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# Doping influence on intrinsic stress and carrier mobility of LP-MOCVD-deposited ZnO:B thin films

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ABSTRACT

Textured boron-doped zinc oxide (ZnO:B) films, suitable as transparent and conductive layers in thin film silicon-based solar cells, have been obtained by low-pressure metalorganic chemical vapour deposition (LP-MOCVD) technique. The complex role of the boron doping in ZnO layers was examined and its influence on the morphological and structural properties was analysed. Furthermore, a correlation between such properties, intrinsic stress and carrier mobility in the film has been analysed. ZnO:B films have a polycrystalline structure with a columnar texture shape, they show a rough surface with pyramidal large grains. At the increase of the boron doping the pyramidal shape of the grains deteriorates and the average grain size reduces. Furthermore the *a*-lattice parameter decreases indicating that the boron incorporation introduces a deformation in the crystal. In addition to these large structural modifications, the decrease of the carrier mobility at the increase of the doping content is observed. At the same time, the boron content also plays a meaningful role on the intrinsic stress inside the film. Stress behaviour in ZnO films has been investigated by X-ray diffraction measurements using the $\sin^2\psi$ method. Tensile stresses have been observed and the thermal and intrinsic components have been calculated. Respect to undoped ZnO films, boron incorporation on substitutional or interstitial sites increases the tensile stress by means of a lattice strain mechanism that reduces the *d*-spacing value.

## 1. Introduction

Zinc oxide is the most promising transparent conductive oxide (TCO) for its application as front electrode in photovoltaic technology based on amorphous and microcrystalline silicon solar cells [1]. It is characterised by low resistivity and high transparency in the visible wavelength range. When used as front electrode, it is extremely important that it shows a suitable surface texture able to give a high light scattering. Different deposition techniques such as RF or DC sputtering, e-beam evaporation, spray pyrolysis and chemical vapour deposition (CVD) are utilized for its preparation [2–5]. The CVD process can produce at low temperature a naturally textured material showing excellent and very stable electrical properties. Also the magnetron sputtering technique, with the addition of water ($H_2O$) [6–8] or $H_2$ [9] to the sputtering gas and with the substrate heating at high temperature ($>350\,^\circ C$), can be used to prepare textured TCO films. Unfortunately the electrical properties of such TCO layers are not excellent or deteriorate in the time. CVD technique, compared to other thin film deposition methods, is characterised by the following advantages

- High deposition rate.
- Good thickness uniformity.
- Natively textured material.
- Low deposition temperature ($<200\,^\circ C$).
- Scalability to large area fabrication (up to 1 $m^2$ and more).

Furthermore, being a low energy process, CVD does not produce surface bombardment, avoiding damage to the underlying layer. As a consequence, it is suitable for both front contact and optical back reflector deposition.

The influence of the deposition parameters on the electrical and optical properties of boron-doped zinc oxide (ZnO:B) films has been widely investigated, whereas on their mechanical properties it has been scarcely considered. Adhesion loss and fracture appearance in the time are strongly determined by "as grown" film mechanical properties. Stresses generated during or after the deposition process can result in either film adhesion failure or significant substrate bending, a serious problem for most device applications. On the other hand, in thin film photovoltaic technology it is well known that mechanical stress

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of the underlying film influences not only its mechanical stability but also the electrical parameters of the overlying films [10,11]. Furthermore, the structure of ZnO films strongly depends on the preparation conditions. ZnO thin films obtained by low-pressure chemical vapour deposition (LP-CVD) exhibit high (1 1 0) texture. However, the extent of the texture, the grain size and the mechanical stress also significantly depend on the growth conditions. In ZnO:B films, the introduction of a large concentration of boron atoms on substitutional or interstitial sites may both promote meaningful changes in film lattice parameters and increase impurity defects at the grain boundaries: both phenomena may produce stress. Therefore, the knowledge and the control of the residual stress in such films represent an important goal.

In the present study, the microstructure of CVD-deposited ZnO films has been analysed as a function of the doping content. Micro-structural aspects contributing to the film's state of stress have been considered. Furthermore, the evolution of the internal stress state with doping level is studied in more detail by applying the measurement technique of angle-dependent lattice strains by X-ray diffraction (XRD), using the $\sin^2\psi$ method. Finally, electrical properties have been studied as a function of the doping level.

## 2. Experimental details

Undoped and boron-doped ZnO films were deposited on Corning glass by low-pressure metalorganic chemical vapour deposition (LP-MOCVD) technique. Measured quantities of the precursors, diethylzinc (DEZ) and $H_2O$, vaporised and diluted with an inert gas (Ar), were separately transported up to the reactor chamber where, through a homogenising vapour shower, they reached the heated substrate maintained at a fixed temperature. The deposition system was elsewhere described [12]. In order to obtain the optimised doped-ZnO material, as first step, it is necessary to define the process parameters by which both a good intrinsic doping level (oxygen vacancies) and an appropriate surface texture are obtained [12]. Subsequently, at these fixed process parameters ($H_2O$/DEZ ratio, deposition temperature and process pressure), diborane ($B_2H_6$) diluted at 2% in helium has been added in order to increase the doping level and, as a consequence, the films conductivity.

ZnO layers with different $B_2H_6$/DEZ ratio (ranging from 0 to 1.2) were deposited to analyse the effect of boron incorporation, maintaining the other parameters constant (substrate temperature at 150 °C, process pressure at $1.3 \times 10^{-2}$ Pa).

The thickness of all the ZnO layers was about 1.7 μm and has been measured using a profilometer.

A detailed analysis of the structural, morphological, optical and electrical changes induced by doping level was carried out. The optical properties of the ZnO layers were analysed by Perkin-Elmer UV–vis-NIR spectrophotometer, the surface morphology and the structure were observed using a LEO S360 scanning electron microscope (SEM) and the surface properties by Veeco NSIV atomic force microscope (AFM). Panalytical X'PERT PRO MRD ($\lambda = 1.54806$ Å for Cu Kα) X-ray diffractometer was used to determine the structure and the residual stress of the films. Residual stress measurements permit the evaluation of an average stress in a large sample area and were carried out in order to study the deformation of the samples as result of their native history.

In order to obtain the total residual stress of deposited ZnO thin films, XRD technique was carried out by using the $\sin^2\psi$ method. In XRD stress experiment, the stress cannot be directly determined, but can be calculated from the angular lattice strain distribution of a chosen set of lattice planes. That is, we choose a reflection at high $2\theta$ angles that are generally more sensitive to strains/stresses (due to the steep incidence of X-ray beam at highest $2\theta$ angle and a higher relative $d$-spacing variation) and we measure the change of the $d$-spacing value (used as an internal gauge) with different orientation (tilt angles $\psi$) of the sample. The lattice strain is observed as a shift of the $2\theta$ angle of the diffraction peak, by recording the peak shift as a function of the sample tilt $\psi$, the amount of the residual stress present can be determined from the strain values ($\varepsilon$) using the elasticity theory, according to the following equation [13]

$$\varepsilon = \frac{d_\psi - d_0}{d_0} = \frac{1+v}{E}\sigma_{\text{tot}}\sin^2\psi \tag{1}$$

where, $\psi$ is the tilt angle, $E$ is the Young's modulus, $v$ is the Poisson's ratio, $d_\psi$ is the lattice spacing at each $\psi$ angle, $d_0$ is $d$-value for $\psi = 0°$ (perpendicular exposure) and $\sigma_{\text{tot}}$ is the total residual stress.

Finally, Hall measurements using a Van der Pauw configuration were used to evaluate the electrical properties of the different deposited films.

## 3. Results and discussion

### 3.1. Morphological and structural properties

ZnO thin films deposited by LP-CVD at appropriate deposition temperature are highly textured. The SEM image of the cross-section and the related XRD pattern of ZnO:B film deposited at substrate temperature of 150 °C are displayed in Fig. 1(a and b), respectively. The film was made of small grains in the region near the substrate, followed by the growth of larger crystals, having a columnar shape whose width increases with the thickness, emerging out of the surface as pyramids. These grains, as can be observed in Fig. 1, have their growth axis oriented perpendicularly to the (1 1 0) crystallographic planes. For both ZnO and ZnO:B films, the dominant diffraction peak is the (1 1 0) peak at around 56.8°, whereas only small amount of (1 0 0) and (0 0 2) peak are present, confirming the strong (1 1 0) texture of these films. The dominant peak arises from diffraction of ZnO planes of grains oriented with $c$-axes parallel to the substrate. Non equilibrium conditions, typically realised in CVD processes operating at high deposition rate, give rise to this grain orientation although it has been shown that the (0 0 1) direction in ZnO, obtained in equilibrium growth conditions, has the lowest surface energy [14]. In the insert of the Fig. 1(b) the SEM image shows the packaging of the crystallographic planes on the pyramid face during the crystal growth. In crystalline hexagonal system the growing of the pyramidal shape grain is realized by means of sequentially packaging of (1 1 0) planes along the vertical direction and by means of (0 0 2) planes along the horizontal direction with a vertical growth faster than the horizontal growth. These two different growth rates justify the pyramidal shape of the grains emerging out of the surface, whereas the observed columnar shape results from coalescence phenomena of several grains.

In Fig. 2 the relative intensities of the XRD peaks, in terms of (1 1 0/0 0 2) and (1 1 0/1 0 0) peak intensity ratios, are reported as a function of the $B_2H_6$/DEZ ratio. Increasing the doping level the (1 1 0/1 0 0) peak ratio remains low and almost constant and the (1 1 0/0 0 2) increases, in any case the (1 1 0) peak remains dominant and also at higher process pressure and boron content the zinc oxide films are composed of highly oriented crystallites.

The surface morphology is strongly affected by boron content. In Fig. 3 the surface morphologies of undoped zinc oxide and ZnO:B thin films with 0.65 and 1 $B_2H_6$/DEZ ratios are compared. The SEM images show that all the obtained films have a textured surface, but the surface morphology changes with the boron content in the film. The undoped film shows large pyramidal