Plasma enhanced chemical vapor deposition of thin ZnO layers at low temperatures♣

M. MINCHEV*, S. KITOVA, G. DANEV
Central Laboratory of Photographic Processes, Bulgarian Academy of Sciences, Acad. G.Bonchev Str., Bl. 109, 1311 Sofia, Bulgaria

The plasma enhanced chemical vapor deposition (PECVD) is a powerful and flexible instrument for depositing thin layers, nanocomposites or nanostructures. In this work, thin ZnO layers have been grown by PECVD (RF - 13.56 MHz) on optical glasses (BK7), Si wafers and polycarbonate (PC), at a substrate temperature of ~ 40℃. Zn acetylacetonate contained in a resistively heated Knudsen cell has been used as a precursor, and oxygen as an oxidant. A system for dosed injection of the precursor or oxidant into the plasma reactor has been developed. The influence of the RF power and oxygen pressure on the composition, structural and optical properties of the ZnO layers has been studied. The results show that the carbon content in the layers decreases, and more Zn atoms are bound to oxygen, with increasing RF power and oxygen pressure. The layers obtained at the highest RF power and O_2 gas ambient pressure were amorphous, with high optical transmission in the visible region and and E_g of 3.36 eV, which is very close to that of bulk ZnO material. These characteristics make the layers suitable for applications as transparent windows for the visible and infrared regions, and as optical filters for the UV region.

1. Introduction

Recently, zinc oxide (ZnO) has been being paid significant scientific and technological interest, due to its high chemical and thermal stability, high mechanical strength, high piezoelectric coefficient, high exciton binding energy (60 meV) and wide band gap (3.37 eV) [1]. ZnO layers are widely used in gas sensors, transparent electrodes, thin layer transistors, displays, solar cells and other optoelectronic devices [1, 2]. In all these applications, the formation of high quality ZnO on amorphous substrates, which are in most cases temperature sensitive, is necessary in order to improve the performance of such devices and to develop novel devices.

It is well known than the ZnO layer properties depend to the great extent on the deposition methods and the processing variable used. ZnO layers can be synthesized by a variety of methods such as pulsed laser deposition, sputtering, sol-gel deposition, spray pyrolysis and metal-organic chemical vapor deposition (MOCVD) [1-4]. Among these, MOCVD can offer high growth efficiency, large area uniformity and the suitability for growing components containing volatile elements [3]. Plasma enhanced MOCVD (PECVD) technology is one of the most attractive for the synthesis of ZnO layers at low and moderate substrate temperatures, and minimal impact upon them. Diethylzinc and dimethylzinc are usually applied as precursors in the PECVD process [1, 4]. Nevertheless, these precursors are less desirable because of their high toxicity. Zinc acetylacetonate ($Zn(acac)_2$) has a lot of advantages such as non-toxicity, inflammability, low vaporization temperatures (250℃), and low thermal decomposition temperatures (150-500℃). However, in the most studies $Zn(acac)_2$ is used as a precursor in atmospheric or low pressure CVD, at substrate temperatures above 250℃ [4-6].

In this paper, the ZnO layers have been grown by PECVD using $Zn(acac)_2$ and O_2 gas as reactants. The effect of the technological parameters of PECVD on the composition, structural and optical properties of the ZnO layers grown at a low substrate temperature (~ 40℃) on BK7 glasses, optical grade polycarbonates and Si wafers has been investigated.

2. Experimental

ZnO layers were grown in PECVD equipment (GENUS 8720). The gas plasma was excited by a 13.56 MHz RF generator. The RF power (W_p) was varied in the

---

range 600 - 2500 W. The base unit was equipped with a resistively heated cell of Knudsen type, where a Zn(acac)$_2$ hydrate powder tablet was placed in a Mo crucible. The Zn source was heated to 140⁰C. The stable precursor temperature resulted in a stable precursor flow rate, even if we could not directly measure the it. O$_2$ gas was introduced into a gas line between the cell and chamber at a constant flow rate. By varying the gas flow rate, the chamber pressure was kept at different ranges from 60 to 300 mTorr. A system for dosed injection of the precursor and oxidant in the plasma reactor was developed.

All substrates of BK7 glass, optical grade polycarbonate and Si wafers were carefully cleaned. In order to improve the adhesion of the deposited layers, especially on the PC substrates, we treated substrates with a 3:1 Ar/O$_2$ plasma gas mixture of short duration (from 20 to 40 s) [7]. Our study showed that the substrate temperature rose to about 40⁰C during the layer deposition process.

The thickness of the layers was measured by a profilometer type Talystep with an accuracy of ±5nm.

The crystal structure of the layers was characterized by XRD diffraction (XRD), using a DRON-3 automatic powder diffractometer.

The surface morphology of the layers was examined by a scanning electron microscope (Philips 515).

The analysis of the composition of the layers deposited on Si wafers was done using an ESCALAB MkII electron spectrometer. The spectra were excited with a AlKα source with energy 1486.6 eV. The photoelectron lines of C 1s, Zn 2p and O 1s were recorded from the layer surfaces, without preliminary ion cleaning. All spectra were calibrated using the C1s line at 285eV as a reference.

The transmittance (T) and specular reflectance (R) of the samples were measured at normal light incidence in the spectral range λ = 300-1000 nm, by a Cary 5E spectrophotometer with an accuracy of ±0.5%. The measured transmittance and reflectance data, corrected for the contributions of the glass substrates [8], were used for determining the absorption coefficient of the layers, according to:

$$T_f = (1 - R_f)\exp(-\alpha d) \qquad (1)$$

where T_f and R_f are the transmittance and reflectance of the layer, and d is the layer thickness.

Since ZnO is a direct band gap material, the optical gap was determined as [9]

$$(\alpha h\nu)^2 = A(h\nu - E_g) \qquad (2)$$

where $h\nu$ is the photon energy, E_g is the optical band gap, and A is a constant.

3. Results

In this study, layers deposited at different RF powers, O$_2$ gas ambient pressures and low temperature of the

substrate (~ 40⁰C), without additional heating, have been characterized. The deposition rate was kept at 0.3 - 0.4 nm s^{-1}. One of the most effective ways of determining the layer composition quantitatively and the chemical state of the constituent elements is to analyze the XPS spectra. Fig. 1 presents the O 1s, Zn 2p and C 1s spectra of layers deposited at different RF powers and a fixed ambient oxygen pressure of 240 mTorr. For comparison, spectra of a layer deposited only by thermal evaporation without plasma impact are also shown.

Fig. 1 shows that the O 1s peaks can be consistently fitted with two nearly Gaussian (combination of 80% Gaussian and 20% Lorentzian distribution) curves, centred at 530.3 and 531.8 - 532.2 eV. The high binding energy peaks are usually attributed to the presence of loosely bound oxygen on the surface of the layers belonging to a specific species, e.g. the –CO$_3$ group, adsorbed O-H or O$_2$ [10]. The low energy peak (at 530.3 eV) is assigned to oxygen atoms in a ZnO matrix [10]. The intensity of this peak is a measure of the amount of oxygen atoms in a fully oxidized stoichiometric surrounding. As seen from Fig. 1, the quantity of these oxygen atoms increases significantly with increasing RF power.
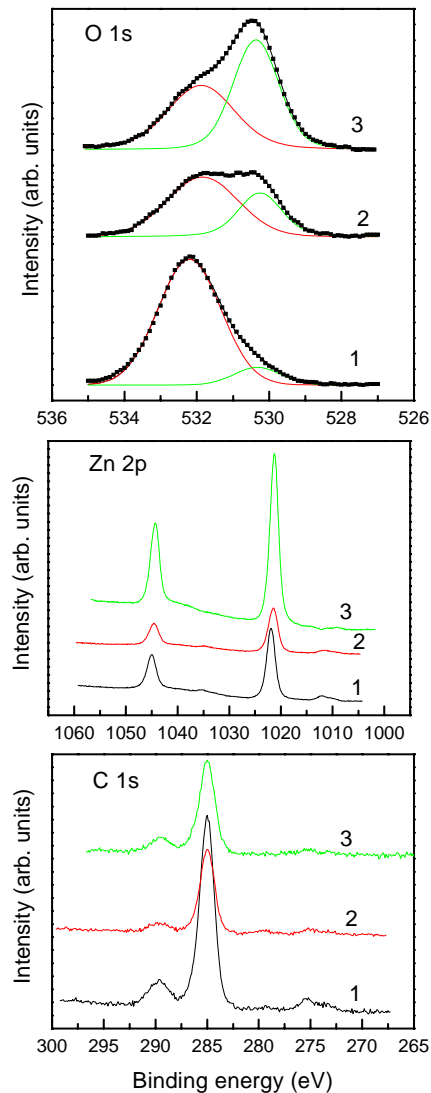
Fig. 1. O 1s, Zn 2p and C 1s spectra of layers deposited at a fixed ambient O_2 pressure of 240 mTorr and different W_p: (1) without W_p; (2) 1200 W; (3) 2500 W. In the case of the O 1s spectra, the dots are the measured data and the full curve is the results of the fit

Fig. 1 indicates that in the Zn 2p region, there are two peaks within the ranges 1021.9 -1021.3 eV and 1045 - 1044.3 eV, which correspond to the binding energies of Zn $2p_{3/2}$ and Zn $2p_{1/2}$ respectively. These values are in good agreement with those in the literature for ZnO [11]. The energy difference between these two peaks is 23-23.1 eV which is the characteristic value for ZnO [11]. From Fig. 1, it is seen that the Zn 2p binding energy shifts slightly (0.6 eV) towards a lower energy as the RF power increases, which shows that more Zn atoms are bound to oxygen.

The C 1s spectra of the layers shown in Fig. 1 indicate a large amount of carbon species on the layer surfaces. The C 1s peak at 285 eV is due to carbon, coming mainly from the exposure of the samples to ambient atmosphere. The smaller C 1s peaks at 289.5 eV are due to C-O and C=O bonds present in acetyl acetate ligands. Those contributions are also found in the O1s peaks at higher binding energies. As seen from Fig. 1, the intensity of the C1s peak at higher energy decreases as the RF power increases. This result indicates that more effective dissociation of acetyl acetate ligands proceeds with increasing RF power. The influence of the RF power and oxygen pressure on the layer stoichiometry is summarized in Table 1

Table 1. Atomic concentration of ZnO layers and atomic ratios Zn/O, Zn/C

W_p (W)	P mTorr	C1s (%)	Zn $2p_{3/2}$ (%)	O1s (%)	Zn2p/ O1s/	Zn2p/ C1s
0	240	48	14	38	0.37	0.29
1200	120	64	6	30	0.2	0.09
1200	240	45	19	36	0.53	0.42
2500	240	25	32	43	0.74	1.28

It is seen that the content of carbon included in the layers decreases, and more Zn atoms are bound to oxygen with increasing the RF power and oxygen pressure, as a result of the more effective dissociation of acetyl acetate ligands and the growth of ZnO. For layers deposited at the highest RF power of 2500 W and an oxygen pressure of 240 mTorr, the atomic ratios Zn/O and Zn/C attain the highest values of 0.74 and 1.28 respectively. Our preliminary results indicate that the deposition of the layer at a substrate temperature of 250ºC or their thermal annealing within the range 250 – 400ºC under an oxygen atmosphere do not improve the layer stoichiometry.
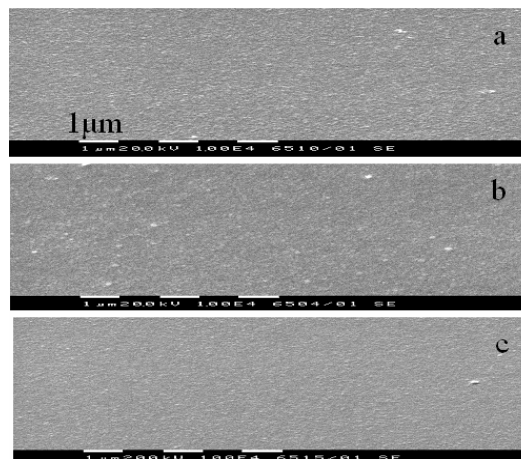

Fig. 2. SEM micrographs of 130 nm thick layers deposited at W_p=2500 W, P=240mTorr on substrates of: (a) BK7 glass, (b) Polycarbonate (c) Si wafers.

The surface morphologies of the layers deposited at different RF powers and O_2 gas ambient pressures was investigated by SEM. The results obtained show that the layer surface is uniform, smooth, and with no defined structures, which is in correspondence with XRD results indicating amorphous layers. Fig. 2 illustrates SEM micrographs of the layers deposited at the highest W_p and P on different substrates.

Fig. 3 shows the optical transmittance curves of 130 nm thick layers deposited on BK7 glass substrates at different RF powers and gas pressures. For comparison, the transmittance of BK7 glass is also given. The transmission of all layers in the visible and near infrared region is over 80%, and the layers are highly transparent in the UV region between 360 and 390 nm, where the absorption edge of the intrinsic ZnO is located. The transmission of sample 3 decreases more sharply than that of the samples 1 and 2. This result is an indication of the higher content of stoichiometric ZnO in sample 3.
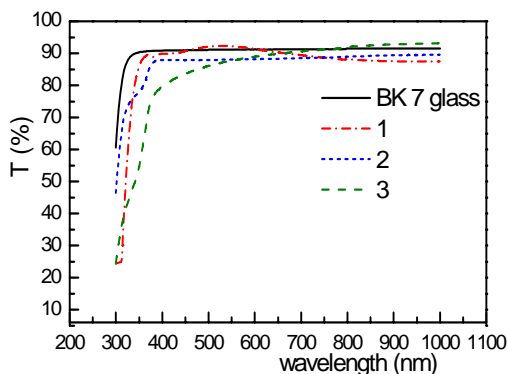
Fig.3. Optical transmittance spectra of BK7 glass and 130 nm thick ZnO layers deposited on BK7 glasses at different W_p and P: (1) 1200 W/120 mTorr; (2) 1200 W/240 mTorr; (3) 2500 W/240 mTorr.

By plotting $(\alpha h v)^2$ vs $(h v)$ and extrapolating the linear portion of this curve to $(\alpha h v)^2 = 0$, the values of the optical band gap E_g obtained for samples 1, 2 and 3 are 3.62 eV, 3.39 eV and 3.36 eV respectively. Obviously, the layers obtained at the highest RF power and O_2 gas ambient pressure have Eg values very close to that of the ZnO bulk semiconductor (3.37 eV) due to the highest content of stoichiometric ZnO, as found by the XPS analysis.

4. Conclusions

Thin ZnO layers were obtained by PECVD at low substrate temperatures of glass, PC and Si wafers. The raw material was $Zn(acac)_2$ which is non-toxic and easy to handle. The results from XPS analysis indicated that the layers obtained at the highest RF power and O_2 gas ambient pressure had the high content of stoichiometric ZnO. These layers were amorphous, with high optical transmission in the visible region and E_g values very close to that of ZnO bulk material. Due to these characteristics, the layers obtained can be used as transparent windows for the visible and infrared region, and optical filters for the UV region. The layers are also potential materials for producing transparent conducting electrodes, most probably after doping with a metal (e.g. Al). The investigation of their electrical properties is under further investigation.

References

[1] V. Karpina, V. Lazorenko, C. Lashkarev, V. Dobrowolski, L. Kopylova, V. Baturin, S. Pustovoytov, A. Karpenko, S.Erimin, P. Lytvyn, Cryst. Res. Technol. **39**, 98 0 (2004).
[2] B. Zhang, C. Liu, Y. Segawa, Y. Kashiwaba, H. Haga, Thin Solid Films **474**, 165 (2005).
[3] Y. Ma, G. Du, J. Yin, T. Yang, Y. Zhang, Semicond. Sci. Technol. **20**, 1198 (2005)
[4] U. Ozgur, Y. Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. Dogan, V. Avrutin, S. J. Cho, H. Morkoc, J. Appl. Phys. **98**, 041301 2005.
[5] K. Haga, P. Wijesena, H. Watanabe, Appl. Surf. Sci. **169-170**, 504 (2001).
[6] M. Purica, E. Budianu, E. Rusu, M. Danila, R. Gavrila, Thin Solid Layers **403-404**, 485 (2002).
[7] S. Kitova, M. Minchev, G. Danev, JOAM **7**, 2607 (2005).
[8] A. Djurisic, T. Fritz, K. Leo, E. Li, Appl. Opt. **39**, 1174 (2000).
[9] K. Kim, K. Park, D. Ma, J. Appl. Phys. **8**1, 7764(1997).
[10] M. Chen, X. Wang, Y. Yu, Z. Pei, X. Bai, C. Sun, R. Huang, L. Wen, Appl. Surf. Sci. **158**, 134 (2000).
[11] Handbook of X-ray and Ultraviolet Photo-electron Spectroscopy; ed. D.Briggs, Heidlin, London (1988).

*Corresponding author: misho@clf.bas.bg