Effect of the substrate surface topology and temperature on the structural properties of ZnO layers obtained by plasma enhanced chemical vapour deposition

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Abstract. In this work thin ZnO layers were grown by metal-organic PECVD (RF 13.56 MHz) on Si wafers. Zn acetylacetonate was used as a precursor and oxygen as oxidant. A system for dosed injection of the precursor and oxidant into the plasma reactor was developed. The influence of the substrate surface topology and temperature on the structural properties of the deposited layers was studied. ZnO and graphite powder dispersions were used to modify the silicon wafers before starting the deposition process of the layers. Some of the ZnO layers were deposited on the back, unpolished, side of Si wafers. Depositions at 400 °C were performed to examine the effect of the substrate temperatures on the layer growth. The film structure was examined by XRD and SEM. The results show that all layers are crystalline with hexagonal wurtzite structure. The crystallites are preferentially oriented along the c-axis direction perpendicular to the substrate surfaces. ZnO layers deposited on thin ZnO seed films and clean Si surface exhibit well-developed grain structures and more c-axis preferred phase with better crystal quality than that of the layers deposited on graphite seed layer or rough, unpolished Si wafer.

1. Introduction

Zinc oxide is a unique material with 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, 2]. In the last years, nanostructured ZnO, such as nanotubes, nanowires, nanoribbons, nanofibres and etc. have attracted extraordinary attention due to their potential application in chemical sensors, light-emitting diodes, field emitters, solar cells, nanogenerators and other optoelectronic devices [3, 4]. However, the performance of these devices is strongly affected by the material properties and, therefore, numerous attempts have made to improve the crystallinity of ZnO layers. So far, various deposition techniques, 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, have been used in attempts to grow highly crystalline ZnO layers on substrates of practical importance, such as sapphire and Si wafers (for reviews see [3, 4] and the reference cited therein). Among them, MOCVD can offer high growth efficiency, large area uniformity and suitability for growing components containing volatile elements [5].

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The plasma enhanced MOCVD (PECVD) technology is one of the most attractive for synthesis of ZnO layers at low and moderate substrates temperatures and minimal impact on them. Diethylzinc and dimethylzinc are usually applied as precursors in the PECVD process [1, 6]. However, 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, non-explosiveness and non-flammability, low vaporization temperatures (250 °C), low thermal decomposition temperatures (150-500 °C), high vapor pressure [6]. However, (Zn(acac)₂) is rarely used as a precursor in PECVD.

In our previous paper we have studied the effect of the PECVD technological parameters, using Zn(acac)₂ and O₂ as reactants, on the composition, structural and optical properties of ZnO layers grown at low substrate temperature (~40 °C) on glasses, optical grade polycarbonates and Si wafers [7]. The results showed that the layers obtained at the highest RF power of 2000 W and O₂ gas ambient pressure (about 300 mTorr) are amorphous, with high optical transmission in the visible region and E_g of 3.36 eV, which is very close to that of the bulk ZnO material. It is known that among the important parameters for producing high-quality crystalline ZnO films are the deposition temperature and the substrate surface [3, 4]. A selective growth of high-quality ZnO nanorods on Si substrates at 800 - 900 °C was demonstrated using a pattern thin film of ZnO as a seed layer [8].

In this paper, the effect was studied of the temperature and the surface topology of the substrate on the structural properties of ZnO layers deposited on Si wafers. The layers were grown by PECVD, using Zn(acac)₂ and O₂ as reactants. Depositions were performed at 400 °C to examine the effect of temperature on the growth. To facilitate the formation of ZnO nuclei, two different very thin seed layers of graphite and ZnO were spin coated prior to the ZnO deposition. In order to study the influence of the surface roughness on the layer growth, some of the ZnO layers were deposited on the back, unpolished, side of Si wafers.

2. Experimental

The 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. Oxygen and Zn(acac)₂ (Zn(C₅H₇O₂)₂.xH₂O) (Sigmas-Aldrich) were used as precursors. The Zn source was sublimated by heating up to 140 °C and carried by nitrogen to the growth chamber. A system was developed and attached to one of the chamber windows to enable dosed injection of the precursor to the plasma reactor. The stable precursor temperature resulted in a stable precursor flow rate, even if we could not directly measure it. The O₂ gas was introduced separately into the reaction chamber. All gas flows were controlled by mass flow meters controllers at a constant flow rate. Chamber pressure of 250 mTorr and gas ratio O₂/N₂ of 4:1 were kept constant during the deposition process. The substrates were heated to 400 °C. The deposition time was typically 20 min. The thickness of the layers was about 1.2 µm measured by a Talystep type profilometer.

The substrates used to deposit the layers were Si wafers. Preliminarily cleaning of the substrate surface is very important to grow ZnO layers with good crystal quality and to enhance ZnO nucleation. For this purpose, the Si wafers were dipped in a 10% dilute HF acid solution and then rinsed in deionized water and isopropyl alcohol. Two different very thin seed films were formed by spin coating (1000 rpm, 60 s) of graphite powder dispersion (1 vol.% ) in isopropyl alcohol and ZnO powder dispersion (1 vol.% ) in isopropyl alcohol.

The crystal structure of the layers was characterized by X-ray diffraction (XRD) using a Philips (PW 1710) apparatus with Cu-Kα radiation separated by a focusing graphite monochromator. The alignment of the diffractometer is in the symmetrical Bragg-Brentanno focusing geometry. Scherrer’s equation was used to estimate the average crystallite sizes, without making the corrections for the instrumental geometrical broadening of the peaks and stripping the α1 component from the α2 component radiation. The value of λ was taken as 0.154 nm. The surface morphology of the layers was examined by a scanning electron microscope (SEM Philips 515).
3. Results and discussion

X-ray diffraction patterns of the layers deposited at 400 °C on Si wafers, ZnO seed film; C seed film; and unpolished side of a Si wafer (samples 1 - 4) are presented in figure 1. The XRD results show that all ZnO layers are polycrystalline. Three peaks at 31.7°, 34.3° and 36.2° are observed. These peaks can be indexed to the (0002), (0002) and (1011) planes of the hexagonal wurtzite structure of the ZnO crystal with cell parameters a = 3.25 Å and c = 5.22 Å, which agree well with the values reported in JCPDS card # 89-1397 [9].

The results show that the crystallites are preferentially oriented along the c-axis direction perpendicular to the substrate surface, as the (0002) reflection is greatly enhanced with respect to the usual (1011) maximum reflection of ZnO. In order to quantify the intensity ratio of the (0002) crystal orientation, $\alpha_{(0002)}$ was defined as:

$$\alpha_{(0002)} = \frac{I_{(0002)}}{I_{(0002)} + I_{(1000)} + I_{(1011)}} \quad \text{(1)}$$

where $I_{(0002)}$, $I_{(1000)}$ and $I_{(1011)}$ denote the intensities of the (0002), (1000) and (1011) planes, respectively. $\alpha_{(0002)}$ is found to be 0.63, 0.69, 0.49 and 0.46 for sample 1 to 4. The full width at half maximum (FWHM) is 0.51, 0.47, 0.76 and 1.92 respectively. The highest value of $\alpha_{(0002)} = 0.69$ and the narrow FWHM of 0.47 found for the layers deposited on a ZnO seed film (sample 2) are indications for a more c-axis preferred phase with better crystal quality than that in the rest of the
samples. The lower values of $a_{0002}$ and the increased FWHM values found for layers deposited on a graphite seed film and on a rough Si surface (samples 3 and 4) point to a more randomly oriented polycrystalline wurtzite phase with smaller size. Based upon Scherrer’s equation, the average crystallite size of samples 3 and 4 is 11.1 nm and 4.3 nm, while that of samples 1 and 2 is 16.3 and 17.8 nm, respectively.

Top-view SEM images of samples 1 - 4 are shown in figure 2. The images show the well-developed grain structures of layers deposited on clean Si and a ZnO seed film, and the denser, without well defined grains, smoother surface of layers deposited on a C seed film and rough unpolished Si.

Most probably, the preferred orientation observed of deposited polycrystalline layers and their related structure are connected with the so called preferential nucleation (PO). For the case of ZnO, c-axis PO nucleation has been considered to arise because of the lowest surface free energy of this plane among the hexagonal crystallographic planes [10]. Therefore, it could be assumed that initial nuclei with predominant c-axis PO were formed in the ZnO seed film and at the onset of the growth of the layer; their PO have determined the PO of the layers obtained. On the contrary, initial nuclei with random orientation dominate on the substrates with the C seed film and on the rough unpolished side of the Si wafer, which have many active centers with different energy on crystal imperfections. The results obtained indicate that these nuclei cause the growth of also a-axis phases (with \(10\bar{1}0\) and \(0\bar{1}1\) planes) and, as a whole, to the smaller grain size of the layer obtained.

4. Conclusions

Crystalline ZnO layers were produced by PECVD at 400 °C on Si substrates with different topography. The raw material was Zn(acac)$_2$ which is non-toxic and easy to handle. The XRD results indicate that all layers exhibit a hexagonal wurtzite structure. The crystallites are preferentially oriented along the c-axis direction perpendicular to the substrate surfaces. It was found that ZnO layers deposited on thin ZnO seed films and clean Si have well developed grain structures with more c-axis preferred phase and better crystal quality than that of the rest of the samples. Due to this characteristic, the layers deposited on ZnO seed layers and Si are potential materials for preparing chemical and biosensors where an inherently large surface to volume ratio of structured materials is an important prerequisite for enhanced sensitivity.

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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] Wang X, Song J and Wang Zh 2007 J. Materials Chemistry 17 711
[3] Mende L and Driscoll L 2007 Materialstoday 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, Lazorenko V, Lashkarev C, Dobrowolski V, Kopylova L, Baturin V, Pustovoytov S, Karpenko A, Ermin S and Lytvyn P 2004 Cryst. Res. Technol. 39 980
[7] Minchev M, Kitova S and Danev G 2009 JOAM 11 1312
[8] Conley J, Stecker L and Ono Y 2006 J. Electronic Mater. 35 795
[9] Powder Diffraction File 89-1397 for hexagonal Zinc oxide (2001 JCPDS-International center for Diffraction data)
[10] Kajikawa Y 2006 J. Crystal Growth 289 387