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Low Temperature Plasma Enhanced CVD Synthesis of Piezoactive ZnO Films

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Abstract. Plasma-enhanced organometallic chemical vapour deposition process has been developed to obtain piezoelectric ZnO films with a highly preferred orientation of the crystallites on sapphire and on SiO_2/Si substrates. The volatile organic precursor of zinc acetylacetonate $Zn(AA)_2$ decomposes under r.f. discharge plasma at low temperature in controlled atmosphere of $Ar+O_2$ gas mixture.
The optimal deposition conditions of high quality ZnO film were deduced and investigated. The films obtained have high resistivity and transparency.

1. INTRODUCTION

ZnO thin films due to their interesting properties have a lot of different applications. For example, films with high conductivity and transparency in the visible spectral range can be used as transparent electrodes [1-3], while highly oriented films with low conductivity can be used in acousto- and electrooptic devices [4,5].

Techniques for zinc oxide thin films deposition such as spray pyrolysis [3,6], sputtering [1,2], various kinds of chemical vapour deposition (CVD) [8,9,10] chemical deposition from solutions [11] are described .

Plasma enhanced metalorganic chemical vapor deposition (PE MOCVD) allows to prepare high quality ZnO films at lower temperatures than usual CVD techniques [12,13]. However such technologically unsuitable compounds as diethylzinc (DEZ) and dimethylzinc (DMZ) are usually used as precursors in CVD process.

In this paper we discuss the PE MOCVD of ZnO films with a highly preferred orientation. Zinc acetylacetonate $Zn(AA)_2$ (AA=acetylacetonate) used as precursor is advantageous with respect to early used reagents due to its non-toxicity, non-inflammability and non-explodity.

2. FILMS PREPARATION

Figure 1 shows a scheme of the experimental setup. It consists of a continuously pumped horizontal quartz tube placed between copper plates on which r.f. power (13,56 MHz) is applied to produce plasma in the reaction chamber and to dissociate $Zn(AA)_2$ vapor. The base unit was equipped with a resistive-heated cylindrical evaporator where $Zn(AA)_2$ powder was placed in a quartz ampule with calibrated orifice (d=0.2-1 mm).

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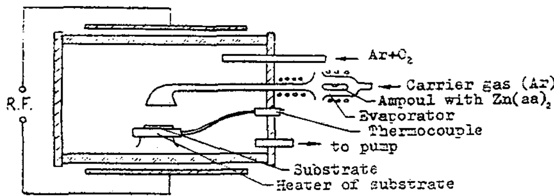

Figure 1: Schematic representation of the PEMOCVD apparatus

The substrate was chemically purified under plasma discharge power of W_p=700 W and system pressure of P=0.2 mTorr before the deposition. When the reaction chamber is evacuated to the base pressure of 100 mTorr and mixture of Ar+O_2 is introduced into discharge tube, the pressure reaches the value of 200-500 mTorr. The total pressure during the film deposition increased to 0.4--1.4 Torr due to evaporation of organometallic compound.

The PEMOCVD experiments show that the film properties are extremely affected by deposition conditions. The dependence of the characteristics of ZnO films grown on crystalline sapphire (001), silicon (100) and SiO_2/Si substrates on the technological parameters of PE MOCVD process is investigated. The temperature of substrates Ts has been varied from 50 to 250°C and r.f. power from 200 to 600 W.

3. RESULTS AND DISCUSSION

The study of chemical composition of ZnO films using Auger spectrometer "JAMP-10S" and X-ray microprobe analyzer "JCXA-733" showed the absence of impurities, including carbon. Error of both methods was less than 0.1 at.%. Auger spectroscopy was also used to determine the elemental distribution profiles. Figure 2 shows the elemental distribution profiles in zinc oxide/silicon sample. A transition region (III) where chemical composition changes can be seen. The existence of a transition region between the film and the substrate may be explained considering a solidphase chemical reaction of the system ZnO/Si [14]. Within this region nearly 20 nm wide a change of relative oxygen and zinc contents takes place.

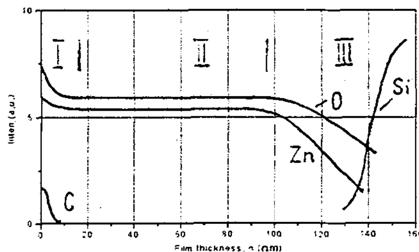

Figure 2: Element distribution profile in the ZnO/Si sample (h:film thickness)

The existence of a transition region was also verified by photoluminescence measurements of the ZnO films deposited on sapphire. As a result of nitrogen laser excitation (λ_{ex}=338 nm), the photoluminescence spectrum of the sample taken on the film side is considerably different from that obtained fon the substrare side (Fig.3). In the last case the evident maxima displacement to yellow-orange region may be explained by nonstoichiometricity of chemical composition and by structural changes in the transition area [15].

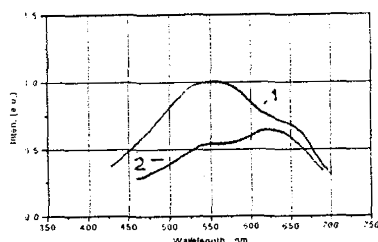

Figure 3: Photoluminescence spectrum of ZnO film on sapphire (001) from the side of film (1) and substrate (2)

As-deposited ZnO films have a polycrystalline structure. Phase analysis carried out by X-ray and electron-diffraction methods showed the presence of a single phase corresponding to the hexagonal ZnO structure. Small-angle X-ray diffraction spectrum of the film deposited at gas carrier flow rate of 55 ml/min is shown in Figure 4b. The diffractogram reveales pronounced (001) texture in the film with preferred orientation of crystallites along c axis, normal to the substrate surface [16]. The only one diffraction peak (002) located at 2θ=34.5° is observed. On the other hand (101) and (100) peaks at 2θ=36.2° and 2θ=31.7° respectively are indicated for the films deposited at gas carrier flow rate of 55 ml/min (Fig.4a).

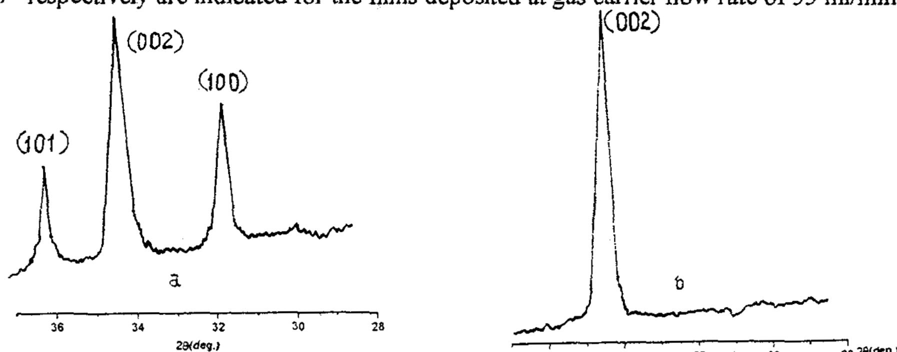

Figure 4: X-ray diffraction spectra of ZnO thin films deposited on sapphire substrates at r.f.power of 380 W, substrate temperature of 200°C, pressure in reaction chamber of 500 mTorr, Ar flow rate 90 ml/min (a); 55 ml/min (b)

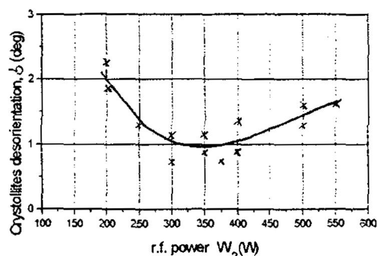

Figure 5: The degree of crystallites disorientation σ in ZnO films on sapphire as a function of r.f.power W_p. T_s=220°C; P=450 mTorr; Q=55 ml/min.

The crystallographic orientation of deposited ZnO film was essentially determined by the technological parameters such as the gas carrier flow rate Q (Fig.4), the r.f. power W_p (fig.5), the substrate temperature Ts and the pressure in reaction chamber P (Fig.6).

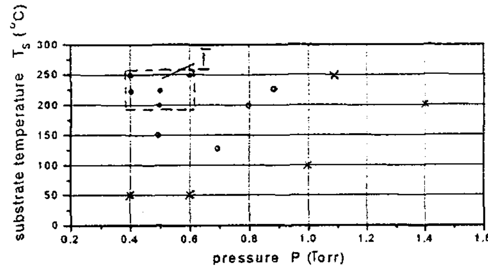

Figure 6: The degree of crystallites disorientation σ in ZnO films on sapphire substates as a function of pressure P and substrate temperature T_s. W_p =350 W; Q=50 ml/min. x-amorphous film,◦-low textured film,•-high textured film (I)

As it follows from the X-ray diffraction pattern, the optimal technological conditions of ZnO films growth by PEMOCVD are: T_s=200-250°C, W_p=250-400 W, Q=50-60 ml/min, P=400-600 mTorr. X-ray diffraction spectrum of ZnO film deposited on sapphire under these optimum parameters is shown in Fig.4b. The films deposited on silicon substrates has no texture in agreement with literature data. Preoxidized silicon substrates were used to obtain textured layers.

The deposited films show a resistivity as high as 10^8 Ohm·cm owing to their rather good stoichiometry. Dielectric strength of ZnO films of 1μm thick is ~10^6 V/cm.

Optical measurments ("PYE UNICAM-8800" spectrophotometer) show that transmission of 0.8 μm thick ZnO films is very similar to that of semiconductor materials: step-by-step change in transmission coefficient takes place (Fig.7) and a high transmission region (over 90%) can be seen. Upon change of film structure from polycrystalline with highly preferred orientation to amorphous the transformation of the form of fundamental absorption edge from steplike to smeared is observed.

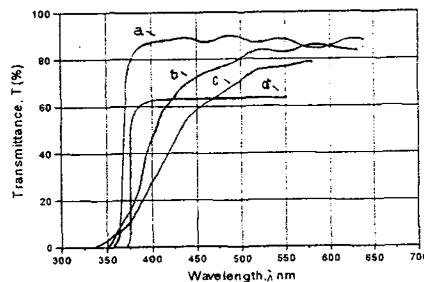

Figure 7: Optical transmission spectra of high textured (a), low textured (b), amorphous (c) ZnO film and ZnO single crystal of thickness 1.5 mm (d)

At λ=630 nm the refractive index of film is equal to 1.97. Experimental studies of optical losses in ZnO films carried out on the basis of waveguide effect of light extending allowed us to determine optical attenuation in planar waveguide to be less than 2 dB/cm.

Piezoelectric modulus d of the obtained films was determined by dynamical method [17] using etalon sample. Its magnitude d_{33}=6-7· 10^{-12} C/N is close to the same characteristic of monocrystalline sample ZnO.

4.CONCLUSIONS

High quality piezoelectric ZnO films were deposited on sapphire and SiO_2/Si substrates at low temperature using plasma-enhanced chemical vapor deposition and zinc acetylacetonate as a precursor. The film deposited under optimal technological parameters were uniform and had highly preferred orientation of crystallites. High piezoelectric and optical characteristics of films are essential for their application in acuosto-optical devices.

The proposed method of ZnO films synthesis could be attractive for deposition on partially formed structures with developed surface relief and on materials which do not allow high temperature influence.

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