JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 9, No. 12, December 2007, p. 3715 - 3719

Investigation of third order nonlinear optical properties in ZnO:Al thin films

Y. HAMAIZI[a,b*], W. BALA[c,d], B. KRAJEWSKI[c], Z. ESSAÏDI[a], A. EL-AKRMI[b]
[a]*Laboratory of Optical Properties of Materials and Applications (POMA), UMR CNRS 6136, University of Angers. 2, Bd Lavoisier, 49045 Angers, France*
[b]*Radiation Physics Laboratory, Department of Physics, P.O.Box 12, University of Badji Mokhtar, 23000 Annaba, Algeria*
[c]*Institue of Physics, N. Copernicus University, Grudziądzka 5/7, 87-100 Torun, Poland*
[d]*Institute of Physics, Kazimierz Wielki University, Weyssenhoff Sq. 11, 85-072 Bydgoszcz, Poland*

Third harmonic generation (THG) in thin films of zinc oxide doped aluminium (ZnO:Al) was studied. The thin layers were deposited on glass substrates by the dip-coating technique. Third order nonlinear optical effect were investigated by Maker fringes method for samples annealed at temperature varying between 390 °C and 600 °C, as well as for the samples with different thicknesses. It is observed that the third order nonlinear optical property increases for samples post-heated above 445 °C due to the crystallisation of ZnO:Al films. This effect is also observed as thickness of samples increases from 2 to 8 deposited layers. The influence of deposition parameters on the film quality and THG efficiency is also discussed.

(Received October 3, 2007; accepted December 4, 2007)

Keywords: ZnO, ZnO:Al, Nonlinear optical properties, Third harmonic generation (THG)

1. Introduction

Zinc oxide is a II-VI semiconductor with 3.4 eV direct band gap at room temperature (RT). It shows high chemical stability, has high melting point and is amenable to wet chemical etching (opportunity for fabrication of low dimensional devices). Especially it high exciton binding energy (60 meV) makes it an interesting photoluminescent material [1,2] because it creates a possibility for an intense near band edge excitonic emission at RT and at higher temperature (it is 2.4 times higher than the RT thermal energy). This also gives to ZnO a strong resistance to high temperatures electronic degradation during operation (laser diode). By controlling the doping level, electrical properties can be changed from insulator, through n-type semiconductor to metal maintaining optical transparency. Many techniques including molecular beam epitaxy (MBE) [3], metal organic chemical vapour deposition (MOCVD) [4], pulse laser deposition (PLD) [5], spray pyrolysis, sputtering, dip-coating etc., can be employed to deposit the film of ZnO onto different substrates. The dip-coating technique is simple, low cost, and can be very useful for large-area applications.

Both linear and nonlinear optical properties of thin films are generally influenced by the specific growth technique and by the deposition parameters. ZnO is also much more resistant to radiation damage [6] than the others common semiconductor materials, such as Si, GaAs, CdS and even GaN which are suitable for space applications. It has strong two photon absorption and negative nonlinear refractive index, so that, high quality bulk crystals of ZnO can be good material for applications in optical power limiting [7]. ZnO is also predicted as a promising future material for spintronics applications [8]. Recently ZnO thin films have been studied extensively due to their potential applications in various fields, such as: gas sensors, varistors, optical wave-guides, transparent conductive layers and electro chromic devices [9-12].

The most common crystal structure of zinc oxide at ambient atmosphere and at RT is the wurzite structure. Another possible crystal structure is the zinc blende structure, for which the lattice energy is slightly higher; therefore it is not so stable at 300 K as the wurzite structure [13].

Moreover, ZnO films have attracted considerable attention because they can be made to possess high electrical conductivity, high infrared reflectance and high visible transmittance. Among all others nonlinear materials applicable to the near-IR or visible spectral range, ZnO is a very promising candidate for film deposition given the large band gap and demonstrated high conversion efficiencies. Its second and third order nonlinear [14-17] optical properties have been investigated and discussed only in recent years and are still under discussion.

The enhanced electrical conductivity in ZnO doped Al films is essentially due to the contribution from Al^{3+} ions on substitutional sites of Zn^{2+} and Al interstitials atoms. As the Al-dopant concentration increases, free electron concentration increases but it saturates for high Al doping levels (< 2 at %) [18]. The above behaviour suggests that Al atoms in the film do not contribute to the dopants, thus, an increasing amount of Al atoms remains in the layer of ZnO electrically inactive above some doping level. This

can be explained by the formation of the neutral impurities from the extra Al atoms. Electronic mobility also shows similar [18] behaviour as free electron carrier concentration, because it can be diminished by any type of disturbance of the periodic lattice potential. Major scattering centres are grain boundaries, ionized point defects and neutral impurities which all arise with too big Al-doping.

Moreover, at high Al-dopant concentration there is a drastic degradation in the film crystallinity [18], because Al-dopant tends to create more nucleation centers during the deposition process and as a consequence, the doped films have smaller crystallite sizes.

For ZnO:Al one can observe wider band gap due to Burstein-Moss effect caused by Al-dopant [19]. Since ZnO is naturally n-type material, it Fermi level will be inside the conduction band when it is heavily doped, thus, the states below the Fermi level are filled and the absorption edge should shift to the higher energies which results in observed wider energy band gap.

The valence electrons of the transition metals (Zn) or the electrons which they use to combine with other elements are present in more than one shell, thus, they often exhibit several common oxidation states. Metal (Al), unlike the transition metal, does not exhibit variable oxidation states and its valence electrons are only present in their outer shell [20].

In this paper, zinc oxide doped aluminium films (ZnO:Al) were prepared by dip-coating technique. Optical properties of ZnO:Al thin film were characterized by THG experiment. The effect of post-heating temperature and thicknesses (number of layers), on the structural and optical properties were investigated.

2. Theoretical approach

The third harmonic generation is a third order nonlinear optical process where a coherent field at the pulsation 3ω is generated through nonlinear polarization in the material from the fundamental field at the pulsation ω. The output intensity of the third harmonic generated in the nonlinear medium, which is optically transparent, is given by the well known relation [21]:

$$I_{3\omega} = \frac{2304\pi^6}{n_{3\omega} n_\omega^3 \lambda_\omega^4 c^2} \left|\chi^{(3)}\right|^2 I_\omega^3 L^2 \frac{\sin^2\left(\frac{\Delta kL}{2}\right)}{\left(\frac{\Delta kL}{2}\right)^2} \qquad (1)$$

where I_ω and λ_ω are the intensity and the wavelength of the fundamental beam, respectively. L is the thickness of the medium. $\chi^{(3)}$ is the third order nonlinear optical susceptibility, c corresponds to the light speed in the vacuum. Δk is the wave-vector mismatch between the fundamental and third harmonic waves.

In the case of thin films that possess weak absorption, Wang et al. [22] derived a simplistic and useful formula (2) that we use for our study.

$$\chi_f^{(3)} = \left(\frac{2}{\pi}\right)\left(\frac{l_{C,S}}{d_f}\right)\left(\frac{I_{f,M}^{TH}}{I_{S,M}^{TH}}\right)^{1/2} \chi_S^{(3)} \qquad (2)$$

where the subscribed letter S and f refers to the silica used as reference material and the film, respectively. $\chi_i^{(3)}$ ($i = f, S$) is the third order nonlinear optical susceptibility. $I_{f,M}^{TH}$, $I_{S,M}^{TH}$ are the maximum intensities of the envelope of TH generated by the layer and by the reference material, respectively. d_f and ($l_{C,S}$) are the thickness of the thin layer and the coherence length of the silica, respectively.

3. Samples preparation

ZnO:Al samples were prepared by the dip-coating technique. The details of the sol preparation are given in [23]. Zinc oxide precursor sol was prepared by mixing zinc acetate ($Zn(CH_3CO_2)_2$,$2H_2O$ and aluminium nitrate ($Al(NO_3)_3$,$9H_2O$ with isopropanol by molar ratio of 1:55 and 1:55, respectively. The atomic ration of Al/Zn atoms in the final solution was estimated to be about 0.8%. The solution was stirred thoroughly for 15 min on magnetic stirrer after which 0.57 ml of diethanolamine (DEA, $C_4H_{11}NO_2$) was added to further dissolve ZnAc. The mixture was stirred for 2h before used for dip coating deposition. Every layer of the sample was done by the same way. First, the substrate was dipped into the solution withdrawn at the rate of 6 cm/min and after 3 seconds was removed with the same speed. The coated substrates were dried for 10 minutes at RT and next, after each dipping were heated at 200°C for 10 minutes in the air. Thickness of one layer was estimated equal (30 ± 5) nm. By repeating the above procedure, ZnO:Al films of different thicknesses were obtained. Finally after depositing all the layers, sample was baked in the oven for 1 hour in high constant temperature (the speed of putting sample by hand into oven and taking out it was as slow as was possible). Pre-heat treatment of the film expelled the water and solvent molecules resulting in the film. Post-heat treatment relieved the stresses in the film and induced the crystallization of the film. There were investigated two sets of the double-sided samples. First set contains six samples with five layers on the quartz substrate (SiO_2), post-heated at different temperatures T. Second set contains six samples with different number of layers on the glass substrate, post-heated at the constant temperature (T=500°C). For the both sets of samples the substrates were dipped into the solution and withdrawn at a rate of 6 cm/min.

4. Experimental setup

THG experiment was performed using a Q-switched Nd:YAG laser (continuum) working at the fundamental wavelength λ_ω = 1064 nm, with 10 Hz rate repetition and 16 ps pulse duration. The experimental set up is depicted in Fig. 1. The fundamental beam is firstly split in two parts by a beam splitter. One part of the beam is detected by the photodiode synchronising all electronics with the pulse repetition rate. The other part of the beam passes through "half-wave plate – Glan polarizer" system which allows adjusting the intensity of incident beam. This latest beam is also split in two parts. One is spitted to the photodiode recording the incident beam intensity, and the other part passes through a convergent lens before reaching the sample placed on a rotating stage. In order to avoid sample thermal damages, the focal point is located before the sample. The third harmonic beam generated from the sample is weakened by neutral density filters and selected by an interferential filter, then is recorded by the photomultiplier tube. Measurement is performed by Maker fringes technique that corresponds to the third harmonic intensity variations versus incident angle. The THG measurements were performed at room temperature and calibrated using a thin slab of fused silica.

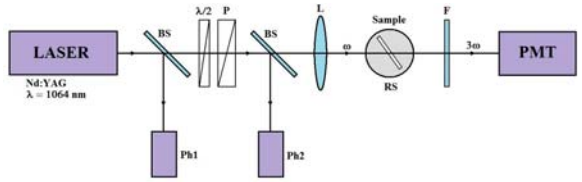

Fig. 1. Third harmonic generation experimental setup. λ/2: is a half wave plate; P: is a Glan polarizer; Ph1 and Ph2 are the synchronisation photodiode and photodiode of control; RS: beam splitter; F is a selective filter at 355 nm and the PMT corresponds to the Photomultiplier Tube.

5. Results and discussion

For THG measurements, only the maximum intensities exhibited by the ZnO:Al samples and observed on the Maker fringes are taken in account in this study. Due to the dipping process during the dip coating technique, the ZnO:Al is deposited on both side of the substrate and can lead to the enhancement of the optical nonlinearities. It is known that thin layers grow to minimize the surface free energy and in the case of ZnO crystallites, the density of surface energy of the wurzite (002) orientation is the energetically lowest which means that orientation of crystallites with c-axis orientation perpendicularly to the substrate is favourable. As we know [24], typical dip-coated ZnO:Al films are mainly polycrystalline structure with c-axis perpendicular to the substrate surface. The relative intensity of the (002) peak change with heating temperature and doping concentration. Structural change of ZnO from amorphous to more ordered state takes place around 445˚C [25]. Fig. 2 shows the increasing of the normalized third harmonic signal intensity as function of the post heating temperature. The studied samples were prepared by the same way and have the same thicknesses (about 150 nm), and were annealed after deposition at the T=500°C. This figure confirms the previous assumptions in which the crystalline structure increases with the increasing of the post-heating temperature. Such trend is observed with the increasing of the normalized third harmonic signal with the temperature. The well-defined increase of the THG response for the samples the post deposition annealing temperature probably is due in part to the increase energy band gap with annealing temperature of ZnO:Al layers and lowering absorption for resonant conditions experienced by the third harmonic wave. By measuring the Maker Fringes of ZnO:Al samples, the electronic contribution of the nonlinear coefficient of the samples can be extracted using equation (2). Because of it well known nonlinear third order optical properties, fused silica was us as reference material [26].The air contribution to these NLO was neglected. In principle, both the deposited films and the substrate contribute to the detected THG signal (the sample was placed before the focal point in order to avoid thermal damages). Moreover, since the film is deposited on both side of the substrate, the experimental configuration is symmetric from a geometrical viewpoint and relations have been developed in order to fit for both side are identical.

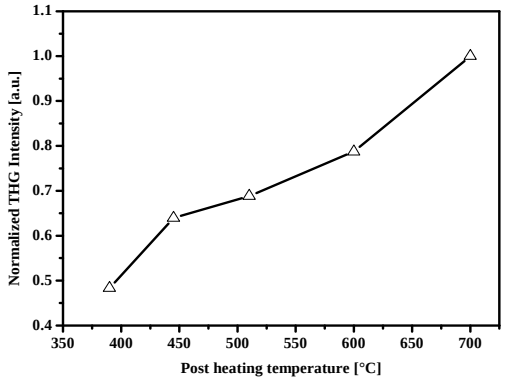

Fig. 2. Normalized THG intensity of ZnO :Al thin film versus post-heated temperature

There is an orientation of the average optical axis normally to the surface. Most crystal grains have c-axis oriented along the normal to the substrate for the ZnO:Al films post heated. Although the increasing crystallization

order degree with the temperature appears as a main potential parameter that can be involved to explain the observed THG signal behaviour, the others parameters should not be forgotten. We can not be sure that this is the main cause because refractive index and thickness of the dip-coated films depends also, on the temperature treatment. In Fig.3 intensities of the third harmonic generated beam of ZnO:Al films, post-heated at the T=500°C with different number of the layers are presented. For only one layer, the initial micro crystallites are deposited randomly on the substrate and possibly acted as the seeds for further growth process. It means that this is only the beginning of the crystallization process when the film does not have predominant c-axis orientation. Doubling the thickness of dip-coated film caused slightly increases the crystallite size but does not change the crystallographic orientation [18], so that, it improves the films crystallinity which can have enhancing effect on the THG. This phenomenon can be connected with the increase of THG signal with the number of the layers (except last sample with 10 layers). However, like in the case of the ZnO:Al films post-heated at different temperatures also here, beside different thickness, some effect can have refractive index increase of dip-coated film with thickness. Therefore in the case of all ZnO:Al samples it is necessary to measure precisely thickness and refractive index, probably for each sample in order, to calculate third order susceptibility from (2), then we can know the nonlinearity of particular sample and connect it with its properties.

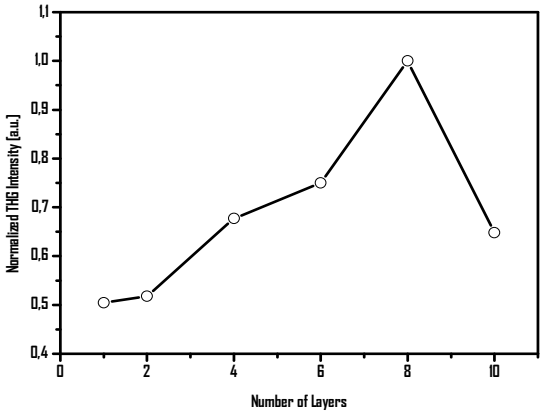

Fig. 3. Normalized THG intensity of ZnO:Al thin film versus number of deposited layers

THG measurements have been performed on a ZnO:Al film deposited on both sides of 1 mm thick silica glass substrates. The thickness of the substrate was chosen in order to optimize Maker fringes data acquisition and analysis. Moreover, since the films are deposited on both side of the substrate, the experimental configuration is symmetric from a geometrical viewpoint.

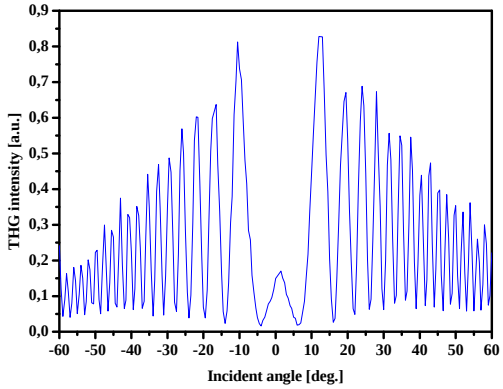

Fig. 4. Experimental Maker fringes of THG of silica glass (1 mm thick) obtained at 1064 nm.

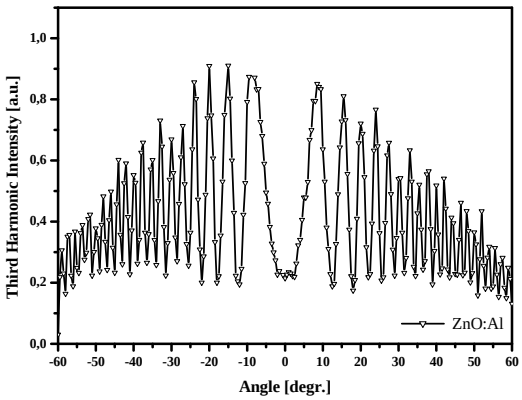

Fig. 5. Experimental Maker fringes of THG of ZnO:Al on both sides of silica glass substrates obtained at 1064 nm.

In Fig. 4, and 5 typical Maker fringe patterns are reported both for the silica glass substrate and for the ZnO:Al film deposited on a 1 mm thick silica glasses at the room temperature and next annealed at 450˚C. Both shown TH intensities are given in arbitrary units. The values of the $\chi^{(3)}$ coefficients are calculated relative to a standard fused silica sample. As we can see from Fig. 5 we obtained good Makers fringes for ZnO:Al layers deposited on silica glass substrates that shows the well crystallization of the sample.

6. Conclusions

Thin films of zinc oxide doped aluminium (ZnO:Al) were prepared by the dip-coating method and their third order nonlinear optical properties investigated using the THG experiment. THG technique applied to the ZnO:Al films heated above 445 °C confirm that the most crystal grains have c-axis oriented along the normal to the substrate. According to the obtained experimental data, we note that the structure and the surface quality of the overall films are reflected by THG results. We demonstrate clearly that ZnO and ZnO:Al thin films are attractive nonlinear optical material for optoelectronic applications. Future studies are expected using others dopants and film structure in order to determine the influence on its nonlinear optical properties and to deduce correlation between nonlinear optical properties and structures.

Acknowledgements

This work is partially supported by Physics, Astronomy and Informatics faculty of Nicholas Copernicus University in Poland and POMA Laboratory at the University of Angers. The authors acknowledge MSc L. Borszewski from N. Copernicus University, Institute of Physics, Torun, Poland, for the help in deposition of zinc oxide layers by dip-coating method.

References

[1] A. Mitra, R. K. Thareja, App. Phys. Lett. **89**, 2025 (2001).
[2] D. M. Bagnall, Y. F. Chen, M. Y. Shen, Z. Zhu, T. Goto, T. Yao, J.Cryst . Growth **184/185**, 605 (1998).
[3] I. Ohkubo, A. Ohtomo, T. Ohnishi, Y. Mastumoto, H. Koinuma, M. Kawasaki, Surf. Sci. L1043 1999.
[4] Z. Fu, B. Lin, J. Zu, Thin Solid Films **402**, 302 (2002).
[5] Y. Nakata, T. Okada, M. Maedo, Appl. Surf. Sci. **197/198**, 368 (2002).
[6] D. C. Look, Mater. Sci. Eng. B **80**, 381 (2001).
[7] A. Zappettini, F. D'Amore, S. M. Pietralunga, A. Terio, M. Martenelli, D. F. Bliss, M. J. Callahan, Phys. Stat. Sol. C **1** (4), 997 (2004)
[8] T. Dietl, H. Ohno, F. Matsukura, J. Cibert, D. Ferrand, Sciences **287**, 1019 (2000).
[9] W. Shen, Y. Zhao, C. Zhang, Thin Solid Films **483**(1-2), 382 (2005).
[10] T. K. Gupta, J. Am. Ceram. Soc. **73**(7), 1817 (1990).
[11] S. Ganesan, Z. C. Feng, D. Mehta, S. Kandoor, E. J. Wornyo, J. Nause, I. Ferguson, Mat. Res. Soc. Sym. Proc. **799**, 249 (2003).
[12] F. Ding, F. Zhengwen, Q. Qizong, Electrochem. Sol. St. Lett. **2**(8), 418 (1999).
[13] J. E. Jaffe, A. C. Hess, Phys. Rev. B **48**, 7903 (1993).
[14] U. Neumann, R. Grunwald, U. Griebner, G. Steinmeyer, W. Seeber, Appl. Phys. Lett. **84**, 170 (2004).
[15] B. Derkowska, B. Sahraoui, X. Nguyen Phu, W. Bala, Nonlinear Optics. **27**, 413 (2001).
[16] Z. Sofiani, A. M. Lamraoui, B. Derkowska, R. Adhiri, L. Dghoughi, N. Fellali, M. Addou, W. Bala, B. Sahraoui, Journal of Applied Physics **101**, 063104 (2007).
[17] Z. Sofiani, S. Dabos-Seignon, B. Derkowska, P. Dalasinski, M. Wojdyla, A. M. Lamraoui, L. Dghoughi, M. Addou, W. Bala, B. Sahraoui, Optics Communications **267**(2), 433 (2006).
[18] R. Bel Hadj Tahar, J. Eur. Cer. Soc. **25**(14), 3301 (2005).
[19] F. K. Shan, Y. S. Yu, Thin Solid Films **435**(1-2), 174 (2003).
[20] http://www.chemicalelements.com/show/name.html.
[21] G. I. Petrov, V. Shcheslavskiy, V. V. Yakovlev, I. Ozerov, E. Chelnokov, W. Marine, Appl. Phys. Lett. **83**(19), 3993 (2003).
[22] X. H. Wang, D. P. West, N. B. McKeown, T. A. King, J. Op. Soc. Am. B **15**, 1895 (1998).
[23] http://www.science.unitn.it/ ~ gcsmfo/facilities/dip-coating.html.
[24] R. Maity, S. Kundoo, K. K. Chattopadhyay, Solar Energy Materials & Solar Cells **86**, 217 (2005).
[25] S. Bandyopadhyay, G. K. Paul, R. Roy, S. K. Sen, S. Sen, Mat. Chem. Phys. **74**, 83 (2002).
[26] F. Kajzar, J. Messier, Phys. Rev. A, **32**, 2352 (1985).

*Corresponding author: hend_ida@yahoo.fr