Optimization of ALD grown Ni-, Co- and Fe-doped ZnO films

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Abstract. Ni-, Co- and Fe-doped ZnO films were grown by atomic layer deposition on Si and glass substrates. The structures prepared were studied and characterized by XRD, XPS, ellipsometry and FTIR. The crystalline ZnO structure showed a strong dependence on the substrate used and the type of transition metal ion despite of the low doping levels.

1. Introduction

The interplay between the magnetic and semiconducting properties of diluted magnetic semiconductors (DMS) is of great interest from both fundamental and practical viewpoints. The semiconductors’ properties and the charge carriers’ spin quantum state of can be controlled by varying the temperature, the pressure, and the strength of the electrical and magnetic fields. Thus, making use of DMS in nano-devices opens-up new frontiers in spintronics and memory device applications. [1, 2].

ZnO films doped with transition metal oxides (TMO) are promising DMS films for optoelectronic and spintronic device applications [3-5]. On the one hand, ZnO possesses a high optical transmittance in the visible range and a low DC resistivity, which makes it suitable for transparent and optical devices. On the other hand, the partially-filled d-shell of transition metals gives rise to exciting and exotic properties of their oxides (TMO), such as colossal magnetoresistance (CMR), resistive switching, magnetism, multiferroism, etc. In view of preparing thin ZnO films, atomic layer deposition (ALD) allows the formation of uniform films on large areas with low level of pin-hole defects.

One can find a large number of publications related to Co-, Fe- or Ni-doped ZnO materials [4-11] but the information on ALD films is scarce [12, 13].

In this work, we studied ZnO films doped with Co, Fe or Ni grown by atomic layer deposition. DEZ (Diethylzinc) and water precursors were used to deposit ZnO. Doped ZnO layers were obtained by repetitively implementing one deposition cycle of TMO to a certain number of ZnO cycles. Nickelocene (NiCp2), cobaltocene (CoCp2) or ferrocene (FeCp2) were used as dopant precursor and ozone (O3) as oxidant.

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2. Experimental

2.1. Thin film preparation
The doped ZnO films were deposited in a thermal ALD reactor (Beneq TFS-200) by alternating ZnO and TMO (Ni, Co or Fe oxides) in 48 supercycles. Each supercycle consisted of 20 cycles ZnO and 1 cycle TMO (figure 1). DEZ followed by H$_2$O for ZnO matrix and metallocene (MeCp$_2$ = NiCp$_2$; CoCp$_2$ and FeCp$_2$) followed by O$_3$ for TMO doping were used. Nitrogen purging was performed after each precursors and oxidant pulses. The pulse duration and purging times (p) for both subcycles were as follows: DEZ/p/H$_2$O/p = 0.2/2/0.2/2 s and MeCp$_2$/p/O$_3$/p = 2/4/1/5 s, respectively. Following this protocol, the as-obtained films were TMO terminated.

A continuous flow of pure nitrogen gas at 300 sccm was used as a precursor carrier gas and for the purging procedure. Thin films of ZnO were deposited on Si and glass substrates and were heated up to 180 °C. The metallocenes are in the form of powder at room temperature. They were heated in order to increase the vapor pressure. The NiCp$_2$ and CoCp$_2$ were heated to 80 °C, while the FeCp$_2$ was heated to three different temperatures: 70 °C (Fe I); 50 °C (Fe II) and 30 °C (Fe III).

![Figure 1. ALD cycles of TMO doped ZnO.](image)

2.2. Ellipsometry
The ellipsometry measurements were performed in reflection mode using a Woollam M2000D rotating compensator spectroscopic ellipsometer with a wavelength range from 193 nm to 1000 nm. The film thickness and the optical constants were determined by fitting the experimental Ψ and Δ data.

2.3. X-ray analysis
The X-ray diffraction patterns were collected within the 2θ range from 10 to 80º with a constant step of 0.02º on a Bruker D8 Advance diffractometer with Cu Kα radiation and a LynxEye detector. The phase identification was performed with the Diffracplus EVA using ICDD-PDF2 Database.

2.4. XPS
The X-ray photoelectron spectroscopy (XPS) was performed on a Kratos AXIS Supra spectrometer with a non-monochromatic Mg X-ray source under vacuum better than 10$^{-8}$ Pa at a 90 degree take-off angle. Each analysis started with a survey scan from 0 to 1200 eV, pass energy of 160 eV at steps of 0.5 eV with 1 sweep. For the high-resolution analysis, the number of sweeps was increased and the pass energy was lowered to 20 eV at steps of 100 meV. The C1s photoelectron line at 285 eV was used for calibration of the recorded spectra.

2.5. FTIR
The FTIR spectra were recorded by using an IRPrestige-21 Shimadzu FTIR Spectrophotometer in the spectral range 350 – 4000 cm$^{-1}$ in a specular reflectance mode (average incident angle of 10°) with a bare Si wafer taken as background.

3. Results and Discussion
The thickness of each ZnO layer was determined by modeling the ellipsometry data Ψ and Δ. The sample was represented by a silicon substrate with three layers on top of it: a native silicon oxide, a ZnO layer and a roughness layer. The roughness layer was simulated by 50% voids and 50% ZnO.
The silicon substrate and the native silicon oxide were modeled using the optical constants from the CompleteEASE software. The ZnO layer was represented by the general oscillator model. For one of the samples, the thickness (about 200 nm, table 1) determined by ellipsometry was checked and confirmed to be the same by cross-sectional SEM (images not shown here). The SEM micrograph showed a smooth uniform surface and an abrupt interface between the film and the substrate. The roughness calculated from ellipsometry was in the range of 6 – 13 nm. The average growth rate of 2 Å/cycle was close to the growth rate reported of pure ZnO films [14-16].

The X-ray diffraction analyses show that the ZnO films doped with Ni, Co and Fe consist of a polycrystalline hexagonal phase with a wurtzite-type structure (figure 2). Even though the TMO are not detectable by XRD due to their low concentrations, there is a visible difference in the crystal structure depending on the type of the doping ion or of the substrate type. The highest intensity of the (002) ZnO reflection appears for pure and Fe-doped ZnO, while the (100) ZnO reflection is characteristic for Co- and Ni-doped ZnO. These results are in accordance with previous investigations based on the ZnO crystal structure dependence on the Al doping concentration, the substrate deposition temperature and the substrate type [16, 17]. The incorporation of a transition metal or/and transition metal oxides in the ZnO crystal lattice could be responsible for the variations in the crystal structure.

The samples were studied further by X-ray photoelectron spectroscopy. The Zn 2p photoelectron line for all thin films, together with the ZnLMM Auger line, show that the ALD process leads to the formation of ZnO. Nickel is detected on the surface, while iron and cobalt are not detected. The binding energy and shape of Ni 2p photoelectron line is typical for the Ni I 2+ oxidation states, most probably Ni(OH)3.

The IR lines at 370 cm−1, around 400 cm−1, and at 420 cm−1 and 455 cm−1 are due to the Zn-O stretching vibrations [18]. The IR peaks at 406 cm−1 and 525 cm−1 are indicative of a wurtzite phase [19]. The absorption band at 470 cm−1 might be related to the Ni-O stretching vibration of NiO6 octahedral in the NiO structure [20]. The analysis demonstrates changes in the absorption bands as a result of the incorporation of nickel (figure 3).

The IR peaks that are characteristic for cobalt oxide have been reported at 665 cm−1 and 577 cm−1 [21]. In our measurements, the ALD Ni-doped ZnO film shows no IR lines related to Co-O bonding, but as can be seen, the absorption bands of the doped samples differ from those of undoped ZnO in their shapes, which is a sign for Co incorporation and changes in the film structure.

The Fe-O vibrations have been reported to appear at 464 cm−1, 575 cm−1 [22], 627 cm−1, 580 cm−1 and 485 cm−1 [23]. In our case, there are no clear IR lines that could be attributed to Fe-O bonding. The incorporation of Fe dopant ions in the ZnO host lattice is manifested by the shifting of the peaks and the change in their shapes [24]. As can be seen in figure 3 for Fe-doped ZnO films, the peaks that

### Table 1. ZnO film thickness and roughness determined by ellipsometry.

| Sample     | Thickness, nm | Roughness, nm | Substrate          |
|------------|---------------|---------------|--------------------|
| ZnO:Ni     | 202.9         | 7.4           | p-Si(111)          |
|            | 207.9         | 10.7          | Knittel Glass      |
| ZnO:Co     | 200.2         | 7.1           | p-Si(111)          |
|            | 198.6         | 8.2           | Knittel Glass      |
|            | 200.2         | 7.5           | n-Si(100)          |
|            | 199.7         | 7.8           | p-Si(100)          |
| ZnO:Fe I   | 206.6         | 8.1           | p-Si(111)          |
|            | 208.5         | 9.5           | Knittel Glass      |
|            | 209.5         | 12.6          | n-Si(100)          |
|            | 199.2         | 7.7           | p-Si(100)          |
| ZnO:Fe II  | 195.2         | 6.4           | p-Si(111)          |
|            | 195.8         | 6.3           | Knittel Glass      |
|            | 206.7         | 8.9           | n-Si(100)          |
|            | 194.6         | 6.6           | p-Si(100)          |
| ZnO:Fe III | 193.6         | 7.0           | Knittel Glass      |
|            | 193.0         | 6.0           | n-Si(100)          |
|            | 192.1         | 6.4           | p-Si(100)          |
correspond to Zn-O vibrations change their shape and position compared to pure ZnO. The shape of the curves depends on the precursor temperature (container temperature), which directly influences the momentary pressure peak in the reactor chamber during the ferrocene (FeCp₂) pulse. Increasing the precursor temperature causes an increase in the pressure in the chamber during the precursor pulse. Additional studies are needed to clarify the effect of the change of the precursor temperature on the dopant incorporation in the ZnO matrix.

Figure 2. X-ray diffraction patterns of TMO-doped ZnO films deposited by ALD on different substrates.

Figure 3. FTIR analysis of Ni-, Co- and Fe- doped ZnO films deposited by thermal ALD on n-Si (100) substrates. During the deposition of the Fe-doped ZnO films, the Fe container was heated to 70 °C (Fe 1); 50 °C (Fe 2) and 30 °C (Fe 3).
4. Conclusions
We presented ALD of ZnO films doped with Ni, Co and Fe. The films were grown into polycrystalline wurzite crystal structures, the latter revealing a strong dependence on the type of substrate and doping. Studying this dependence could be very useful in understanding the mechanism of transition metal ion incorporation in the ZnO crystal lattice. From the practical point of view, ZnO should have different predominant crystal orientations depending on the application.

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