Influence of the processing conditions on the structural properties of ZnO layers obtained by PECVD

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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 have been grown by metal-organic PECVD (RF - 13.56 MHz) on Si wafers. Zn acetylacetonate has been used as a precursor and oxygen as oxidant. The influence of the oxygen content in gas mixture, the total pressure, substrate temperature and ZnO seed layer on the structural properties of the layers deposited on Si wafers has been studied. ZnO layer properties were investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM). XRD data have shown that all layers are crystalline with hexagonal wurtzite structure. The crystallites are preferentially oriented along c-axis direction perpendicular to the substrate surfaces. The results obtained indicate that by controlling the oxygen content in gas mixture, the total pressure and substrate temperature during the film growth one can control the formation of c-axis phase and the crystallite grain size. Nanorods with good alignment, vertically orientated to the substrate surface can be observed in the layers deposited at low content of O2 in plasma at substrate temperature of 400 °C. Due to their structural characteristics these layers are potential materials for preparing chemical- and biosensors where inherently large surface to volume ratio of structured materials are important prerequisite for enhanced sensitivity.

1. Introduction
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 to grow high crystalline ZnO layers on a practical substrate such as sapphire and Si wafer (for reviews see [1, 2] and references cited there in). Among these, MOCVD can offer high growth efficiency, large area uniformity and the suitability for growing components containing volatile elements [3].

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 upon them. Diethylzinc and dimethylzinc are usually applied as precursors in PECVD process [4, 5]. Nevertheless, these precursors are less desirable because of their high toxicity and flammability and high price. 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), and high vapor pressure [4]. 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, 5-8]. 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 seed layer [9].

In this paper, the effect of the oxygen partial pressure, the total pressure, the substrate temperature and ZnO seed layer on the structural properties of ZnO layers deposited on Si wafers has been studied. The layers are grown by PECVD, using Zn(acac)₂ and O₂ as reactants.

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 8 mTorr before the process. Oxygen gas and Zn(acac)₂ (Zn(C₅H₇O₂)₂·xH₂O - Sigma-Aldrich) were used as precursors. A system attached to the one of the chambers windows for dosed injection of the precursor to the plasma reactor was developed. The Zn source was sublimated by heating up to 140 °C and carried by nitrogen gas at constant flow rate to the growth chamber. 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 vary total pressure. All gas flows were controlled by mass flow meters controllers. By varying the gas flow rate the chamber pressure was kept at different ranges from 70 to 900 mTorr. The substrates were heated in the range 400-600 °C. The deposition time was between 60 - 90 min. The thickness of the layers of about 500 µm was measured by a profilometer type Talystep.

The substrates used to deposit the layers were p-type Si wafers with (100) orientation. Preliminary cleaning of the substrate surface was very important to grow ZnO layers with a good crystal quality and to enhance ZnO nucleation. For the clean surface, the Si wafers were dipped in a 10% dilute HF acid solution and then rinsed in deionized water and isopropyl alcohol.

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 2θ range used in XRD measurements was from 20° to 60° in step of 0.05° s⁻¹ and fixed counting time of 5 s per step. A smoothing process of 5-point Fast Fourier transform followed by an appropriate baseline correction was applied to all diffractograms. 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. Scherrer’s equation was used for estimating the average crystallite size. The value of λ was taken as 0.15406 nm.

The surface morphology of the layers was examined by a scanning electron microscope (SEM Philips 515).

3. Results and discussion
Our previous study have showed that the layers obtained at the highest RF power of 2000 W, O₂ gas ambient pressure of about 300 mTorr and low substrate temperature (~ 40 °C) are amorphous, with high optical transmission in the visible region and E₉ of 3.36 eV, which is very close to that of bulk ZnO material [10]. Figure 1 presents X-ray diffraction patterns of the layers grown on Si wafers at different partial oxygen pressure P_{O₂}, constant total pressure P_{tot} of 280 mTorr and substrate temperate Tₛ of 400 °C. The XRD data demonstrate that the all ZnO layers are polycrystalline. Three peaks at 31.7°, 34.3°, and 36.2° are observed. These peaks can be indexed to (10\overline{1}0), (00\overline{2}) and (10\overline{1}1) planes of the hexagonal wurtzite structure of ZnO crystal [11]. 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 relatively to the usual (1011) maximum reflection of ZnO.

In order to quantify the preferred orientation (PO), often called texture, in the crystalline films, the texture coefficient (Tc) was defined as [12]:

\[
Tc(hkl) = \frac{I(hkl)/I_o(hkl)}{N \sum_n I(hkl)/I_o(hkl)}
\]  

(1)

where \(I(hkl)\) is the measured intensities of a (hkl) plane converted into the corresponding intensity of infinitely thick sample. \(I_o(hkl)\) is the intensity of a random oriented ZnO powder standard measured at the same conditions, \(N\) is the reflection number and \(n\) is the number of the diffraction peaks. A sample with randomly oriented crystallites presents \(Tc(hkl) = 1\), while the larger value, the larger abundance of crystallites oriented at the (hkl) direction.

Figure 2 (a-c) presents the influence of the partial oxygen pressure, the total pressure and the substrate temperature on Tc, FWHM and grain size calculated from XRD patterns of the highly oriented (0002) peaks. The high value of Tc of about 4.5, the very narrow full width of 0.22-0.27 and grain size of about 35 nm are the indications of predominant c-axis phase with better crystal quality formed on pure Si wafers at oxygen partial pressure up to 150 mTorr. As it is seen in figure 2a, the further increase in \(P_{O_2}\) in plasma gases leads to decreasing Tc value to 2.2 and to broadening FWHM value to 0.97. Correspondingly, the average crystallite size, which is inversely proportional to FWHM steeply, decreases to the smallest value of 9 nm. These results denote less c-axis preferred phase with smaller size grown at \(P_{O_2}\) higher than 150 mTorr. As a rule with increasing the oxygen partial pressure, the crystalline quality degrades from single oriented crystal to polycrystalline. We have found that there was no film to grow on Si wafers with further increasing the oxygen pressure. The data presented in figure 2a indicate that in the presence of ZnO seed films on Si wafer Tc and FWHM are less dependent on partial \(P_{O_2}\). Figure 2b shows that the increasing the total pressure up to 280 mTorr favors the c-axis phase formation with better crystal quality since Tc has high value and FWHM decreases from 0.5 to 0.22. Further rising \(P_{tot}\) degrades the c-axes PO and leads finally to more random orientation with lower crystal quality. Figure 2c shows that the rising the substrate temperature degrades the c-axes PO and leads finally to more random orientation. The growth of the grain along substrate surface is enhanced and thus grain size of c-phase decreases.

It should be noted that the results illustrated in figure 2 are consistent with the data obtained by SEM observations. Figure 3 shows top- and cross sectional- view SEM images of the layers grown on Si wafers at different partial oxygen pressure and at constant \(P_{tot}\) and \(T_s\). The images show a well

![Figure 1: X-ray diffraction patterns of the layers grown on Si wafers at indicated partial oxygen pressure (a) 1 mTorr, (b) 70 mTorr, and (c) 180 mTorr, with constant total pressure \(P_{tot}\) of 280 mTorr and substrate temperature \(T_s\) of 400 °C.](image-url)
developed grain structures of layers deposited at low $P_{O_2}$ in plasma and denser and smoother surface of layers deposited at high $P_{O_2}$ in plasma. All layers exhibit columnar 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.

Figure 2. $T_c$, FWHM and grain size calculated from XRD patterns of the highly oriented (0002) peaks in dependence of:

(a) the partial oxygen pressure $P_{O_2}$ - for the layers grown on Si wafers without and with ZnO seed layer at constant $P_{tot}$ of 280 mTorr and $T_s$ of 400 °C.
(b) the total pressure $P_{tot}$ - for the layers grown on Si wafers at constant $P_{O_2}$ of 20 mTorr and $T_s$ of 400 °C.
(c) the substrate temperature $T_s$ - for the layers grown on Si wafers at constant $P_{O_2}$ of 70 mTorr and $P_{tot}$ of 280 mTorr.

Most probably, the observed preferred orientation (PO) of deposited crystalline layers and their related structure are connected with so called preferential nucleation and preferential grain growth. The preferential nucleation is a process in which initial nuclei with a specific crystallographic direction preferentially nucleate 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 [8]. Therefore, it could be proposed that the initial nuclei with predominant c-axis PO are formed at the beginning of the layer growth and their PO have determined the PO and the
columnar structure of the layers obtained. The results obtained indicate that the O\textsubscript{2} content in the plasma influences the nucleation process and the growth of ZnO. In plasma with high O\textsubscript{2} concentration ZnO has a high nucleation density and a rapid growth, which leads to formation of dense films with smaller grain size. On the other hand, at low O\textsubscript{2} concentration the activation energy of nucleation is higher which makes the nucleation of ZnO more difficult. Under this oxygen deficient condition, ZnO will grow preferentially on the pre-existing 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.

**Figure 3.** Top- and cross sectional- view SEM images of the layers grown on Si wafers at indicated partial oxygen pressure \(P_{O_2}\) and at constant \(P_{tot}\) of 280 mTorr and \(T_s\) of 400 °C.

4. Conclusion

The crystalline ZnO layers have been obtained by PECVD at \(T_s\) within the range of 400 to 600 °C on Si substrates without and with ZnO seed layer. The XRD data indicate that all layers exhibit the hexagonal wurtzite structure. The crystallites are preferentially oriented along c-axis direction perpendicular to the substrate surfaces. The result obtained show that by controlling the oxygen content in gas mixture during the film growth as well as the total pressure and substrate temperature one can control the formation of c-axis phase and grain size. It has been found that ZnO layers deposited at low O\textsubscript{2} content in the plasma gases and at \(P_{tot}\) of 200 -300 mTorr and \(T_s\) of 400 °C have well developed grain structures with predominant c-axis phase and better crystal quality than that of the samples obtained in plasma with high oxygen concentration and high \(P_{tot}\). However, in the presence of ZnO seed films on Si wafer the formation of c-axis phase and its quality are less dependent on partial \(P_{O_2}\). Nanorods with good alignment, vertically orientated to the substrate surface can be observed in the layers deposited at low content of O\textsubscript{2} in plasma at substrate temperature of 400 °C. Due to their structural characteristics, these layers are potential materials for preparing chemical- and biosensors where inherently large surface to volume ratio of structured materials are important prerequisite for enhanced sensitivity.
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References
[1] Mende L and Driscoll L 2007 Materialstoday 10 40
[2] Lu J, Chang P and Fan Zh 2006 Mater. Sci. Eng. R52 49
[3] Ma Y, Du G, Yin J, Yang T and Zhang Y 2005 Semicond. Sci. Technol. 20 1198
[4] 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
[5] 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
[6] Iwanaga H, Shibata N, Nittono O and Kasuga M 1978 J.Crys.Growth 45 228
[7] Liu X, Wu X, Cao H and Chang R 2004 J. Appl. Phys. 95 3141
[8] Kajikawa Y 2006 J. Crystal Growth 289 387
[9] Conley J, Stecker L and Ono Y 2006 J. Electronic Mater. 35 795
[10] Minchev M, Kitova S and Danev G 2009 JOAM 11 1312
[11] Powder Diffraction File 89-1397 for hexagonal Zinc oxide (2001 JCPDS-International center for Diffraction data)
[12] Barret C and Massalski T 1980 Structure of Metals (Oxford: Pergamon Press)