Deposition conditions for the growth of textured ZnO thin films by aerosol CVD process

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Abstract

The crystalline orientation of ZnO thin films deposited by an aerosol CVD process is studied with regard to the experimental conditions. The quality of the C-axis oriented growth depended on the substrate temperature, on the deposition rate and also on the hygrometric degree of the carrier gas. The quality of the gold sublayer influenced also the quality of the ZnO textured growth. Under a dry gas mixture N_2-O_2 at 495°C and with a deposition rate of 35Å/mn, the texture ratio was less than -3.5 and the misorientation σ_{002} was less than 1.6°.

Introduction

Due to their high piezoelectric properties, the zinc oxide thin films are one of the most important materials among microsensor devices or micromachined actuators [1,2]. The efficiency of these devices strongly depends on the crystalline orientation of the ZnO films. In our laboratory for the growth of textured ZnO layers we used a particular CVD technique which is based on the pyrolysis of an aerosol produced by ultrasonic spraying [3]. This process allowed us to deposit textured ZnO thin films on silicon wafers, whose crystalline orientation depended on the deposition temperature and on the deposition rate [4]. This paper reports new results about the quality of the textured growth of the ZnO films.

Thin films preparation

As starting material, zinc acetate was dissolved in methanol at a concentration of 0,025 Mol/l. This solution was ultrasonically sprayed and the produced mist was carried by a gas towards the reaction zone, where the pyrolysis of the aerosol occurred on the heated silicon wafer. The deposition process is accurately described elsewhere [3]. Typically the substrate temperature ranged from 470°C to 510°C. For each deposition test we used different types of substrates: Silicon wafer, silicon wafer coated with an aluminium sublayer

or with chromium and gold sublayers or with thermal SiO_2 and also glass substrates. As reported earlier [3], the deposition conditions corresponded to the chemical vapour deposition conditions. The deposited ZnO thin films exhibited a good transparency and adherence and the thickness of the films varied between 0,5 and 1 μm .

Samples characterizations

The crystalline orientation of the deposited films has been studied with two automatic diffractometer Siemens D500 (λ_{Fe} θ/θ and λ_{Cu} $\theta/2\theta$). In the classical Bragg Brentano configuration $\theta/2\theta$, the measured diffractograms allowed to obtain the ratio between the intensity of the ZnO X-ray diffraction lines 101 and 002 ($R = \log I_{101}/I_{002}$). The differences in the quality of the textured growth was clearly described by the variation of this ratio. Moreover the growth quality was also described by the measure of the value of the half width at the half maximum (HWHM) σ of the rocking curve of the ZnO 002 diffraction line. The quality of the gold sublayer was also studied by these two X ray diffraction analysis ($R_{\text{Au}} = \log I_{200}/I_{111}$ and σ for the 111 line). The morphological aspect of the ZnO thin layers was observed by scanning electron microscopy with views of the surface and of the cross section of the films. With these different characterization methods we have studied the influence of the hygrometric degree of the carrier gas on the crystalline orientation of the ZnO thin films.

Results and discussion

The first fact which revealed the influence of the hygrometric degree is that under the same deposition conditions, the deposition rate was three times higher with a dry pure gas mixture $\text{N}_2\text{-O}_2$ (80%-20% with $\text{H}_2\text{O} < 5\text{ppm}$, $4\text{mg}_{\text{H}_2\text{O}}/\text{m}^3$) than with air saturated at 20°C with water vapour ($17\text{ g}_{\text{H}_2\text{O}}/\text{m}^3$). In a previous paper [4], it was reported that the texture ratio R depended on the substrate temperature and on the deposition rate. For films deposited with air dried by a condensation system (this dried air exhibited an hygrometric degree of $6\text{ g}_{\text{H}_2\text{O}}/\text{m}^3$) the minima in the texture ratio are obtained at 480°C with a deposition rate of $15\text{ \AA}/\text{mn}$ (figures 1 and 2).

When the substrate temperature and the deposition rate are varied under the pure gas mixture $\text{N}_2\text{-O}_2$, the curves exhibited also minima (figures 3 and 4) and in this case these minima in texture ratio are obtained at higher deposition temperature (495°C) and at higher deposition rate (around $35\text{ \AA}/\text{mn}$). Moreover for the silicon wafers coated with gold, the best value was less than -3,5, whereas for a randomly oriented sample the texture ratio was 0,25.

Figure 1 : Texture ratio of $0.5\mu\text{m}$ ZnO thin films deposited with moist air ($6\text{g}_{\text{H}_2\text{O}}/\text{m}^3$) as function of temperature for different substrates.

Figure 2 : Texture ratio of $0.5\mu\text{m}$ ZnO thin films deposited with moist air ($6\text{g}_{\text{H}_2\text{O}}/\text{m}^3$) and at 480°C as a function of the deposition rate for different substrates.

Figure 3 : Texture ratio of $0.5\mu\text{m}$ ZnO thin films deposited with dry gas mixture $\text{N}_2\text{-O}_2$ ($4\text{mg}_{\text{H}_2\text{O}}/\text{m}^3$) as a function of the temperature for different substrates.

Figure 4 : Texture ratio of 0.5 μ m ZnO thin films deposited with dry gas mixture N₂-O₂ (4mg_{H2O} /m³) and at 485°C as a function of the deposition rate for different substrates.

On the other hand the hygrometric degree didn't influence the HWHM σ of the ZnO 002 line. The σ values were the same, when the films were deposited with the dry gas mixture N₂-O₂ or with moist air (figure 5-B). However these experiments have revealed that the quality of the c-axis orientation depended on the quality of the gold sublayer as shown on the figure 5.(A-B) As reported earlier for ZnO thin films deposited by sputtering [5], the HWHM σ of the ZnO layers decreased when the HWHM σ of the gold 111 line decreased. In our case the lowest σ values are obtained with gold coated silicon wafers which exhibited a poor crystallinity ($R_{Au} = -0,9$ instead of $-2,5$ and $\sigma_{111} = 5,3^\circ$ instead of $3,7^\circ$). We don't yet understand this effect, but it was reproducible in all deposition conditions.

Figure 5 : HWHM σ of 0.5 μ m ZnO thin films as a function of the deposition rate for films deposited on two types of gold coated silicon wafers :

- A dry air ; Si/Cr/Au (250Å/ 4000Å) with a poor crystallinity : $I_{111} = 10^4$ cps ; $\sigma_{111} = 5.2^\circ$
- B moist and dry air ; Si/Cr/Au (250Å/ 3000Å) with a good crystallinity : $I_{111} = 3 \cdot 10^5$ cps ; $\sigma_{111} = 3.7^\circ$

The observation of the morphological aspect of the ZnO thin films confirmed the diffraction results. As shown in figure 6, for the ZnO thin layers deposited on silicon wafers with air saturated by water vapour at 20°C, the ZnO hexagonal plates were randomly oriented and the porosity of the films was large. On the other hand, when the ZnO layers are deposited on gold coated silicon wafers and with the dry gas mixture N_2-O_2 , the films exhibited a columnar growth and a high compactness. This columnar growth was clearly observed by a skew view of the cross section of the ZnO thin films (figure 7). When the films are deposited on silicon wafers or with moist air, the columnar growth disappeared.

Figure 6 : Scanning electron micrographs of 0.5μm ZnO thin films deposited on silicon or on gold coated silicon wafers and with different hygrometric degrees of the carrier gas.

Conclusion

Strongly C-axis oriented ZnO thin films can be deposited by the pyrosol CVD process. The crystalline orientation of the ZnO layers depended on the substrate temperature, on the deposition rate and also on the hygrometric degree of the carrier gas. The best texture ratio was obtained under a dry gas mixture N_2-O_2 at $495^\circ C$ and with a deposition rate of $35 \text{ \AA}/\text{mn}$. The quality of the gold sublayer influenced also the quality of the ZnO texture growth.

Figure 7 : Skew views of the cross section of $0.5 \mu m$ ZnO thin films deposited on silicon or on gold coated silicon wafers and with different hygrometric degrees of the carrier gas.

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