Zinc oxide thin films deposited by magnetron sputtering with various oxygen/argon concentrations

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Abstract. Deposition of zinc oxide thin films onto silicon and thermally oxidized silicon substrates was performed by radio frequency magnetron sputtering. The obtained films were studied in function of percentage of oxygen and argon flow as process gases. Stoichiometric films were obtained in oxygen rich process conditions, which are more suitable to be p-type doped. Growth of zinc oxide films over thermally oxidized substrates resulted in better structural characteristics.

1. Introduction
Zinc oxide (ZnO) is a kind of semiconductor classified as a transparent conductive oxide (TCO), as it may exhibit electrical conductivity and optical transparency. It is a promising substitute to indium-tin oxide (ITO), widely used in optical devices as transparent electrode. ZnO, by nature, is an n-type material due to intrinsic defects as interstitial zinc atoms (Zn_i) and oxygen vacancies (V_o) on its structure [1]. However, it has been recognized that it is very important to grow high-quality both p- and n-type ZnO thin films for the development of ZnO-based optoelectronic devices [2]. Even with poor conductivity, formation of p-type ZnO has been observed when the films were deposited on O_2-rich conditions, without the presence of dopants [3]. These films have excess of oxygen in contrast to normal n-type ZnO films, which have excess of zinc [4].

For the deposition of ZnO, silicon substrates have many advantages, such as large wafer size and the possibility of integrating nitride semiconductors with the silicon technology. For research purposes, they are especially suitable because they are easy to cleave, have low surface roughness and present good chemical purity, facilitating the characterization processes of samples. However, for applications where transparency in the visible range is needed, amorphous materials (such as glass or polymers) are often used as substrates. Besides, the large mismatch of the lattice and thermal expansion coefficients between Si and ZnO makes the direct growth of ZnO on a Si substrate difficult, and frequently results in amorphous or polycrystalline films [5].

Magnetron sputtering is a physical vapor deposition method that creates plasma in the chamber to sputter the target material, commonly using argon as process gas. In this work, radio frequency (RF) magnetron sputtering was used for the deposition of the thin layers. The process is initiated in a glow discharge, produced in the vacuum chamber, under controlled gas flow. ZnO thin films were deposited onto silicon (Si) substrates. The main goal of this study is to find a process gas mixture that results in stoichiometric ZnO thin films, reducing intrinsic defects that impose n-type conductivity. In addition,
thermally oxidized silicon (SiO$_2$/Si) substrates were also used in order to study the difference in the structural characteristics occasioned by the substrate type where films were grown.

2. Experiment

Silicon (p-type, crystallographic orientation (100)) substrates were firstly cleaned with an ammonium hydroxide solution (H$_2$O + H$_2$O$_2$ + NH$_4$OH - 5:1:1, for 10 minutes) to clean organic contamination and particles. They were then rinsed in with deionized water and immersed in a hydrochloric acid solution (H$_2$O + H$_2$O$_2$ + HCl – 4:1:1, for 10 minutes) in order to remove metallic contaminants. The wafers were rinsed again and immersed in fluoridric acid (H$_2$O + HF - 20:1), until the wafers seemed to be dry when taken out of the solution, in order to clean off the native silicon dioxide (SiO$_2$).

Half of the clean Si substrates were thermally oxidized in a wet process for 210 minutes at 1150ºC, resulting in a 288nm layer of SiO$_2$.

Thin films of ZnO were deposited over the previously cleaned silicon and thermally oxidized silicon substrates by RF magnetron sputtering, using a 4” high-purity (99.999%) zinc oxide ceramic target. After placing each substrate in the chamber, the system was evacuated to a vacuum of the order of 5x10$^{-7}$ Torr using a turbomolecular pump. A distance of 10cm was maintained between target and substrate. Argon and oxygen were used as sputtering gases, with 10$\pm$0.5mTorr of process pressure (controlled by gas flow) and 200W of RF power. The percentage of oxygen flow in the process gas varied over the range 7.3 – 12.5% (deposition time: 90 min), and an additional film without oxygen in the gas composition was fabricated (using 100% argon, with 60 min of deposition time). Table 1 summarizes the deposition characteristics, both for Si and SiO$_2$/Si substrates.

In order to obtain the I-V curves of the ZnO/Si samples, aluminum contacts were deposited by thermal evaporation. The Al top electrodes were evaporated through a shadow mask, resulting in various Al cylinders of approximately 1 mm$^2$ each. On the back of each sample, a whole Al layer was deposited.

| Process | Gas flow (scm) | Percentage of gas flow | Deposition time (min) |
|---------|----------------|------------------------|-----------------------|
| a)      | 83.4 (Ar)      | 100% (Ar)              | 60                    |
| b)      | 76.0 (Ar) - 6 (O$_2$) | 92.7% (Ar) - 7.3% (O$_2$) | 90                    |
| c)      | 74.6 (Ar) - 8.1 (O$_2$) | 90.2% (Ar) - 9.8% (O$_2$) | 90                    |
| d)      | 69.5 (Ar) - 9.9 (O$_2$) | 87.5% (Ar) - 12.5% (O$_2$) | 90                    |

3. Results and discussion

The thicknesses of the samples were obtained by surface profilometry. The deposition rates of the ZnO/Si films (figure 1) tend to decrease as oxygen concentration increases. According to the literature, with oxygen content, the amount of Ar ions is decreased in the sputtering ambient, changing the deposition rate. Also, oxygen chemisorbs on the target and forms a surface layer of adsorbed oxygen. This layer inhibits the sputtering of the atoms [6].

The spectra of the ZnO/Si samples obtained by rutherford backscattering spectrometry (RBS) are shown in figure 2. In order to find out the stoichiometry of the films, simulation was performed using the RBS analysis package built on Genplot (RUMP), and simulated spectra were compared to the experimental data. The results shows that films with more oxygen concentration in the process gas tend to incorporate more oxygen in film composition, as expected. When the oxygen flow gets to 9.8%, the films present good stoichiometry (same proportion of Zn and O in the films). According to the RBS simulation, introduction of oxygen in the process gas results in films with higher roughness values, as the FUZZ command, which simulates the roughness of surface or interface, had to be used so the simulation would fit the experimental spectra. It was observed that roughness tends to increase proportionally to the oxygen concentration, until 9.8% of oxygen flow. With a further increase in the
oxygen flow, the roughness value kept constant. The values of surface roughness were not measured in this work, only estimated by the RBS spectra.

**Figure 1.** Deposition rate of ZnO/Si films in function of oxygen flow percentage in the process gas, along with the thicknesses obtained by profilometry.

The crystallinity of the ZnO/SiO₂ films (figure 3(a)) and ZnO/Si films (figure 3(b)) was studied by x-ray diffraction (XRD). The films obtained with oxygen in gas composition are strongly c-axis oriented along the (002) direction, resulted from the hexagonal (wurtzite) ZnO crystal structure. Both samples obtained with 100% Ar as process gas also presented other peaks of low intensity, indicating polycrystalline characteristics. The ZnO/Si with 100% Ar sample also showed an amorphous phase along with low intensity peaks. From the literature, it is known that the usage of SiO₂ buffer layer decreases the stress in the film. Stress in the ZnO thin film deposited on the bare Si substrate mainly results form the mismatch of lattice constants and thermal expansion coefficients between ZnO and Si substrate, resulting in a degradation of cristallinity [7].

An improvement of the crystallinity with the increase in oxygen concentration for both substrates can be observed, probably due to the suppression of defects on the structure. Optimum results were found for films with 7.3 and 9.8% of oxygen in gas composition, as they resulted in highest (002) peaks.

The I-V curves (figure 4) of the samples ZnO/Si were obtained by applying voltage from the top Al electrodes (deposited on ZnO) to the bottom electrodes (deposited under the silicon substrates). The results suggest that the oxygen incorporation influence the resistivity behavior. Although all the samples are poorly conductive, as they are not doped, the oxygen vacancies (specially present on samples obtained with less oxygen in gas composition) act as electron donors, increasing the probable n-type conductivity.

Scanning electron microscopy (SEM) images of ZnO/SiO₂/Si (figure 5) and ZnO/Si samples (figure 6) show that the structures of the films change drastically with the addition of oxygen in gas composition. Figure 5(a) shows clusters of mean size of 110 nm, formed by smaller grains, and figure 6(a) shows grains of different shapes and sized, agreeing with XRD spectra, which presented many small peaks and amorphous phase. Both samples obtained with no oxygen in gas composition appear to be flatter than the other samples, suggesting a lower surface roughness. These observations agree with the RBS spectra. For the films obtained with oxygen partial pressure ((b), (c) and (d) of figure 5 and figure 6), uniformly distributed spherical grains compose the surfaces.
4. Conclusions
Stoichiometric ZnO films were prepared by RF magnetron sputtering using a high-purity ZnO ceramic target. The layers were deposited onto silicon and thermally oxidized silicon substrates using argon and oxygen as sputter gases, 200W of RF power and 10mTorr of total process pressure. Substrate type has influenced the microstructure and crystallinity of the ZnO films, as they show better characteristics when deposited onto SiO$_2$/Si substrates. According to RBS measurements, films with higher oxygen partial pressure tend to incorporate more oxygen on the films, while films fabricated with low or no oxygen in gas composition presented oxygen vacancies. These defects are responsible for increasing n-type conductivity and reducing crystallinity. Best results of chemical composition and structural characteristics were found for samples produced with 7.5% of oxygen in the gas composition. They show good stoichiometry, improved crystallinity and reduced n-type conductivity. Therefore, this composition is more suitable for p-type doping of the films.

Figure 2. RBS spectra of ZnO/Si, showing atomic percentage of zinc and oxygen in film composition for samples obtained with (a) 0% O$_2$, (b) 7.3% O$_2$, (c) 9.8% O$_2$ and (d) 12.5% O$_2$. 
Figure 3. XRD spectra obtained for (a) ZnO/SiO2/Si films and (b) ZnO/Si films.

Figure 4. I-V curves of ZnO/Si films with (a) 0% O2 and 7.3% O2 and (b) 9.8% O2 and 12.5% O2.
Figure 5. SEM images obtained for ZnO/SiO2/Si samples with (a) 0% O2, (b) 7.3% O2, (c) 9.8% O2 and (d) 12.5% O2.

Figure 6. SEM images obtained for ZnO/Si samples with (a) 0% O2, (b) 7.3% O2, (c) 9.8% O2 and (d) 12.5% O2.
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