



High mobility hydrogenated zinc oxide thin films



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ABSTRACT

In this work we present a comprehensive study of the role of hydrogen in the structure, morphology, composition and electro-optical properties of zinc oxide thin films deposited by rf reactive magnetron sputtering at room temperature.

The transparency and conductivity of the in situ hydrogenated zinc oxide films (ZnO:H) are improved with the addition of H₂ to the sputtering atmosphere, where the resistivity dropped one order of magnitude (from 3×10^{-2} to 2.8×10^{-3} Ωcm) for an optimal dilution of 1.5% in argon. The effect of hydrogen in the conductivity of undoped ZnO thin films has been attributed to the shallow donor behaviour. However, we observed that the increase in the conductivity came essentially from the improvement of the mobility that reached 47.1 cm²/Vs for a carrier concentration of 4.4×10^{19} cm⁻³. This improvement in the mobility happens with an effective hydrogen incorporation into the bulk of the sputtered ZnO:H films, being attributed to the passivation of grain boundaries trap states while carrier concentration is dominated by the formation of Zn interstitials.

1. Introduction

Zinc oxide (ZnO) is a wide band gap ($E_g \approx 3.3$ eV) semiconductor that has been the focus of research for many decades due to its multifunctionality making possible to use it on a plethora of applications, that goes from transparent conductive material for electrodes, channel layer in thin film transistors (TFTs), light emitting devices (LEDs), laser diodes, chemical or gas sensors [1–6]. The interest in this material is mainly due to the easiness of tuning the optical and electrical properties, as happens when doping it with elements from group-III (e.g. In, Ga, Al), which occupy substitutional Zn positions in the lattice, increasing the free carrier concentration and optical band gap [7]. Undoped ZnO may also present native defects that affect its electrical and optical properties such as oxygen vacancies (V_O), zinc vacancies (V_{Zn}), zinc interstitial atoms (Zn_i) and antisites, or even incorporated hydrogen [8–10]. Concerning the last, hydrogen is defined as an amphoteric impurity in most of the semiconductors and typically counteracts the dominant electrical conductivity of the material: it acts as acceptor (H^-) in n-type material and as a donor (H^+) in p-type materials [11,12]. However, the role of hydrogen in ZnO is not consensual as well as its ability in compensating native defects, since some theoretical studies suggest that it has a non-amphoteric behaviour, acting instead as donor and resulting in the enhancement of n-type conductivity [9]. One of the first reports dates from the 1950's,

when Thomas et al. observed an increase in the electrical conductivity of a ZnO crystal, after hydrogen diffusion [13]. In spite of the several reports on the improvement in the electrical conductivity when hydrogen is incorporated, the mechanism behind it is not clearly understood. Several explanations have been reported such as the shallow donor behaviour acting as positive charged states; passivation of native defects (oxygen vacancies - V_O filling); occupation of interstitial sites connected to multicenter bonds; or promoting the relaxation of the ZnO lattice [1,9,14–19].

In most of the published reports the hydrogenation of the ZnO films is achieved by ion implantation, H₂ plasma treatment or in-situ through metal organic chemical vapour deposition resulting in a clear improvement of the films' electrical properties [13,20]. In this work the hydrogen was incorporated by mixing it with argon (Ar+H₂) during the films' growth, under reactive sputtering conditions, without any intentional substrate heating or post deposition treatment. The set of films produced under different dilutions were studied aiming to determine the influence on the electro-optical properties of the films and how this is related to the structure and to the chemical state of the hydrogen incorporated in the oxide matrix.

2. Experimental details

ZnO and ZnO:H thin films with around 180 nm were prepared on

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Corning glass by radio frequency magnetron sputtering at 13.56 MHz using an AJA ATC 1800 equipped with a load-lock chamber, from a 3 in. ZnO ceramic commercial target (LTS Chemical Inc., purity > 99.99%). The depositions were performed under a reactive atmosphere where the H₂ (99.9999% purity) dilution ($D_{H_2} = H_2 \text{ flow} / (Ar+H_2) \text{ flow}$) was changed from 0% to 2%. The base pressure, deposition pressure and target/substrate distance were kept constant at 7×10^{-5} Pa, 0.4 Pa and 15 cm, respectively. The rf power density applied to the ZnO target was 4.4 W cm^{-2} and the films were deposited without intentional substrate heating.

The structure of the films was studied by X-ray diffraction (XRD) using a PANalytical X'Pert PRO with Cu K α radiation ($\lambda = 1.540598 \text{ \AA}$) while the morphology was assessed by scanning electron microscopy (SEM) with a ZEISS SEM/FIB AURIGA operated at 2 kV, with an aperture size of 30 μm and a working distance of 5.2 nm. The surface roughness of the films was analysed by atomic force microscopy (AFM) using an Asylum MFP-3D instrument in non-contact mode.

The optical transmittance (T%) was measured between 300 and 2500 nm, using a double-beam UV–vis–NIR spectrometer (Lambda 950). The electrical resistivity (ρ), Hall mobility (μ_H) and free carrier concentration (n) were determined by Hall effect measurements in Van der Pauw geometry in a Biorad HL 5500 equipment using a constant magnetic field of 0.5 T. The electrical properties of the samples were measured at room temperature (RT), and for some selected samples the temperature-dependency was evaluated between 170 and 373 K in a cryostat.

PL measurements were performed in a home-made confocal setup by OSRAM Opto Semiconductors at RT. A HeCd laser was used for excitation at 325 nm with an output power of 30 mW and spot size of approximately 20 μm . Raman spectra were acquired using a confocal Raman microscope (LabRAM HR Evolution, Horiba Jobin Yvon). A 532 nm laser diode was used to excite the sample through a 100X, N.A.=0.90 air objective (MPlan N, Olympus). The Raman signal collected in the backscattering mode was dispersed in the built-in spectrograph by a 600 gr/mm grating and detected by an Open-Electrode CCD (Syncerity, Horiba Jobin Yvon).

The chemical state of oxygen and zinc in ZnO and ZnO:H films was investigated by X-ray photoelectron spectroscopy (XPS) using a PHI VersaProbe I Scanning Microprobe equipped with a monochromated Al K_{α} X-Ray source ($h\nu = 1486.6 \text{ eV}$), while the content of hydrogen in the films was inferred using a secondary ion mass spectrometer (SIMS) (Cameca MIQ256 Ion Microprobe instrument from ISA RIBER). More details about the SIMS data acquisition set-up and conditions are given in [Supplementary information](#).

3. Results

3.1. Structure and morphology

The XRD patterns of ZnO and ZnO:H films deposited with different D_{H_2} are presented in [Fig. 1](#). The data depicted clearly shows that the increase of D_{H_2} enhances the (002) reflex for 2θ around 34° , meaning the films become texturized along the [001] direction (c-axis) of the ZnO hexagonal wurtzite structure, minimizing so the surface energy [20,21]. It has been reported that preferential orientation is less favoured when depositing sub-stoichiometric ZnO as it is the case of the films here presented deposited only with Ar [22]. This also confirms that hydrogen has a similar effect to that of oxygen in determining a preferential growth direction in ZnO thin films.

[Fig. 1](#) also shows that the 2θ position of the (002) reflex shifts towards lower angular with D_{H_2} ([Fig. 1b](#), and [c](#)), which indicates the increase of the lattice's interplanar distance (d_{002}). Van de Walle and Chen et al. associated this to the relaxation of residual tensile strain in the lattice [1,2,20]. The increase of the full width at half maximum (FWHM) for D_{H_2} between 1% and 2%, suggests a decrease in the crystallite dimension, in agreement with previous studies [23,24]. The

average size, estimated using Debye–Scherrer equation, is around 20 and 24–25 nm for the ZnO and ZnO:H films, respectively ([Fig. 2](#)) [25].

The SEM micrographs of the films deposited under D_{H_2} are shown in [Fig. 3](#). When no H₂ is used, the films present a rough surface (RMS = 11.4 nm estimated by AFM) with large agglomerates that are supposed to be formed by small grains, as suggested by the average crystallite size determined from the XRD data ([Fig. 2](#)). When increasing D_{H_2} the surface becomes homogeneous and smooth without agglomerates, while the RMS roughness decreases down to 3.4 nm for $D_{H_2}=2\%$. This effect is attributed to the decrease in the growth rate (from 10.5 to 5–6 nm/min) related to the reduction of the sputtering yield due to the reduction of the Ar⁺ ion density in the plasma and so on cathode bombardment, when hydrogen atoms are added, as predicted by Bogaerts et al. [26], and experimentally observed by Saikia et al. during the deposition of TiO₂ thin films [27].

Another possibility for the decrease of the growth rate is the poisoning of the target's surface due to the presence of hydrogen that may result in the formation of metal hydrates, which leads to changes in the potential of plasma, responsible for a decrease in the deposition yield. Finally we cannot neglect also the re-sputtering (etching) of the growing film promoted by hydrogen atoms that eliminates preferentially weak bonds and small agglomerates, improving the films' crystallinity [25]. Regardless the reason behind the decrease of the growth rate, the roughness of the set of films analysed is reduced to about a half when compared to the ones deposited without H₂, in line to what was already observed by other authors [17,23,28].

3.2. Electrical and optical characterization

The Hall effect data for the ZnO and ZnO:H films ([Fig. 4](#)) show that they are n-type and the resistivity (ρ) decreases significantly as H₂ is added to the sputtering atmosphere. The increment of D_{H_2} from 0% to 1.5% results in a strong improvement of the Hall mobility (μ_H) from 6 to a maximum of $47.1 \text{ cm}^2/\text{Vs}$, while the carrier concentration (n) also increases reaching a value of $4.4 \times 10^{19} \text{ cm}^{-3}$, resulting in a ρ of $3 \times 10^{-3} \Omega\text{cm}$. This behaviour agrees quite well with what was already observed in metal oxide degenerated semiconductors [29]. However a decrease in n was observed when $D_{H_2}=0.5\%$. When using only Ar the resulting ZnO thin films are sub-stoichiometric and carrier concentration is controlled by V_O . When intentionally adding H₂ to the sputtering atmosphere, these defects start to be compensated, which results in improvement of the transparency and a decrease in the number of free electrons generated by V_O , while the μ_H is improved consistently with the increase observed in the crystallite sizes. It is expected that the formation of other donor like defects, such as Zn_i , will dominate at higher H₂ content and so will then increase. Further increase in D_{H_2} above 1.5% leads to an even higher n but μ_H slightly decreases, which does not result in a significant variation on ρ . Several explanations can be found in the literature for the improvement of both ρ and μ_H , such as donor effect either by the creation of interstitial hydrogen (anti-bonding O sites, bond-centred sites O–Zn in the grain boundary with bond like O–H) or oxygen vacancies (V_O) filling ($V_O+H^+ \rightarrow H_O^+$). This leads to ZnO reduction with hydrogen atoms and/or hydride ions or combination of oxygen vacancies with hydrogen creating V_O-H complex [1,2,10,14,15,23,24,30].

The optical characterization of ZnO thin films ([Fig. 5a](#)) shows that the average transmittance in the visible range (AVT) is around 90%, well above the one measured for films deposited without H₂ (AVT $\approx 60\%$). The improvement in the transparency is like that observed when adding oxygen to the gas mixture (see [Fig. 1 Supplementary information](#)). This shows that adding H₂ indeed compensates oxygen vacancies in ZnO thin films.

The optical band gap was obtained using the Tauc law, accordingly to the following equation:

$$ah\nu = A(h\nu - E_{op})^m,$$

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