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Short communication

Modification of electrical properties induced by annealing of ZnO:B thin films deposited by chemical vapour deposition: Kinetic investigation of evolution

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ABSTRACT

In this study temperature dependent Hall effect measurements combined with Fourier Transformed Infra-Red (FTIR) spectroscopy measurements is used to determine the evolution of the scattering mechanisms ascribable to in-grain and grain boundaries on Boron doped ZnO thin films deposited by Low Pressure Chemical Vapour Deposition (LPCVD). Through Hall effect measurements during in situ isothermal annealing, changes in electrical characteristics of zinc oxide could be followed in real time. Whereas only degradation is observed in air, an improvement of layer conductivity could be achieved at low temperatures by annealing under argon atmosphere. A study of the conductivity during isothermal annealing offers the possibility to extract activation energies, which have been compared to migration energies of the different intrinsic defects in ZnO.

1. Introduction

From all Transparent Conductive Oxide (TCO), ZnO thin films is one of the most commonly used as transparent electrode due its good transparency, conductivity, and abundancy as a material [1]. ZnO is an intrinsic n-type semiconductor nevertheless to achieve the conductivity required for solar cell application, an extrinsic doping with B, Al or Ga is used to obtain n-type degenerate semiconductor with free carrier concentration between 10^{19} and 10^{21} cm^{-3} [2]. However increasing the carrier concentration has a drawback, the increase will shift the plasmonic absorption to the visible range [3] and therefore decreases the amount of light available for energy conversion. Improvement of the conductivity by means of mobility increase is therefore preferable to reduce the absorption around the plasma frequency and capture more light in the absorber layer.

The deposition of boron doped ZnO (ZnO:B) by Low Pressure Chemical Vapor deposition (LPCVD) is well suited for deposition of uniform layer at low temperature on large substrate needed in thin film solar modules manufacturing [4]. With this deposition techniques ZnO:B layer can be grown with rough faceted surface ideal to achieve high solar cell efficiency due the enhanced light scattering [5]. Nevertheless this specific layer morphology also induces a lots of grain boundaries that can influence material stability essential for solar cell application to ensure durability as tested during certification [6]. ZnO surface and grain boundaries are known to interact with ambient atmosphere, which is a useful property in other applications such gas sensing [7,8] or photo-catalysis. This study on electrical properties of polycrystalline ZnO thin films brings new contributions for a better understanding of ZnO stability and interactions with the ambient atmosphere during thermal treatment. This paper also aims to optimize thermal treatment conditions to sustainably improve electrical properties.

2. Experimental details

ZnO films are deposited by LPCVD at 180 °C on a silicon (1 0 0) wafer, during deposition, 210 sccm of diboran is added to the gas mixture to increase the layer conductivity via boron doping which leads to an average carrier concentration of $8–9 \times 10^{19}$ cm^{-3}. The deposition time is adjusted to achieve an average layer thickness of 1 μm.

The electrical properties were characterized by Hall effect measurements in a HMS 5300 setup with in situ annealing. These measurements under direct current (d.c) condition sense the mobility of free carrier on macroscopic scale including therefore all scattering mechanisms. Initially performed in air, all of the experiments are repeated in inert atmosphere (Ar) to study the influence of the annealing atmosphere.

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Near-infrared reflectance spectra measured by Fourier transform spectrometer are treated with the standard Drude model with the dielectric function define as:

$$\varepsilon(\omega) = \varepsilon_\infty - \left(\frac{\omega_p^2}{\omega^2 + i\Gamma\omega}\right) \quad (1)$$

where ε_∞ is the dielectric constant at high frequency, Γ the damping frequency and ω_p, the plasma frequency. The simulation of reflectance spectra provides access to electrical parameters (free carrier concentration N and the optical mobility μ_{FTIR}) by means of the Eqs. (2) and (3):

$$\omega_p^2 = \frac{Ne^2}{\varepsilon_0 m^*} \quad (2)$$

$$\mu_{FTIR} = \frac{e}{\Gamma m^*} \quad (3)$$

where ε_0 is the free space permittivity, e is the elementary charge and m^* the electron effective mass.

As the optical mobility results of the free carrier motion under a high frequency electric field confining their motion to few nanometres, the electrical properties extracted are therefore considered as in-grain electrical properties. So, the comparison of Hall effect and optical measurements is very useful for a better description of the evolution of scattering mechanisms, which occur during annealing.

3. Results

3.1. Atmosphere influence

Stability of ZnO is strongly influenced by the ambient conditions. For example long term stability is tested usually in an atmosphere combining the effect of humidity, oxidation and temperature [9–11]. Several annealing experiments on ZnO have clearly demonstrated the influence of the ambient atmosphere during annealing on the evolution of the electrical properties [12–15]. However the stability depends on the deposition techniques [16], initial properties such as doping concentration [17] and thickness [18]. Fig. 1 presents the evolution of ZnO:B thin film conductivity after an annealing between 300 and 570 K in air and in an argon atmosphere. Bellow 440 K the conductivity remains almost constant. Above 440 K significant differences appear in both annealing atmospheres: the conductivity in air decreases quickly and loses 85% within 50 K, whereas in argon the conductivity gains almost 65% up to 500 K. Despite the fact that Hall effect measurements are very sensitive to small electrically active material modifications, information on the origin and the mechanism involved is relatively limited with these techniques. To determine the scattering mechanism involved in these processes, the conductivity extracted from FTIR measurement is added for comparison to the one measured by Hall effect at different annealing temperatures. The changes in conductivity are closely related to the mobility variation. In air annealing the degradation of conductivity is the consequence of a mobility decrease from 18 $cm^2 V^{-1} s^{-1}$ to less than 1 $cm^2 V^{-1} s^{-1}$ (limit of the HMS5300 detection level) while in argon the conductivity follows the mobility behaviour and the small variations observed in the carrier concentration do not significantly affect conductivity. The differences observed at room temperature between the intra-grain conductivity extracted with the optical technique and the conductivity measured by Hall effect indicate that the sample has a non-negligible contribution of grain boundary to the scattering. In air, the degradation of the in-grain electrical properties above 440 K is very low compared to the one measured by Hall effect; this difference points to a degradation of electrical properties during air annealing that is localized at the grain boundaries, and that the effect on the electrical properties within the ZnO grains is minor. On the other hand, for argon annealing measurements exhibit initially an improvement of the both macroscopic and in-grain conductivity. Until 520 K σ_{Hall} and σ_{FTIR} follow the same trend, but a closer inspection shows a progressive decrease in the differences between them. The ratio $\sigma_{Hall}/\sigma_{FTIR}$ is almost directly proportional to μ_{Hall}/μ_{FTIR}. According to Matthiessen's rule, this ratio can be interpreted as grain boundary scattering, and the minimum difference between μ_{FTIR} and μ_{Hall} observed at 520 K consequently indicates a decrease of grain boundary scattering associated with in-grain conductivity improvement. It is only at the highest temperature that degradation of the macroscopic electrical properties is measured while the in-grain mobility is still increasing. As in air, this degradation phenomenon acts at the grain boundaries but with a significant shift to higher temperatures.

3.2. Isothermal annealing

The role of temperature and atmosphere on the electrical properties described in the previous section is not sufficient to completely understand the modification of the film properties. All phenomena occurring during annealing are not only temperature dependent but also time dependent. The conductivity measured during in situ isothermal annealing as a function of time in different atmosphere offers the possibility to extract an activation energy that can be discussed in terms of migration, adsorption and diffusion processes.

Isothermal annealing confirms that regardless of the temperature, the macroscopic conductivity decreases when annealing is carried out in air (Fig. 2). For argon annealing, the evolution is completely different and two temperature range can be defined: in a first range corresponding to temperature bellow 440 K, the conductivity only increases with time (Fig. 2a), and in a second range with $T > 440$ K this improvement stage is followed by a degradation process (Fig. 2b). In order to extract quantitative values characteristics of these different thermally activated phenomena, isothermal annealing is carried out at different temperatures. The evolution of conductivity with time is described by Eq. (4) for degradation and with Eq. (5) for the improvement:

$$\sigma(t) = \Delta\sigma^-(T) \times \left[\exp\left(\frac{-t}{\tau}\right) - 1\right] + \sigma_0 \quad (4)$$

$$\sigma(t) = \Delta\sigma^+(T) \times \left[1 - \exp\left(\frac{-t}{\tau}\right)\right] + \sigma_0 \quad (5)$$

where σ_0 is the conductivity at $t = 0$ and $\Delta\sigma^+(T)$ and $\Delta\sigma^-(T)$ are the amplitude variation for the improvement and degradation case respectively. The relaxation time τ is defined by an Arrhenius-type equation:

$$\tau = A \times \exp\left(\frac{E_a}{kT}\right) \quad (6)$$

here E_a is the activation energy, k is the Boltzmann's constant and A the pre-exponential factor.

For the highest annealing temperature in argon where both process simultaneously occur the variation was fit according to the following equation:

$$\sigma(t) = \sigma_0 + \Delta\sigma^-(T) \times \left[\exp\left(\frac{-t}{\tau_1}\right) - 1\right] + \Delta\sigma^+(T) \times \left[1 - \exp\left(\frac{-t}{\tau_2}\right)\right] \quad (7)$$

For degradation during air annealing the activation energy E_a, the pre-exponential factor and $\Delta\sigma$ were determined by fitting a series of 5 isotherms between 400 K and 440 K with Eq. (4) (Fig. 3). For the lowest annealing temperatures ($T \leq 440$ K) in argon where the conductivity is only increasing (Fig. 4a) Eq. (5) have been used