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From ZnF_2 to ZnO thin films using pulsed laser deposition: Optical and electrical properties

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ABSTRACT

The growth of Zn-based thin films, from pure ZnF_2 to pure ZnO, has been investigated as a function of the oxygen partial pressure and substrate temperature using pulsed laser deposition. Starting from $(1-x)$ $ZnO-x\cdot ZnF_2$ target compositions, ZOF films containing a low fluorine content ($x<0.10$) have been successfully deposited. These films exhibit typical ZnO wurtzite structure while maintaining the (002) preferred orientation. The fluorine doping does not modify the film transparency ($T\approx 90\%$), whereas for a high fluorine content, a large haze effect is observed. Such effects are associated with increased surface roughness. The Hall effect measurements show a beneficial effect with the addition of F corresponding to a decrease in resistivity for ZOF thin films accounting for oxygen to fluorine substitution in the ZnO structure. In contrast, attempts at annealing in air of successfully deposited pure ZnF_2 thin films does not lead to increased conductivity in the films; this is associated with a progressive transformation from ZnF_2 to ZnO. Finally, improvements in the electrical properties are proposed for F and Si co-doping, and resistivities as low as $7.2\times10^{-4}\,\Omega$ cm for SZOF thin films deposited at RT from a ZnO (87 at%)–ZnF_2 (10 at%)–SiO_2 (3 at%) target are achieved.

1. Introduction

Transparent conducting oxides (TCOs) are currently attracting significant attention in numerous applications, including use in solar energy [1,2], flat panel displays, electrochromic devices, and transparent electronics [3,4]. In particular, TCOs play a key role as the transparent conducting layer in current photovoltaic technologies, ranging from inorganic Si-based cells to organic and Grätzel cells. The required characteristics for TCOs across all photovoltaic technologies are similar to those desired for flat panel displays, including high transmittance and high electrical conductivity. Additionally, with more applications requiring flexibility, light weight, small volume, and low preparation temperatures, TCO layers deposited on plastic are becoming more desirable. ZnO thin films have been reported as suitable alternatives to other TCOs such as the state of the art Sn-doped In_2O_3, or ITO, due to their abundant resources, environmental safety, and their relatively low cost. High conductivities in ZnO thin films can be achieved through both intrinsic and extrinsic doping. For the latter, both n-type and p-type conductors have been reported, depending on the nature of the dopants [5]. However, despite several years of study, intrinsic and stable p-type conductivity [6–9] remains questionable. N-type conductivities have been reported for either intrinsic doping (via O deficiency and/or Zn interstitials) or for extrinsic doping (the most common dopants being Al and Ga) [10–12]. With our recent investigation on the influence of +4 dopants, we demonstrated similar or better TCO properties for ZnO:Si thin films deposited at low temperature relative to ZnO:Al or ZnO:Ga thin films [13]. N-type conductivity by anionic substitution is much less reported. The addition or substitution of fluorine remains the most common route for doping ZnO thin films grown using electron beam evaporation [14] and sputtering [15–17]. These depositions are mostly performed at elevated temperatures or followed by an annealing step. Taking advantage of its high versatility, pulsed laser deposition (PLD) has been shown to be highly suitable for the growth of a wide range of materials, including hydrides [18], oxides [19,20] and fluorides [21]. In this paper, we demonstrate the successful deposition of Zn-based thin films with PLD. We investigated two routes for the preparation of fluorine-doped conductive films (ZOFs) that were dependent on the target composition; these were ZnF_2 (i) and mixed $(1-x)$ $ZnO-x\cdot ZnF_2$ $(0<x<1)$ compositions (ii). Herein, the effect of annealing on the structural and optical properties of as-deposited ZnF_2 thin films are first reported, and the properties of ZOF thin films deposited from mixed targets are also discussed.

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Modeling of the optical data nicely supports the experimental data. Finally, a novel approach for F and Si co-doping of ZnO thin films is discussed.

2. Experimental

The "$(1-x)$ ZnO–$x$$ZnF_2$" thin films were grown by pulsed laser deposition using a KrF excimer laser Compex 102 ($\lambda=248$ nm) with a laser energy of 180 mJ pulse. Thin film depositions were performed on glass substrates with various O_2 pressures. ZnO and ZnF_2 targets were prepared from commercially available (Sigma-Aldrich) ZnO (99.99%), and ZnF_2 targets with $4H_2O$ (98%) and $(1-x)$ ZnO–$x\cdot ZnF_2$ samples were prepared by mixing ZnO (99.99%) and ZnF_2 targets with $4H_2O$ (98%) powders in stoichiometric proportion and pressing at 10 tons for 10 min. Pellets were sintered at 500 °C for 24 h under Ar atmosphere. Five target compositions with the following x values: $x=0$, 0.05, 0.1, 0.5 and 1 were prepared. XRD patterns of the targets show the presence of only ZnO ($P6_3mc$) and ZnF_2 ($P4_2/mnm$) diffraction peaks with various intensity ratios as a function of the x value. The film thicknesses were determined by profilometry and confirmed by transmittance modeling. Faster deposition rates were recorded for ZnF_2 thin films (≈ 4 nm/s) compared to ZnO (≈ 0.6 nm/s). All films were subjected to structural identification by X-ray diffraction (XRD) analysis using a D8 BRUKER diffractometer with $CuK_{\alpha 1}$ radiation. The surface morphology was characterized by Scanning Electron Microscopy (SEM, PHILIPS XL30) and atomic force microscopy (AFM, NTegra NT-MDT Serial number TS-150 used in the tapping mode). The composition of the films was determined by energy dispersive X-ray spectrometry (EDS) analysis and by X-ray photoelectron spectroscopy (XPS) analysis. XPS was performed on a VG 220i-XL ESCALAB spectrometer equipped with a monochromatized $Al_{K\alpha}$ source (1486.6 eV). Once deposited, thin films were kept under vacuum to prevent contamination. However, during the transfer from the substrate holder to the spectrophotometer, films were exposed to air for a few minutes. All XPS spectra have been corrected to C1s at 284.0038 eV. The optical transmittance was measured using a Varian double beam, UV–vis–NIR spectrophotometer CARY-5E, between 250 and 2500 nm with a direct method and an integrated method (sphere device). The experimental transmittance spectra were fitted with a commercial computer program [22]. The carrier type, carrier concentration and mobility were determined with an MMR Technologies, Inc., Hall setup in the Van der Pauw geometry at a magnetic field of 0.3 T.

3. Results and discussion

3.1. Deposition from the ZnF_2 target

The influences of the substrate temperature (from room temperature (RT) to 450 °C) and of the oxygen pressure (from 2.5×10^{-3} to 1.0 Pa) during thin film deposition have been investigated.

3.1.1. Structural characterization

The films deposited under an oxygen pressure (PO_2) of 1 Pa are polycrystalline and exhibit the typical ZnF_2 rutile structure (space group: $P4_2/mnm$) (Fig. 1) over all substrate temperatures. A slight increase in crystallinity is observed as the substrate temperature increases, with no evolution of the cell parameters. The average cell parameters are $a=b=4.71$ Å and $c=3.13$ Å; these are similar to the values reported in the literature [23]. Using the Scherrer formula, average crystallite sizes of 11 nm (for the film deposited at RT) and 12 nm (at 450 °C) were found. Depositions under lower (2.5×10^{-3} Pa) and higher (1.0 Pa) oxygen partial pressures led to similar XRD patterns with typical ZnF_2 structure. Interestingly, an increase in the oxygen partial pressure is associated with an increase in the cell volume (inset of Fig. 1). The latter trend can be correlated to steric effects, as the radius of fluorine ions is smaller than one of oxygen ions ($rF^- = 1.36$ Å $< rO^{2-} = 1.40$ Å). This trend may be interpreted as a first sign of an oxygen-doped ZnF_2 structure.

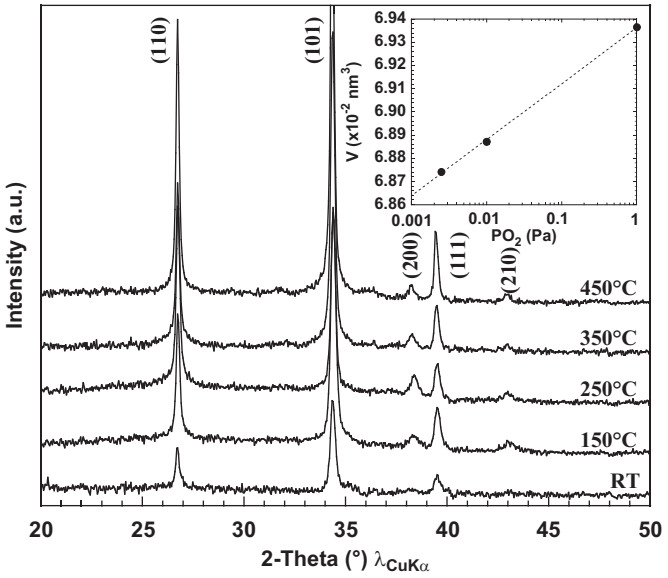

Fig. 1. Evolution of the XRD patterns of ZnF_2 thin films deposited under 1 Pa of oxygen as a function of the substrate temperature (From RT to 450 °C). The inset shows the evolution of the ZnF_2 cell volume with the O_2 pressure.

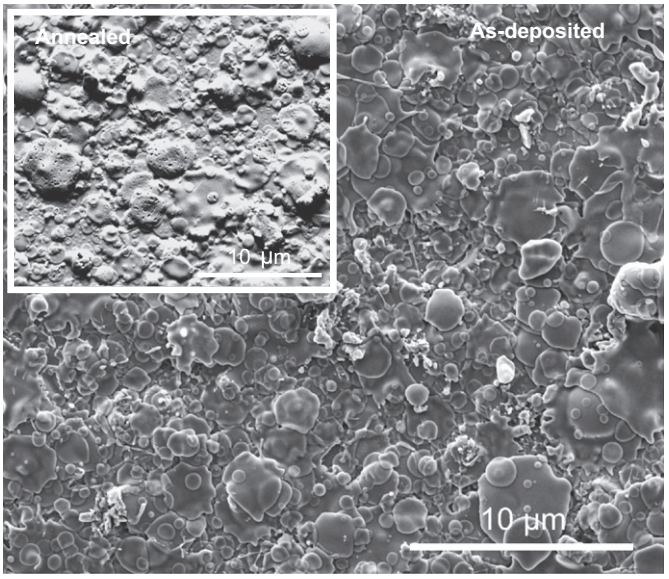

Fig. 2. SEM picture of a 450-nm ZnF_2 thin film deposited at 450 °C under 1 Pa of oxygen. The inset is an SEM picture of a 450-nm ZnF_2 thin film deposited at 450 °C under 1 Pa of oxygen and annealed under air at 300 °C.

3.1.2. ZnF_2 thin film morphology

The surface of the ZnF_2 thin films is very rough (Fig. 2) and does not depend on the substrate temperature. AFM measurements indicate an RMS roughness of 250 nm for a 450 nm thick