

where $\Delta^{\rm exp}$, $\Psi^{\rm exp}$ are the experimentally determined values; $\Delta^{\rm calc}$, $\Psi^{\rm calc}$ are the values calculated using the acceptable model of surface; $\sigma_\Delta$, $\sigma_\Psi$ are the point-wise experimental errors of the respective measured values $\Delta$, $\Psi$; $n$ is the number of data points, and $m$ is the number of unknown model parameters.

Often, it is necessary to enter additional layers into a physical model for adequate specification of complex surface structure. The structural heterogeneities in transitional regions between different materials (ambient-film, film-substrate) cause the presence of these layers in the model. Obviously, the simpler surface model is the more reliable and suitable for interpretation one. Therefore, we begin from the simplest variant (monolayer model ZnO:Cu film on the glass substrate).

Priori information about the thickness of the ZnO:Cu film significantly eases the procedure of the model selection and data fitting.

However, achievement of satisfactory fitting between the experimental and calculated data is impossible within the mono- and two-layer surface models. Experimental ellipsometric parameters depending on the angle of incidence (Fig. 1(a–d)) can be satisfactorily described only within the three-layer surface model that is shown in Fig. 2.

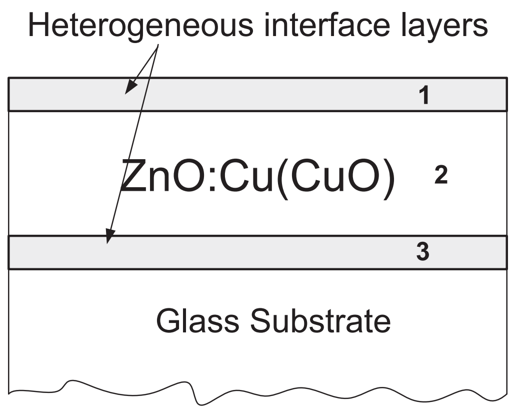


**Fig. 2.** Three-layer model of surface under investigation. 1 and 3 are the layers simulated the heterogeneities of film-ambient and film-substrate interfaces correspondingly.

The main ZnO:Cu(CuO)-layer with thickness about 1200 nm is limited top and bottom by two thin absorbing layers with thicknesses changing from 5 nm to 20 nm. Thicknesses of transitional layers 1 and 3 are the characteristics of the film-ambient and film-substrate interfaces with dislocated structure and approximately correlate with the values of mean square roughness (MSR) of film and substrate surfaces respectively. Only the thickness of bottom layers localized on the film-substrate interfaces exceed a value of 10 nm. This effect can be explained by additional heterogeneities that arise at initial stages of the film formation.

AFM micrograph analysis indicates the granular character of the deposited films. Fig. 3 shows the AFM images of ZnO films doped with different concentration of copper dopant from 0.5 at.% to 5.0 at.%, respectively. The average grain size and the surface roughness obtained from those data (Table 1) are connected with the amount of Cu dopants, i.e. they decrease with increase of Cu concentration. It is evident that the thickness of transition layers 1 and 3 (Fig. 2) and the MSR of the ZnO:Cu-film as well as the substrate roughness are the values of the same order.

**Table 1**
Superficial parameters of ZnO films, doped with Cu.

| Film | Roughness $R_q$ (nm) | Average height $D$ (nm) |
|---|---|---|
| ZnO:Cu (0.5 at.%) | 5.12 | 18.0 |
| ZnO:Cu (1.5 at.%) | 6.22 | 23.4 |
| ZnO:Cu (3.3 at.%) | 5.48 | 21.0 |
| ZnO:Cu (5.0 at.%) | 4.90 | 16.6 |
| Glass substrate | 6.86 | 24.4 |

Complex refractive indices of the transitional interface layers obtained by fitting procedure are characterized by high values of imaginary part (extinction coefficient $k$) for all structures within the three-layer model. There are a number of works, which explored the influence of surface roughness on the optical parameters of the material in the block [10] and on the parameters of a thin uniform film, which simulates the properties of heterogeneous structures [11–14]. It is shown in these works that the increase of the surface roughness $R$ increases the effective absorption coefficient $\kappa = k/n$, defined as the ratio of imaginary $k$ and real $n$ parts of complex refractive index $N = n - ik$ of effective medium or effective surface layer. This conclusion applies when the condition $R \ll \lambda$ satisfies. Then we can conclude that existence of additional layers in the model is caused by roughness on the top and bottom of principal Cu doped ZnO-layer.

However, the relationship between the optical characteristics of effective layer and dimensional parameters of the heterogeneous surface microstructure is a problematic question and it has not found definitive final solution till now. Then we will focus only

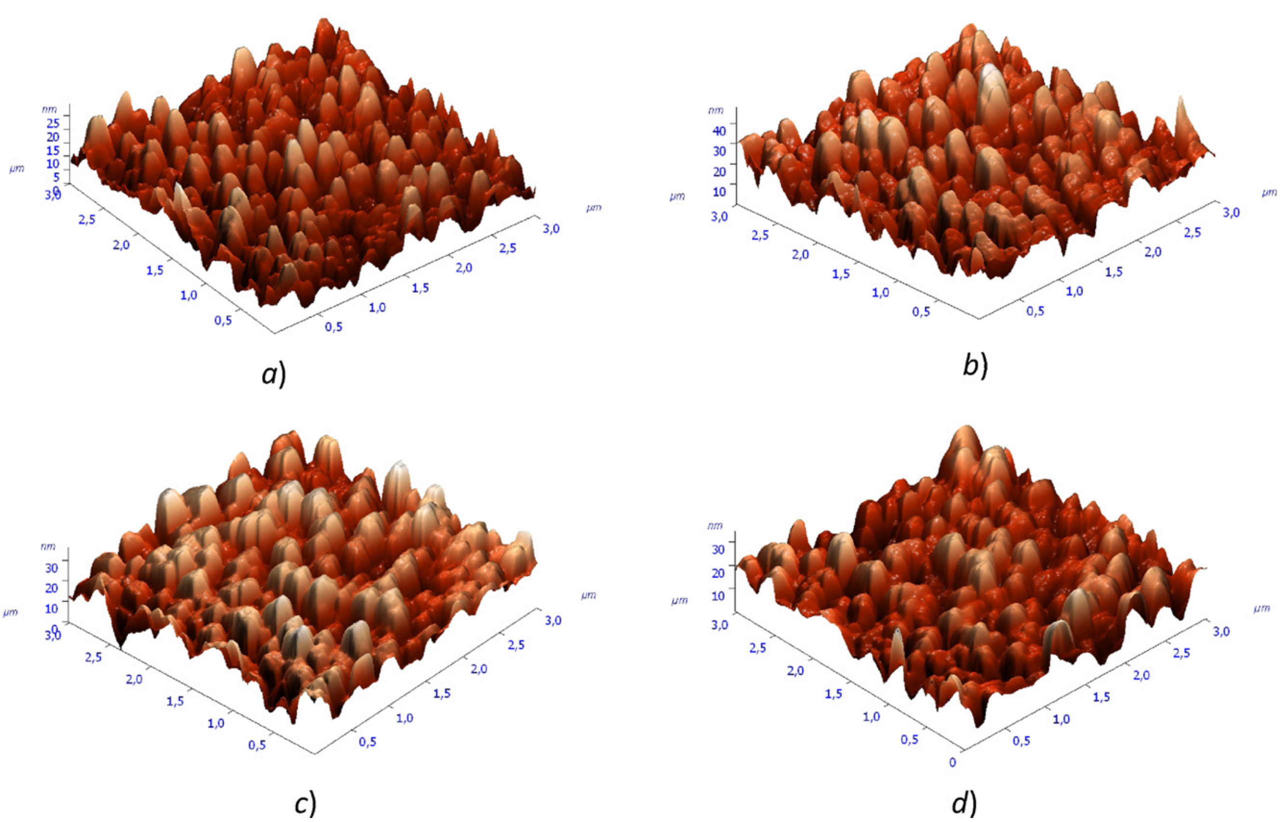


**Fig. 3.** 3D AFM images of ZnO films doped with different concentration of copper dopant: (a) 0.5 at.%; (b) 1.5%; (c) 3.3%; and (d) 5.0%.

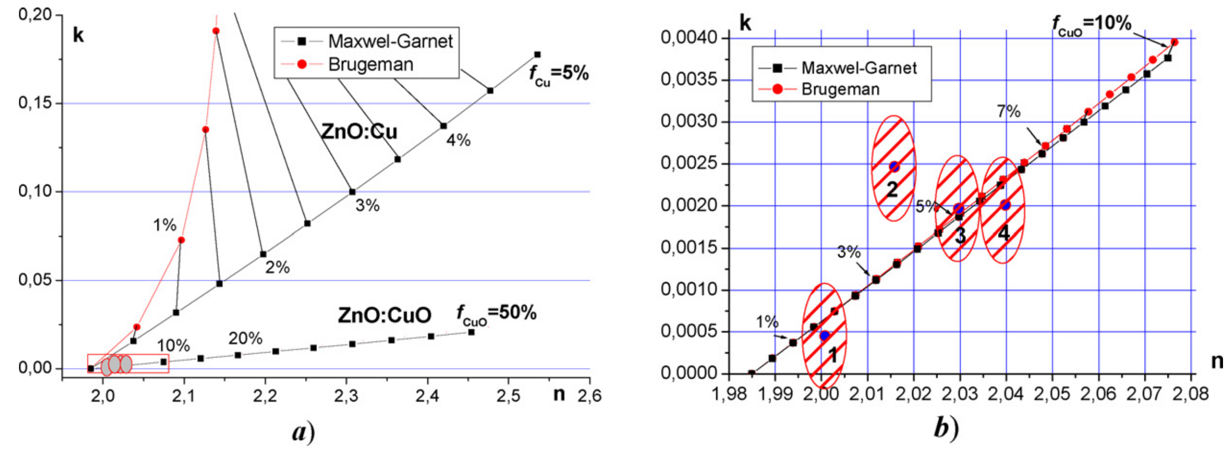


**Fig. 4.** Dependencies of optical parameters ($n$ is the refractive index, $k$ is the extinction coefficient) of effective media (ZnO:Cu and ZnO:CuO) on the volume fraction of dopants ($f_{Cu}$ or $f_{CuO}$) calculated in accordance with MG (full squares) and B (full circles) approximations. Panel (b) represents the rectangular element marked on the panel (a). Full elliptic areas indicate error band of uncertainty (area of feasible solutions of inverse ellipsometry problem) for the optical parameters of ZnO:CuO-layers with different atomic amount of CuO dopant: (1) 0.5%; (2) 1.5%; (3) 3.3%; and (4) 5.0%.

**Table 2**
Dielectric functions and refractive indexes of major components of the Cu doped ZnO-film.

| Components of ZnO:Cu-film | $\varepsilon_1$ | $\varepsilon_2$ | $N=n-j\cdot k$ |
|---|---|---|---|
| ZnO [1,16] | 3.940 | 0.0 | $1.98-j\cdot 0$ |
| Cu [17–19] | −7.500 | 1.670 | $0.241-j\cdot 3.458$ |
| CuO [20] | 8.990 | 0.300 | $3.0-j\cdot 0.05$ |

**Table 3**
Optical parameters and thickness of ZnO:Cu layers with different amount of dopant.

| Layer parameters | Atomic amount of Cu dopant (%) | | | |
|---|---|---|---|---|
| | 0.5 | 1.5 | 3.3 | 5.0 |
| $n$ | 2.002 | 2.015 | 2.030 | 2.040 |
| $k$ | 0.0005 | 0.0025 | 0.0019 | 0.002 |
| $d$ (nm) | 1280 | 1270 | 1225 | 1320 |

on the parameters of the composite ZnO:Cu-layer that in general determine the angular dependencies obtained experimentally and presented in Fig. 1(a–d). Result of the fitting procedure obtained within the tree-layer model for each four specimens is shown also in Fig. 1 (solid lines) and demonstrate a satisfactory agreement with experimental data.

For estimation of optical parameters of the Cu doped ZnO-film we use the Bruggeman (B) and Maxwell Garnett (MG) [15] models of effective media approximation (EMA). Dielectric functions and complex refractive indexes of major components of the ZnO:Cu(CuO)-structure at wavelength $\lambda = 632.8$ nm were obtained from the literature data and are presented in Table 2. Here, we assume that the copper-doped ZnO layer contain not only separate $Cu^{+2}$-ions substitutional at the lattice positions $Zn^{+2}$-ions but the cluster structure of metallic copper too.

EMA theory allows the determination of permittivity $\varepsilon$ of microscopically heterogeneous but macroscopically homogeneous media, consisting of two or more components with different dielectric properties. The MG model assumes a structure in which the phase with permittivity $\varepsilon_b$ is surrounded by the phase of $\varepsilon_a$ and their volume ratio determines by $f_b$:

$$\frac{\varepsilon-\varepsilon_a}{\varepsilon+2\varepsilon_a} = f_b\frac{\varepsilon_b-\varepsilon_a}{\varepsilon_b+2\varepsilon_a} \quad (2)$$

On the other hand, Bruggeman model assumes random mixture consisting of two phases $\varepsilon_b$, $\varepsilon_a$ with volume fractions $f_a$ and $f_b$ correspondingly:

$$0 = f_a\frac{\varepsilon_a-\varepsilon}{\varepsilon_a+2\varepsilon} + f_b\frac{\varepsilon_b-\varepsilon}{\varepsilon_b+2\varepsilon} \quad (3)$$

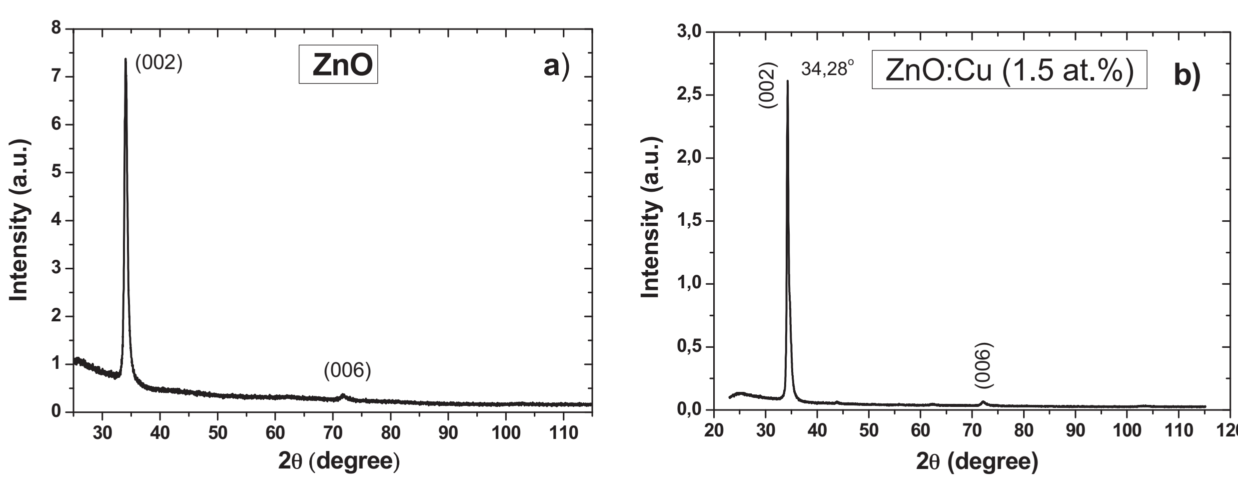


**Fig. 5.** XRD spectra of ZnO films: (a) ZnO undoped and (b) ZnO:Cu (1.5 at.%).

**Table 4**
Parameters of Cu-doped ZnO films taken from XRD spectra.

| Film | (0 0 2)-peak position |
|---|---|
| ZnO | 34.04° |
| ZnO:Cu (0.5 at.%) | 34.05° |
| ZnO:Cu (1.5 at.%) | 34.28° |
| ZnO:Cu (3.3 at.%) | 34.33° |
| ZnO:Cu (5.0 at.%) | 34.29° |

We consider two different materials: (a) consisting of ZnO with Cu metallic clusters; (b) consisting of ZnO with CuO grains (substitution of $Zn^{2+}$ ions by $Cu^{2+}$).

Dependencies of the effective media optical parameters on the volume fraction of dopants ($f_{Cu}$ or $f_{CuO}$) calculated in accordance with MG and B approximations are presented in Fig. 4(a and b). Data of Table 2 were used for calculation procedure by varying of the dopant volume fraction within limits from 0 to 0.5.

Optical parameters ($n$, $k$) of ZnO:Cu layers generating the three-layer structure, which is presented in Fig. 2, are marked also in Fig. 4(a and b) as full ellipses. The ellipse dimensions indicate approximately the error values for real and imaginary parts of the layer complex refractive index. These parameters were obtained as result of fitting procedure for four specimens with different atomic amount of Cu dopant and are presented also in Table 3. The low values of extinction coefficient $k$ of ZnO:Cu layers evidence the occupation of the lattice sites of ZnO by Cu ions that were confirmed by the data of XRD spectra [21,22].

The X-ray diffraction spectra of ZnO and ZnO:Cu thin films of wurtzite structure are shown in Fig. 5. As one can see, the doping of ZnO film by a few percents of copper does not affect the crystalline structure of the film considerably. Besides, the peaks which correspond to phase of copper do not appear in XRD spectra, therefore the presence of metallic clusters in such films is hardly probable.

Moreover, with the increasing of copper dopant amount, in the XRD spectra the shift of (0 0 2)-peak into direction of higher values of $2\theta$ takes place in the XRD spectra due to isomorphous substitution of $Zn^{2+}$ ions by $Cu^{2+}$ ions. This peculiarity can be explored by decreasing of the lattice constant when $Cu^{2+}$ ions substitute $Zn^{2+}$ ions [23]. The parameters taken from XRD spectra are presented in Table 4.

It is obviously from the EMA analysis, that presence of metallic copper in the ZnO:Cu structure leads to it optical extinction rapid increase. Moreover, the occurrence of metallic copper due to the delocalized d-Cu states may lead to additional plasmon absorption. On the contrary, ellipsometry data indicate very gradual increasing of the extinction coefficient with increase of the copper dopant concentration.

## 4. Conclusion

Both the MG and Bruggemans EMA models for the ZnO films including the metal phase of Cu give results differing sufficiently from the fitting parameters of explored layers. Extinction of such effective media on two orders exceeds the values of extinction coefficients of ZnO-layers with Cu-dopant obtained as result of ellipsometric measurements. This result confirms absence of Cu metal phase (metallic clusters) in the structure of doped ZnO-layers. The data of ellipsometry are in good agreement with data of EMA analysis for the ZnO:CuO-system. Therefore, the substitution of $Zn^{2+}$ ions by $Cu^{2+}$ ions with close radii in the crystalline structure and formation of ZnO:CuO-mixture can by confirmed using ellipsometry technique as well as by the data of XRD spectra.

Multiple angle of incidence ellipsometry can be successfully used for analysis of complex surface structure under the previous assumption on the values of several structure parameters. The second essential requirement is acquisition of experimental data in maximally wide range of the incident angle.

## References

[1] X.W. Sun, H.S. Kwok, J. Appl. Phys. 86 (1999) 408–411.
[2] N.Y. Garces, L. Wang, L. Bai, N.C. Giles, L.E. Halliburton, G. Cantwell, Appl. Phys. Lett. 81 (2002) 622–625.
[3] Z. Zhang, J.B. Yi, J. Ding, L.M. Wong, H.L. Seng, S.J. Wang, J.G. Tao, G.P. Li, G.Z. Xing, T.C. Sum, C.H.A. Huan, T. Wu, J. Phys. Chem. C 112 (2008) 9579–9585.
[4] Y. Kanai, Jpn. J. Appl. Phys. 30 (1991) 703–707.
[5] R. Janisch, P. Gopal, N.A. Spaldin, J. Phys.: Condens. Matter 17 (2005) R657–R691.
[6] J. Ebothe, I.V. Kityk, S. Benet, B. Claudet, K.J. Plucinski, K. Ozga, Opt. Commun. 268 (2006) 269–272.
[7] K. Ozga, T. Kawaharamura, A. Ali Umar, M. Oyama, K. Nouneh, A. Slezak, S. Fujita, M. Piasecki, A.H. Reshak, I.V. Kityk, Nanotechnology 19 (2008) 185709.
[8] M. Losurdo, M. Bergmair, G. Bruno, D. Cattelan, C. Cobet, J. Nanopart. Res. 11 (2009) 1521–1554.
[9] D. Mardare, P. Hones, Mater. Sci. Eng. B 68 (1999) 42–47.
[10] C.A. Ferstermaker, F.L. McCrackin, Surf. Sci. 16 (1969) 85–96.
[11] S. D'Elia, N. Scaramuzza, F. Ciuchi, C. Versace, G. Strangi, R. Bartolino, Appl. Surf. Sci. 255 (2009) 7203–7211.
[12] L. Rolland, C. Vallée, M.-C. Peignon, C. Cardinaud, Appl. Surf. Sci. 164 (2000) 147–155.
[13] D. Bhattacharyya, A.K. Poswal, M. Senthilkumar, P.V. Satyam, A.K. Balamurugan, A.K. Tyagi, N.C. Das, Appl. Surf. Sci. 214 (2003) 259–271.
[14] M. Gaidi, A. Amassian, M. Chaker, M. Kulishov, L. Martinu, Appl. Surf. Sci. 226 (2004) 347–354.
[15] D.E. Aspnes, Thin Solid Films 89 (1982) 249–262.
[16] V. Kapustianyk, B. Turko, A. Kostruba, Z. Soani, B. Derkowska, S. Dabos-Seignon, B. Barwinski, Yu. Eliyashevskyi, B. Sahraoui, Opt. Commun. 269 (2007) 346–350.
[17] L.G. Schulz, F.R. Tangherlini, JOSA 44 (1954) 362–367.
[18] L.G. Schulz, JOSA 44 (1954) 357–362.
[19] H.J. Hagemann, W. Gudat, C. Kunz, JOSA 65 (1975) 742–744.
[20] B. Balamurugan, B.R. Mehta, Thin Solid Films 396 (2001) 90–96.
[21] M. Öztas, M. Bedir, Thin Solid Films 516 (2008) 1703–1709.
[22] B. Kulyk, B. Sahraoui, V. Figa, B. Turko, V. Rudyk, V. Kapustianyk, J. Alloys Compd. 481 (2009) 819–825.
[23] X. Peng, J. Xu, H. Zang, B. Wang, Z. Wang, J. Lumin. 128 (2008) 297–300.