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Plasma Enhanced Chemical Vapor Deposition of Thin ZnO Layers on Glass Substrates*

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Abstract. The plasma enhanced chemical vapor deposition (PECVD) is a powerful and flexible instrument for depositing thin layers, nanocomposites or nanostructures. In this work ZnO layers were grown by metal-organic PECVD (RF – 13.56 MHz) on glass substrates coated with ZnO seed films. Zn acetylacetonate was used as a precursor and oxygen as oxidant. The influence of the oxygen content in gas mixture on the morphology, optical and electrical properties of the deposited layers was studied. ZnO film properties were investigated by scanning electron microscopy (SEM), UV-VIS optical spectrophotometry and current-voltage (I-V) measurements. The results obtained show that the oxygen content in the deposition atmosphere influences the morphology, the optical properties and the electrical resistivity of the obtained ZnO layers. Nanorods with good alignment, vertically orientated to the surface of glass substrate can be observed in the layers deposited at low content of O_2 in plasma at substrate temperature of 400°C.

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1 Introduction

Zinc oxide (ZnO) thin films are being extensively studied due to their interesting electro-optical properties, high electro-chemical stability, a large band gap (between 3.2 and 3.4 eV at room temperature), abundance in nature and absence of toxicity [1-3]. ZnO has wide range of technological applications as sensors, heat mirrors, transparent electrodes, solar cells, piezoelectric and other optoelectronic devices [1,3-5]. However, the performance of these devices is strongly affected by the material properties and, therefore numerous attempts have been made to improve the crystallinity of ZnO layers. So far, various deposition techniques, such as thermal evaporation, pulsed laser deposition, sputtering, electrochemical and sol-gel deposition, template assisted and solution processes, molecular beam epitaxy, metal-organic chemical vapor deposition (MOCVD) have been attempted to grow high quality crystalline ZnO layers on a practical substrate,

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such as sapphire, Si wafer and glass substrates (for reviews see [4,5] and reverence cited there in, as well as [6]). Among them MOCVD can offer high grown efficiency, large area uniformity and the suitability for growing components containing volatile elements [7].

Plasma enhanced MOCVD (PECVD) technology is one of the most attractive for a synthesis of ZnO layers at low and moderate temperatures of substrates and minimal impact on them. Diethylzinc and dimethylzinc are usually applied as precursors in PECVD process [1,8]. Nevertheless these precursors are less desirable because of their high toxicity and flammability. Zinc acetylacetonate ($Zn(acac)_2$) should be a good candidate for use in low temperature fabrication of crystalline ZnO layers because of its non-toxicity and inflammability, low vaporization temperatures (250°C), low thermal decomposition temperatures (150–500°C), high vapor pressure [8]. However, ($Zn(acac)_2$) is rarely used as precursor in PECVD.

It is well known that structures of synthesized ZnO are dependent on processing conditions, such as working pressure, substrate temperatures, deposition power and gas mixture. Several authors have already synthesized different crystalline nanostructured ZnO by adjusting substrate temperatures, reaction gases, and starting material during CVD [1,4,9-11].

In this paper, the effect of the oxygen partial pressure on the structural, optical and electrical properties of ZnO layers deposited on glass substrates has been studied. The layers are grown by PECVD, using $Zn(acac)_2$ and O_2 as reactants. To facilitate the formation of ZnO nuclei thin ZnO seed film was spin coated on glass substrate prior ZnO deposition.

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 was 2000 W. The reaction chamber was evacuated to 20 mTorr before the process. Oxygen gas and $Zn(acac)_2$($Zn(C_5H_7O_2)_2.xH_2O$) were used as precursors. The Zn source was sublimated by heating up to 140°C and carried by nitrogen gas to the growth chamber. O_2 gas was introduced separately into the reaction chamber in order to prevent any pre-reaction of the two precursors. Additional Ar gas was injected for varying the oxygen concentration in the chamber. All gas flows were controlled by mass flow meters controllers. The total pressure was kept constant of 280 mTorr. The temperature of the substrates was 400°C. The thickness of the layers within the range of 100–500 nm was measured by a profilometer type Talystep.

The layers were deposited on Corning glass substrates, preliminary carefully cleaned. Very thin ZnO seed films of about 3–5 nm were formed by spin coating (500 rpm, 180 s) of 20 mM $Zn(CH_3COO)_2.2H_2O$ solution in ethanol followed by thermal treatment for 1 h at 400°C in air.

The surface morphology of the layers was examined by a scanning electron microscope (SEM Philips 515). The transmittance and specular reflectance of the samples were measured in the spectral range $\lambda = 300$–800 nm by a Cary 5E spectrophotometer. The procedures for deriving the optical band gap and Urbach energy on the basis of the measured values were described in details elsewere [12]. The resistivity measurements were provided with 2 mm planar narrow strip Al electrodes. Current-voltage (I-V) measurements were performed in dark at 25°C with Keithley 230 voltage source and Keithley 617 electrometer.

3 Results

Our previous study has shown that crystalline ZnO layers are deposited on glass substrates with ZnO seeds at substrate temperature of 400°C. The XRD data have indicated that all layers exhibit hexagonal wurtzite structure with a predominant c-axis phase and good crystalline quality [12,13]. Figure 1 shows top- and cross sectional view SEM images of the layers grown at different partial oxygen pressure P_{O_2}. The images show a well-developed grain structures with grain size increasing with oxygen partial pressure. All layers exhibit columnar

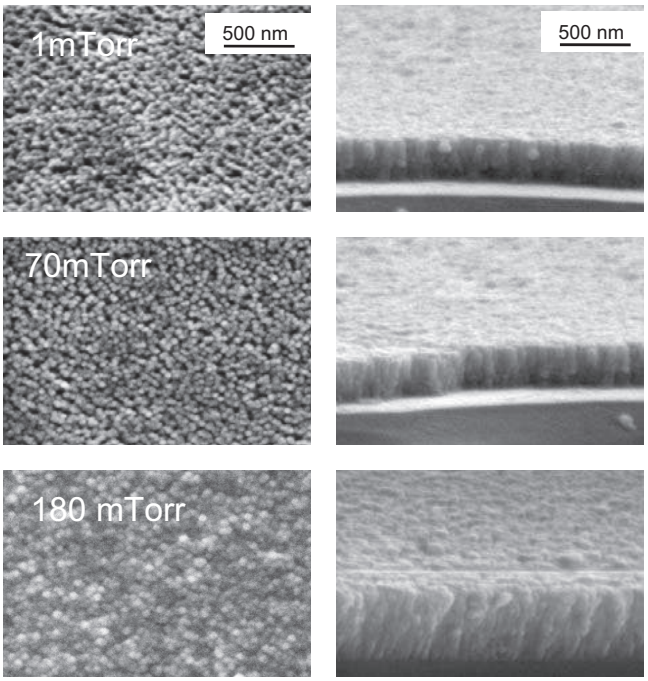

Figure 1. Top- and cross sectional- view SEM images of ZnO layers grown at the indicated partial oxygen pressure P_{O_2}.

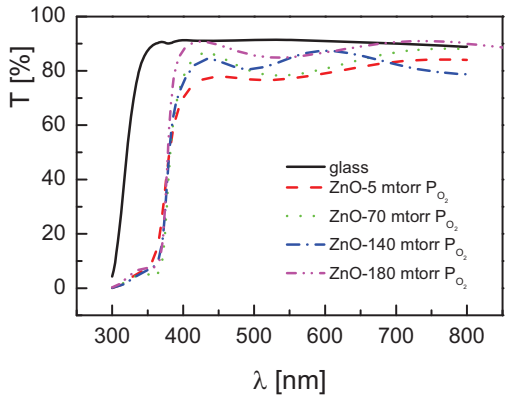

Figure 2. Optical transmittance spectra of glass substrate and 100 nm thick ZnO layers deposited at different oxygen partial pressure P_{O_2}.

structure. Nanorods with good alignment, vertically orientated to the substrate surface can be seen in layers deposited at low content of O_2 in plasma gases.

Most probably the observed preferred orientation (PO) of deposited crystalline layers and their related structure are connected with the so-called preferential nucleation and preferential grain growth. The preferential nucleation is a process in which initial nuclei with a specific crystallographic direction preferentially nucleates on the substrates. For the case of ZnO c-axis PO nucleation has been considered to arise because of the lowest surface free energy of the plane among hexagonal crystallographic planes. Under 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 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 formation of dense films with smaller grain size and more random orientation. Further the excess of O_2 may induce defects in ZnO which influences the nucleation and the growth of the films. This results in the degradation of the crystal quality or even to the inhibition of the grain growth.

Figure 2 presents optical transmittance curves of 100 nm thick ZnO layers deposited at different partial oxygen pressure. For comparison the transmittance (T) of pure glass substrate is also given. It is seen that all layers are highly transparent in the visible region. They have transmission over 80% which increases with P_{O_2} increasing. A step decrease in T is observed in the UV region between 360 and 390 nm, where the absorption edge of the intrinsic ZnO is located.

Figure 3 shows the influence of partial oxygen pressure on the optical band gap (E_g), Urbach energy (E_U) and resistivity (ρ) of deposited ZnO layers. It is seen

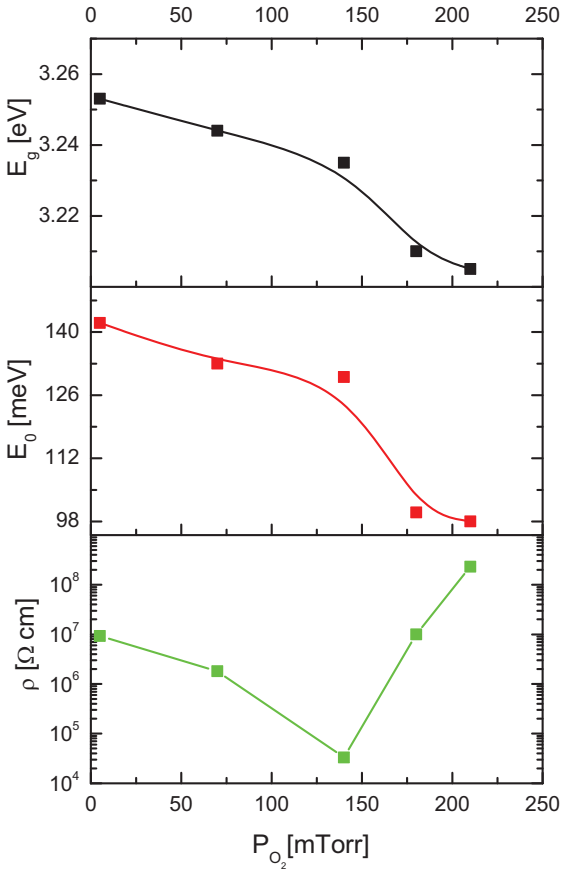

Figure 3. The optical energy gap E_g, Urbach energy E_{U} and the resistivity ρ of 100 nm thick ZnO layers in dependence of the partial oxygen pressure P_{O_2}.

that optical band gap shifts from 3.25 eV to 3.22 eV with P_{O_2} increasing. The values obtained are very close to those cited in the literature [1]. Urbach energy also varies with the oxygen content in plasma gases. E_{U} values of layers grown at low P_{O_2} are greater than that of the layers grown at high P_{O_2}. The Urbach energy characterizes the effects of all possible defects in the films. It has been shown that, in crystalline solids, Urbach's tail occurs due to static disorder (structural disorder). The increasing of the structural disorder results in an increase in Urbach energy [14-16]. This means that the films grown at low P_{O_2} have the most number of structural defects. The results obtained indicate that deposited ZnO layers have high resistivity within the range 3.3×10^4–2.3×10^8 $\Omega\,$cm. The lowest ρ exhibit ZnO layer deposited at P_{O_2} of about 140 mTorr.

4 Conclusions

The crystalline ZnO layers with hexagonal wurtzite structure and predominant c-axis phase were obtained by PECVD on glass substrates coated with ZnO seeds. The SEM studies show that all layers exhibit columnar structure. Nanorods with good alignment, vertically orientated to the substrate surface are formed in the layers deposited at low content of O_2 in plasma gases. All layers exhibit high resistivity and high optical transmission in the visible region (over 80%) and optical band gap of about 3.22–3.26 eV. The layers grown at oxygen deficient conditions have the most number of structural defects as followed from the E_U values obtained. All the above results, concerning the characterization of the ZnO layers, can contribute towards the optimization of their growth conditions and the achievement of the required performance, in order to be used for the production of chemical- and biosensors or other electronic devices characterized by high efficiency, sensitivity and lifetime.

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