Structural properties of ZnO layers deposited on glass substrates by PECVD

S Kitova1, R Kazakov and G Danev

Acad. J. Malinowski Institute of Optical Materials and Technologies,
Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bl. 109, 1113 Sofia, Bulgaria

E-mail: skitova@clf.bas.bg

Abstract. Thin ZnO layers were grown by metal-organic plasma-enhanced CVD (RF - 13.56 MHz) on glass substrates without and with ZnO seed film. The properties of the ZnO layers obtained were studied in dependence of the partial oxygen pressure by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The results obtained show that by controlling the partial oxygen pressure during the layer growth one can control the crystallinity and texture of the layers obtained on pure glass substrates. It was found that ZnO layers deposited at low O2 pressure have well-developed grain structures with a predominant c-axis phase and better crystalline quality than that of the samples obtained at high partial oxygen pressure. In the presence of ZnO seed films, the formation of c-axis phase and its quality are less dependent on partial $P_{O_2}$. Nanorods with good alignment and orientated vertically with respect to the substrate surface can be observed in the layers deposited on glass substrates with ZnO seeds and substrate temperature of 400°C at low content of O2 in the plasma. This behavior is interpreted in the framework of the so-called preferential nucleation and preferential grain growth.

1. Introduction
Zinc oxide (ZnO) thin films find a wide range of technological applications as sensors, heat mirrors, transparent electrodes, solar cells, piezoelectric and other optoelectronic devices [1-4]. So far, various deposition techniques have been applied, such as thermal evaporation, pulsed laser deposition, sputtering, sol-gel deposition, template assisted and solution processes, molecular beam epitaxy, metal-organic chemical vapor deposition MOCVD, in order to grow high-quality crystalline ZnO layers on substrates of practical importance, such as sapphire, Si wafer and glass substrates (for review see [3, 4]). Among them, MOCVD can offer high growth efficiency, large area uniformity and suitability for growing components containing volatile elements [5]. The plasma enhanced MOCVD (PECVD) technology is one of the most attractive for the synthesis of ZnO layers at low and moderate substrate temperatures and a minimal impact on the substrate. Diethylzinc and dimethylzinc are usually applied as precursors in the PECVD process [1, 6]. However, the use these precursors is not desirable because of their high toxicity and flammability. Zinc acetylacetonate (Zn(acac)2) should be a good candidate for use in th low-temperature fabrication of crystalline ZnO layers because of its
non-toxicity and inflammability, low vaporization temperatures (150–250 °C), high vapor pressure [6]. However, (Zn(acac)2) has rarely been used as a precursor.

It is well known that structures of synthesized ZnO are dependent on the processing conditions, such as working pressure, substrate temperature, deposition power and gas mixture [1, 3, 7-9]. Selective growth of high-quality ZnO nanorods on Si substrates at 800-900 °C has been demonstrated using a pattern thin film of ZnO as a seed layer [10].

In this work, the structural properties of ZnO layers deposited on glass substrates with and without ZnO seeds were studied in dependence of the partial oxygen pressure. The layers are grown by PECVD using Zn(acac)2 and O2 as reactants.

2. Experimental

ZnO layers were grown in a PECVD equipment (GENUS 8720). The gas plasma was excited by a 13.56 MHz RF generator at RF power of 2000 W [11]. Oxygen gas and Zn(acac)2 (Zn(C5H7O2)2.2H2O) (Sigma-Aldrich) were used as precursors. The Zn source was sublimated by heating up to 140 °C and carried by nitrogen gas to the growth chamber at a constant partial nitrogen pressure, PN2, of 70 mTorr. The stable precursor temperature resulted in a stable precursor flow rate, even if we could not directly measure it. O2 gas was introduced separately into the reaction chamber in order to prevent any pre-reaction of the two precursors. Additional Ar gas was injected through a separately connected gas line in order to keep a constant total pressure, Ptot, of 280 mTorr. The temperature of the substrates, Ts, was 400 °C. The thickness of the layers of about 300-500 nm was measured by a profilometer type Talystep. The layers were deposited on Corning glass substrates, preliminary carefully cleaned. The cleaning procedure first involved washing by a 1% detergent solution and then with deionized water in an ultrasonic cleaner. Very thin ZnO seed films of about 3-5 nm were formed by spin coating (500 rpm, 180 s) of 20 mM Zn(CH3COO)2.2H2O (Sigma Aldrich) solution in ethanol followed by thermal treatment for 1 h at 400 °C in air.

The crystal structure of the layers was characterized by XRD diffraction (XRD), using a Philips (PW 1710) apparatus with Cu-Kα radiation separated by a graphite focusing monochromator. The intensity and full width at half maximum (FWHM) of a (hkl) plane were determined by profile fitting procedure using a Voight or Gaussian peak shape. Schererrer’s equation was used to estimate the average crystallite size. The surface morphology of the layers was examined by a scanning electron microscope (SEM Philips 515).

3. Results and discussion

The results obtained show that the deposition rate Rd of the layers depends on the partial oxygen pressure PO2. As seen in figure 1, the layers deposited at low PO2 grow more slowly that those deposited at higher PO2. The presence of a seed film on the glass substrate facilitates the layer growth at low PO2. The XRD analysis indicates that all the ZnO layers deposited at different PO2 and at substrate temperature of 400 °C are polycrystalline. Three peaks are observed which can be indexed to (1010), (0002) and (1011) planes of the hexagonal wurtzite structure of the ZnO crystal. The results show that the crystallites are preferentially oriented along the c-axis direction perpendicular to the substrate surface, as the (0002) reflection is enhanced relatively to the usual (1010) maximum reflection of ZnO. In order to quantify the preferred orientation (PO), often called texture, in the crystalline films, the texture coefficient (Tc) was calculated [11]. The sample with randomly oriented crystallites exhibits Tc(hkl) = 1, while the higher value of Tc indicates the larger abundance of crystallites oriented at the (hkl) direction.

Figure 2 presents the influence of the partial oxygen pressure on Ts, the FWHM and the grain size calculated from the XRD patterns of the highly oriented (0002) peaks. The high value of Tc, of about 4.5, the narrow full-width of 0.22 – 0.35 and the grain size of 33 – 23 nm are indications of a predominant c-axis phase with good crystalline quality formed on pure glass substrates at oxygen partial pressure of up to 150 mTorr. As it is seen in figure 2, the further increathease of PO2 in the
plasma gases leads to a steep decrease in $T_c$ to 1.6 and to FWHM broadening 1.5. Correspondingly, the average crystallite size, which is inversely proportional to the FWHM, decreases to the smallest value of 6 nm. These results are indicative of a lesser amount of a $c$-axis preferred phase with smaller size and worse crystalline quality grown at $P_{O_2}$ higher than 150 mTorr. As a rule, as the oxygen partial pressure is increased, the crystalline quality degrades from a single oriented crystal to a polycrystalline structure. Further raising the oxygen pressure resulted in preventing the film growth on the glass substrates. It should be noted that we observed a similar dependence for ZnO layers deposited on a Si wafer [11], but the partial oxygen pressure influence is expressed more strongly in the case of amorphous glass substrates. The data presented in figure 2 indicate that $T_c$, FWHM and grain size are less dependent on the partial pressure $P_{O_2}$ in the presence of ZnO seeds on the glass substrate.

![Figure 1: $R_d$ vs the partial oxygen pressure $P_{O_2}$.](image1)

![Figure 2: $T_c$, FWHM and grain size calculated from XRD patterns of the highly oriented (0002) peaks vs $P_{O_2}$ for layers grown on glass substrates without and with ZnO seeds.](image2)

The results obtained are consistent with the data by SEM observations. Figure 3 shows top- and cross-sectional view SEM images of the layers grown on glass substrates with and without ZnO seeds at different partial oxygen pressures. The images show the well-developed grain structure of the layers deposited on pure glass substrates at low $P_{O_2}$ in plasma and the denser and smoother surface of layers deposited at high $P_{O_2}$ in plasma. Only the layers deposited at low $P_{O_2}$ in plasma exhibit columnar structure. In accordance with the results by XRD study all layers deposited on glass substrates with ZnO seeds exhibit a well developed grain structure. Nanorods with good alignment, vertically oriented to the substrate surface can be seen in the layers deposited at low content of O$_2$ in the plasma gases.

![Figure 3: Top- and cross-sectional view SEM images of the layers grown on glass substrates without and with ZnO seeds at the indicated $P_{O_2}$.](image3)
Most probably, the preferred orientation (PO) observed of the crystalline layers deposited and their related structure are connected with the so-called preferential nucleation and preferential grain growth. For the case of ZnO, c-axis PO nucleation has been considered to take place because of the lowest surface free energy of this plane among the hexagonal crystallographic planes [9]. At low $P_{O_2}$, when the layer deposition rate is low, once the condensation process begin, the initially condensed molecules form seed crystals serving as the nucleation sites with predominant c-axis PO; their PO determines the PO of the layers obtained. No preliminary created nucleation sites are necessary. On the contrary, initial nuclei with relatively more random orientation dominate in the substrates with ZnO seeds. Under this oxygen deficient condition, ZnO will grow preferentially on the pre-existing ZnO nuclei of the seed film or on the ZnO nuclei that have been formed during the beginning of the layer growth. In addition, due to the faster vertical growth rate along the c-axis compared to the lateral direction, rod shaped ZnO crystal are developed. In plasma with high O$_2$ content, ZnO has a high nucleation density and a rapid growth which leads to the formation of dense films with smaller grain size and more random orientation. A further excess of O$_2$ may induce defects in ZnO, which may influence the nucleation and the growth of the films. This results in a degradation of the crystal quality, or even to the inhibition of the grain growth.

Conclusions
Crystalline ZnO layers were obtained by PECVD at 400 °C on glass substrates with and without ZnO seeds. The SEM and XRD studies show that the crystallinity and texture of the ZnO layers depend strongly on the oxygen pressure in the case of layers grown on glass substrates without a seed film. It was found that ZnO layers deposited on pure glass substrates at low O$_2$ pressure have well developed grain structures with predominant c-axis phase and better crystalline quality than that of the samples obtained in plasma with high O$_2$ pressure. In the presence of ZnO seed films on the glass substrates, the formation of a c-axis phase and its quality are less dependent on partial pressure $P_{O_2}$. Nanorods with good alignment orientated vertically with respect to the substrate surface can be observed in the layers deposited on glass substrates with ZnO seeds at low content of O$_2$ in the plasma. This behavior can be explained by the so-called preferential nucleation and preferential grain growth. The above results can contribute to optimizing the growth condition of ZnO layers and achieving the performance required for the production of chemical- and bio-sensors or other electronic devices characterized by high efficiency and sensitivity and long lifetime.

Acknowledgements
The authors wish to thank Prof. D.Sc. I. Tomov for XRD measurements, and G. Maleshkova for the SEM observations. This study was supported by the Bulgarian National Science Fund Grant # DO02-207/2009.

References
[1] Ozgur U, Alivov Y, Liu C, Teke A, Reshchikov M, Dogan S, Avrutin V, Cho S, and Morkoc H 2005 J. Appl. Phys. 98 041301
[2] Djurisic A and Chen A 2010 Progress in Quantum Electronics 34 191-259
[3] Mende L and Driscoll L 2007 Materials Today 10 40
[4] Lu J, Chang P and Fan Zh 2006 Mater. Sci. Eng. R52 49
[5] Ma Y, Du G, Yin J, Yang T and Zhang Y 2005 Semicond. Sci. Technol. 20 1198
[6] Karpina V, Lazarekno V, Lashkarev C, Dobrowolski V, Kopylova L, Baturin V, Pustovoytov S, Karpenko A, Erimen S and Lytvyn P 2004 Cryst. Res. Technol. 39 980
[7] Iwanaga H, Shibata N, Nittono and Kasuga M 1978 J. Cryst. Growth 45 228-32
[8] Liu X, Wu X, Cao H and Chang R 2004 J. Appl. Phys. 95 3141-7
[9] Kajikawa Y 2006 J. Cryst. Growth 289 387-94
[10] Conley J, Stecker L and Ono Y 2006 J. Electr. Mater. 35 795
[11] Kitova S and Danev G 2010 J. Phys.: Conf. Series 253 012031