Available online at www.sciencedirect.com
ScienceDirect
Thin Solid Films 516 (2008) 4620–4627
www.elsevier.com/locate/tsf

Carrier transport in polycrystalline transparent conductive oxides: A comparative study of zinc oxide and indium oxide

Klaus Ellmer [a,*], Rainald Mientus [b,1]

[a] Hahn-Meitner-Institut, Department Solar Energetics, Glienicker Str. 100, 14109 Berlin, Germany
[b] Opto-Transmitter-Umweltschutz-Technologie e.V., D-12555 Berlin, Köpenicker Str.325[b] Germany

Available online 14 June 2007

Abstract

Highly doped indium-tin oxide films exhibit resistivities ρ as low as 1.2×10^{-4} Ω cm, while for ZnO films resistivities in the range of 2 to 4×10^{-4} Ω cm are reported. This difference is unexpected, if ionized impurity scattering would be dominant for carrier concentrations above 10^{20} cm^{-3}. By comparing the dependences of the effective Hall mobility on the carrier concentration of ZnO and ITO it is found that grain barriers limit the carrier mobility in ZnO for carrier concentrations as high as 2×10^{20} cm^{-3}, independently, if the films were grown on amorphous or single crystalline substrates. Depending on the deposition method, grain barrier trap densities between 10^{12} and 3×10^{13} cm^{-2} were estimated for ZnO layers. Also, crystallographic defects seem to reduce the mobility for highly doped ZnO films. On the other hand, for ITO films such an influence of the grain barriers was not observed down to carrier concentrations of about 10^{18} cm^{-3}. Thus the grain barrier trap densities of ZnO and ITO are significantly different, which seems to be connected with the defect chemistry of the two oxides and especially with the piezoelectricity of zinc oxide.

Keywords: Transparent conductive oxides; Carrier transport; Degenerate semiconductors; Grain barriers; Electron mobility

1. Introduction

Transparent conductive oxides constitute a material class that combines high transparency in the visible and near infrared spectral range with a high electrical conductivity of up to 10^3 to 10^4 S cm^{-1}.

Today, films of indium, zinc and tin oxide are widely used as transparent electrodes in flat panel displays, thin film solar cells, as heating or antistatic layers. Up to now, tin-doped indium oxide (ITO) yields the lowest resistivities of about 1×10^{-4} Ω cm. This, together with its very good etchability, are the reasons why ITO is presently used exclusively as transparent electrode material for flat panel displays, based on liquid crystals, microplasmas or organic light emitting diodes (OLED). Zinc oxide, which is much less expensive than indium oxide, would be an alternative to replace ITO in flat panel displays. It can be doped by group III elements (boron, aluminium, gallium or indium) up to carrier concentrations of more than 10^{21} cm^{-3}. However, for ZnO only resistivities in the range of 2 to 4×10^{-4} Ω cm have been reported, particularly when prepared by large area coating methods like magnetron sputtering. Furthermore, compared to ITO it is much more difficult to prepare doped ZnO films of such low resistivities, i.e., the "process window" is much narrower.

It has been stated by Bellingham et al. and others [1–3] that the carrier scattering at ionized impurities (for instance Sn^+ or Al^+) limits the mobility in these TCO materials for carrier concentrations above 10^{19} cm^{-3}. For a degenerately doped semiconductor the mobility due to ionized impurities μ_{ii} is proportional to the square of the ratio of its relative dielectricity constant and its effective mass [4–6]: $\mu_{ii}\sim(\varepsilon_r/m^*)^2$. This ratio is listed in Table 1 for the three oxides. The data of silicon are included for comparison, since this semiconductor is best investigated for carrier concentrations $>10^{19}$ cm^{-3}.

If ionized impurity scattering would be the dominant scattering mechanism for carrier densities $>10^{19}$ cm^{-3}, comparable resistivities for ITO and ZnO are expected for the same carrier concentrations. For SnO_2 even higher mobilities can be calculated,

* Corresponding author. Tel.: +49 30 80622770; fax: +49 30 80622434.
E-mail addresses: ellmer@hmi.de (K. Ellmer), r.mientus@t-online.de (R. Mientus).
[1] Tel.: +49 30 65762673; fax: +49 30 65762672.

0040-6090/$ - see front matter © 2007 Published by Elsevier B.V.
doi:10.1016/j.tsf.2007.05.084

Table 1
Static dielectric constants ε_r, effective masses m^*/m_e and ionized impurity limited mobilities of TCOs and of silicon

Material	ε_r	m^*/m_e	$(\varepsilon_r\, m_e/m^*)^2$	Normalized ratio	μ_{ii} [cm^2/Vs]
In_2O_3	9	0.35	661	0.53	50
SnO_2	11.5	0.26	1956	1.57	30
ZnO	8.3	0.28	879	0.70	50
Si	11.9	0.337	1247	1.0	68.5(n)/44.5(p)

about a factor of 2 to 3 higher than that of ZnO or ITO. However, this is not found experimentally [2].

Therefore, in the present study the carrier transport processes in ITO and ZnO are compared in order to get a deeper understanding of the differences between these TCO materials. For this purpose conductivity and Hall mobility measurements on ZnO:Al and ITO films were undertaken for films deposited on amorphous as well as single crystalline substrates (sapphire) in order to determine the dominant scattering processes (ionized impurities, grain barriers, crystallographic defects). Our own data are compared with literature data reported for ZnO and ITO to show the general trends. Theoretical and semiempirical models are used to fit the experimental data and to derive characteristic material parameters for these three oxides.

2. Theoretical models

The theoretical models on ionized impurity scattering were already reviewed in 2001 by one of the authors when estimating the mobility limit of highly doped zinc oxide [3]. In the following a short summary is given to lay the basis for the further discussion.

2.1. Ionized impurity scattering

This scattering process is caused by ionized dopant atoms and dominates for carrier concentrations above about 10^{19} cm^{-3}. An analytical expression for the mobility μ_{ii} of degenerately doped semiconductors, taking into account the nonparabolicity of the conduction band, was given by Zawadzki [7] and refined by Pisarkiewicz et al. [6]:

$$\mu_{ii}^{ZP} = \frac{3(\varepsilon_r\varepsilon_0)^2 h^3}{Z^2 m^{*2} e^3}\frac{n}{N_i}\frac{1}{F_{ii}^{\mathrm{np}}(\xi_d)} \quad \text{with} \quad \xi_d = \left(3\pi^2\right)^{1/3}\frac{\varepsilon_r\varepsilon_0 h^2 n^{1/3}}{m^* e^2} \tag{1}$$

where the screening function F_{ii}^{np} is given by

$$F_{ii}^{\mathrm{np}} = \left[1 + \frac{4\xi_{\mathrm{np}}}{\xi_d}\left(1 - \frac{\xi_{\mathrm{np}}}{8}\right)\right]\cdot\ln(1+\xi_d) - \frac{\xi_d}{1+\xi_d} - 2\xi_{\mathrm{np}}\left(1 - \frac{5\xi_{\mathrm{np}}}{16}\right) \tag{2}$$

with the parameter $\xi_{\mathrm{np}} = 1 - m_0^*/m^*$, which describes the nonparabolicity of the conduction band (m^*, m_0^* — effective masses in the conduction band and at the conduction band edge, respectively). The prefactor in Eq. (1) shows that the ionized-impurity limited mobility depends as $\mu_{ii} \sim (\varepsilon_r/m^*)^2$ on the material constants of the semiconductor and as $\mu_{ii} \sim Z^{-2}$ on the charge of the dopants.

The theoretical model given above as well as the models of Conwell and Weisskopf [8,9], Shockley [4], and Dingle [5] are based on the assumption of a statistically homogeneous distribution of scattering centers, i.e., dopants. However, this is no longer valid for extremely high dopant concentrations, where the dopants form clusters which lead, due to their higher charge ($\mu_{ii} \sim Z^{-2}$), to lower mobilities. This effect was already proposed in 1971 by Dakhovskii et al. [10]. Klaassen applied this cluster model to fit accurate measurements of mobilities in p- and n-type single crystalline silicon [11,12]. He calculated cluster charges up to 2 for boron-doped and 3.5 for phosphorous-doped silicon at a carrier concentration of 10^{21} cm^{-3}. Recently, such clusters of zinc dopants were verified by atomically resolved analysis in GaAs [13]. The carrier mobility in highly doped semiconductors is best investigated for p- and n-type silicon. Masetti et al. [14] measured the mobility of arsenic-, phosphorus-, and boron-doped silicon up to carrier concentrations of 5×10^{21} cm^{-3} and fitted their experimental values by the empirical curve

$$\mu^{\mathrm{Ma}} = \mu_{\min} + \frac{\mu_{\max} - \mu_{\min}}{1 + \left(n/n_{ref1}\right)^{\alpha_1}} - \frac{\mu_1}{1 + \left(n_{ref2}/n\right)^{\alpha_2}} \tag{3}$$

The fit parameters $\mu_{\max}$, $\mu_{\min}$ and $\mu_{\min} - \mu_1$ describe the lattice mobility at low carrier concentrations, the mobility limited by ionized impurity scattering and the clustering mobility, discussed above (see Table 2).

Unfortunately, experimental mobility data for single crystalline oxides are not available for $N > 10^{20}$ cm^{-3}. For zinc oxide mobilities up to $N \approx 8\times10^{19}$ cm^{-3} have been measured by Rupprecht about 50 years ago [15]. His data are shown in Fig. 1 together with other data for single crystalline ZnO as well as the fit curves for the experimental data of silicon given by Masetti et al. [14]. The ZnO mobility values were fitted using the empirical formula (3) and the fit parameters are summarized in Table 2 together with the corresponding values for silicon. In the transition region from lattice to ionized scattering for $5\times10^{16} < N < 5\times10^{18}$ cm^{-3} a large scattering of the experimental ZnO data can be observed. Therefore, the data have been fitted in analogy to the silicon data, which exhibit a much higher accuracy [14]. However, the exact transition does not influence the conclusions much since we are interested predominantly in ionized impurity scattering in the region $N > 10^{19}$ cm^{-3}.

Table 2
Fit parameters for $\mu = f(N)$ (Masetti's formula, Eq. (3)) for phosphorous- and boron-doped silicon [14] and zinc oxide, indium oxide and tin oxide ($\mu_{\max}$ — lattice mobility, $\mu_{\min}$ — ionized impurity mobility, $\mu_{\min}$–μ_1 — clustering mobility)

Fit parameter	Si:P	Si:B	ZnO	ITO	SnO_2
$\mu_{\max}$ [cm^2/Vs]	1414	470.5	210	210	250
$\mu_{\min}$ [cm^2/Vs]	68.5	44.9	55	55	50
$\mu_{\min}-\mu_1$ [cm^2/Vs]	12.4	15.9	5	5	10
n_{ref1} [10^{17} cm^{-3}]	0.92	2.23	4	15	20
α_1	0.711	0.719	1	1	1
n_{ref2} [10^{20} cm^{-3}]	3.41	6.1	6	20	6
α_2	1.98	2.0	2	2	2