Preparation and characterization of transparent ZnO thin films obtained by spray pyrolysis

R. Ayouchi, D. Leinen, F. Martín, M. Gabas, E. Dalchiele, J.R. Ramos-Barrado

*Laboratorio de Materiales y Superficie (Unidad Asociada al CSIC), Departamento de Física Aplicada & Departamento de Ingeniería Química, Universidad de Málaga, Campus de Teatinos, E29071 Malaga, Spain

bp Instituto de Física, Facultad de Ingeniería, Universidad de la República, Herrera y Reissig 565, C.C. 30, 11000 Montevideo, Uruguay

Received 24 July 2002; received in revised form 19 December 2002; accepted 20 December 2002

Abstract

Structural, optical, chemical and electrical properties of thin films of ZnO obtained by spray pyrolysis over Pt or silica substrates are determined at temperature ranges between 223 and 373 K. The thin films are pure ZnO with a preferred crystalline orientation of (0 0 2). Grain-boundary barriers are created by the band bending and the mobility of charge carriers is limited by the thermal field emission of electrons at the grain-boundary barriers. The density of ionized acceptor atoms and the width of the space charge, both obtained from the capacitance–voltage (C–V) method, are consistent with the theory of the depletion layer in the Schottky barrier device. The density of states of defect, obtained from admittance spectroscopy, only presents a maximum at approximately 0.44 eV, whose position in the band gap does not change under bias.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Spray pyrolysis; ZnO; Electrical properties; Schottky barrier

1. Introduction

Zinc oxide is an n-type semiconductor with very important properties, which make it commonly used in electronic and optoelectronic applications [1]. Polycrystalline ZnO varistors have been widely used as surge protection devices in the electronic industry [2]. Thin films with low conductivity and highly oriented grains can be used as ultrahigh frequency electroacoustic transducers due to their piezoelectric properties [3]. Moreover, thin films of ZnO are used in solar cell manufacturing as transparent and antireflective coatings [4]. The antireflection coating thickness and smoothness must be optimized to take full advantage of the solar spectrum. There are several reports of d.c. conductivity [5] in thin films and crystals of insulating ZnO. Band conduction has been suggested with donor levels close to the conduction band produced by interstitial Zn.

However, only a few reports are available on the conduction mechanism in ZnO films [5–7].

Spray pyrolysis is a useful alternative to the traditional methods for obtaining thin films of ZnO. It is of particular interest because of its simplicity, low cost and minimal waste production. The spray pyrolysis process allows the coating of large surfaces and it is easy to include in an industrial production line. With spray pyrolysis, the solution is sprayed directly onto the substrate. A stream of gas, e.g. compressed air, can be used to help the atomization of the solution through the nozzle. Sometimes, posterior thermal treatment is necessary to ensure the elimination of precursor waste, and avoid sintering or crystallographic phase transformation.

The aim of this work has been to obtain thin films of ZnO by spray pyrolysis using aqueous solutions of compound precursors of the oxide and to compare their electrical and optical properties with the properties of other thin films obtained with methods employing a high vacuum environment.
2. Experimental details

In this paper work, ZnO thin films were prepared by spray pyrolysis from $4 \times 10^{-3}$ M of zinc acetate dihydrate dissolved in ultra pure water. All the films were deposited onto fused silica and Pt substrates; the substrate temperature was $573 \pm 2$ K. The solution flow rate and gas pressure were kept constant at 50 ml h$^{-1}$ and $3 \times 10^5$ Pa, respectively. The nozzle to substrate distance was 10 cm and the spraying time was 30 min. In this procedure, compressed air is used to atomize the solution containing the precursor compounds through a spray nozzle over the heated substrate; air is compressed from the atmosphere, using filters to remove water and oil. The precursor is pyrolyzed on the heated substrate. The substrate holder is equipped with thermocouples and heating elements equipped with a temperature controller. The substrate is moved forward and backward at a fixed frequency (0.5 Hz) by an electronically controlled step motor; the amplitude of displacement was twice the length of substrate. The solution was pumped into the air stream in the spray nozzle by means of a syringe pump. The nozzle consists of two concentric pipes, through the inner pipe flows the solution and between inner and outer the air stream; the spray is produced by the Ventury effect at the end of both pipes. The thickness of the films was measured ex situ by means of X-ray absorption with an accuracy of ±5 nm. Film structure was characterized by X-ray diffraction using Cu Kα radiation in a conventional goniometer with a θ–2θ scanning mechanism.

Chemical composition of the films were studied by X-ray photoelectron spectroscopy with a physical electronic instrument (PHI 5700). A standard X-ray source of 15 kV, 300 W and Mg Kα radiation (1253.6 eV) was used. The energy scale of the spectrometer was calibrated using Cu 2p, Ag 3d and Au 4f$_{3/2}$ photoelectron lines at 932.7, 368.3 and 84.0 eV, respectively. PHI ACCESS ESCA-V6.0F software package was used for data acquisition and analysis. Atomic concentrations were determined from the photoelectron peak areas using Shirley background subtraction [8] and sensitivity factors provided by the instrument manufacturer. All sample spectra were referred to the C1s line of the residual carbon set at 284.6 eV. Depth profiling was carried out using 4 keV Ar$^+$ bombardment at a current density of $\sim$3 μA cm$^{-2}$. A sputtering rate of 0.5 nm min$^{-1}$ is assumed as determined for Ta$_2$O$_5$ under the same sputtering conditions.

Observation of surface morphology was performed using a scanning electron microscope (SEM JEOL model JSM5300).

Electrical properties were determined by dielectric spectroscopy using a Broadband Dielectric Converter from Novocontrol with a Solartron 1255 frequency response analyzer for a frequency range between 10 Hz and 1 MHz. The ZnO thin film, over a Pt substrate, was placed in a Novocontrol sample holder modified in our laboratory. The temperature range was between 223 and 353 K, which was controlled by a Quatro temperature controller from Novocontrol.

3. Results and discussion

3.1. Structural and optical properties

Fig. 1 shows a typical X-ray diffractogram obtained from a 150 nm thick film. As we can see, only the ZnO (0 0 2) peak is observed at $2\theta = 34.68^\circ$ (JCPDS card 6-0416), which indicates that under the conditions described in the previous section, the films grow preferentially along the c-axis orientation, vertical to the substrate. The shift of the diffraction peak position to a value higher than its normal position in ZnO powder ($2\theta = 34.42^\circ$) is attributed to a surface effect which originate a lattice distortion and decrease the lattice parameter along the c-axis direction [9]. As determined from the XRD data, the lattice parameter c is estimated to be 5.17 Å.

The mean crystallite size of the sample is evaluated by means of the Scherrer formula

$$D = \frac{0.9\lambda}{B\cos\theta_B}$$  

(1)

where $\lambda$, $\theta_B$ and $B$ are the X-ray wavelength (1.5418 Å), Bragg diffraction angle and full width at half maximum of (0 0 2) diffraction peak, respectively; using $B = 0.01^\circ$, $\theta_B = 17.34^\circ$, the grain size is estimated to be $\approx 146$ Å [10].

Fig. 2 shows the transmittance spectra in the wavelength range from 300 to 900 nm, for ZnO deposited on fused silica. The films are highly transparent in the
visible range of the electromagnetic spectrum with an average transmittance reaching values up to 95%, and present a sharp ultraviolet cut-off at approximately 380 nm.

Fig. 3 shows the plot of \((\alpha h\nu)^2\) vs. \(h\nu\), where \(\alpha\) is the optical absorption coefficient and \(h\nu\) is the energy of the incident photon. Since the ZnO is a direct transition semiconductor, \(\alpha\) is related to the optical energy band gap \((E_g)\) by, [11].

\[
(\alpha h\nu)^2 = \beta (h\nu - E_g)
\]

where \(\beta\) is a parameter; \(E_g\) is determined by extrapolating the straight line portion \(h\nu\alpha = 0\), in this case \(E_g\) is estimated to be 3.31 eV. However, the optical band gap for pure bulk ZnO, is known to be 3.2 eV [12]. This difference was also observed in ZnO thin film obtained by the photochemical vapor deposition technique and can be interpreted as the Burnstein-Moss effect [12], which is supported by the XPS and XRD data.

3.2. Morphology characterization

Fig. 4 presents the microphotograph, obtained by SEM, of the surface of a ZnO thin film obtained at 573 K and the cross section of the same film. We can observe that the surface is flat without holes, cracks, protrusions, or other defects. In the cross section we can see the substrate (SiO₂), after a thin film of Pt of 300 nm, deposited by d.c. sputtering, and the 2.5 μm of a thick ZnO film. Others relevant properties about the growth of ZnO thin films, as its columnar growth, are studied in another paper [13].

3.3. Chemical characterization

Fig. 5 shows the wide scan XPS spectra of ZnO thin film prepared at 573 K, before (curve a) and after (curve b) 30 s of Ar⁺ etching in the binding energy range of 0–1200 eV.
range of 0–1200 eV. XPS spectrum of the film after Ar$^+$ sputtering showed no evidence of C 1s or C KLL peaks. These results suggest that carbon found on the surface of the film is probably due to contamination caused by specimen handling.

Fig. 6a and b, shows the high-resolution spectra of O1s and Zn2p photoelectron lines, respectively, for ZnO thin film. It can be seen from this figure, that the O1s peak consists of two components at 530.2 eV (O1s(a)) and 532.01 eV (O1s(b)). The first one can be attributed to O–Zn bonds [13], while the second one which disappears completely after a few minutes of Ar$^+$ sputtering corresponds to adsorbed oxygen from O–H bonds in adsorbed H$_2$O molecules as reported by Futsubara [14]. For the Zn2p$_{3/2}$ line, only one peak at 1021.49, which corresponds to Zn–O bonds, can be observed. The atomic ratio of Zn/O was 1.02/1.00 (±2%) as determined from XPS spectrum by using the integrated peak area and sensitivity factors. These results confirm the highly resistant characteristic of the film. Table 1 shows the most relevant results.

3.4. Electrical conduction mechanism

The measurement of electrical conductivity at different temperatures allows us to obtain information about important properties of the film, for example, the activation energy and the donor level and from the comparison between the average grain size and the Debye screening length, we can determine if a potential barrier is created because of band bending, and even if the mobility of charge carriers is limited by the thermionic or thermo field emission of electrons.

The a.c. method is an easy procedure for measuring the electrical conductivity of a film because at low frequencies the conductivity dependence can be expressed by the so-called Jonscher power law [15].

$$\sigma'(\text{low freq.}) = \sigma_{dc} + A\omega^n \quad n < 1$$  
(2)
Fig. 8. Arrhenius plot for d.c. conductivity.

Here $\sigma_{dc}$ is the d.c. conductivity, $A$ a temperature dependent parameter and $n$ a fractional exponent between 0 and 1. Fig. 7 shows a log–log representation of $\sigma'(\omega)$ vs. experimental frequency, $\omega$, for the different temperatures. The second term in Eq. (2) represents the a.c. or polarization conductivity. This power law has been widely observed in many disordered materials like ionically conducting glasses [16], ferroelectric materials [17], semiconductor materials [18], etc.; this behavior is generally related to the mechanism of charge transport as well as many-body interaction among of charge carriers [19].

The variation of $\sigma_{dc}$ with temperature obtained from a fitting of the experimental values of the frequency-dependent conductivity is shown in Fig. 8. These values of $\sigma_{dc}$ are identical to the d.c. values obtained from a complex plane analysis. The d.c. conductivity shows a linear Arrhenius behavior indicating band conduction of carrier electrons. From these data, we obtained an activation energy of 0.37 eV, which is in good agreement with the values obtained by other authors [20,21].

The donor level from the bottom of the conduction band is given by $E_d=2E_x$, so if the donor level is produced by interstitial Zn atoms, then $E_d=0.74$ eV. The electron transport at low temperature in polycrystalline semiconductor can be discussed by comparing average grain size $l$ with the Debye screening length [22] $L_d$, expressed as $L_d=(\varepsilon\varepsilon_0 kT/q^2N_d)^{1/2}$, where $\varepsilon$ is the specific dielectric constant, $\varepsilon_0$ the dielectric constant in vacuum, and $N_d$ the donor concentration of the sample. Then, if the average grain size is larger than $2L_d$, a potential barrier is created because of band bending, and the mobility is thermally activated. On the other hand, if $l$ is less than $2L_d$, the conduction band becomes flat. As a result the potential barrier does not exist around the grain-boundary for the electron transport, and the mobility is hardly activated.

To determine the value of $L_d$ for the ZnO film obtained by spray pyrolysis in the above indicated conditions, it is necessary to estimate the electron concentration from the Mott–Schottky plot (Fig. 15). The value obtained by this method, $5 \times 10^{23}$ m$^{-3}$, is similar to the value obtained in the work of Natsume et al. [23], $4.2 \times 10^{24}$ m$^{-3}$. We have assumed this electron concentration and $\varepsilon=8.5$ at 300 K [24]. Providing that most donors are ionized at room temperature, $N_d=5 \times 10^{23}$ m$^{-3}$, we estimate $L_d=5.75 \times 10^{-9}$ m. Since electrons are transported in the conduction band in the ZnO film, we must take into account the effects of the grain-boundary barriers created by the band bending since the criterion $2L_d<1$ is satisfied, that is agreement with the work of Natsume et al., even the grain seize in our films is lower [23].

Some authors [25] discuss the effects of the grain-boundary barrier using the criterion of the material tunnelling constant [26], given as $E_0=(N/m^*\varepsilon)^{1/2}$ eV, where $N$ is the impurity concentration and $m^*$ the effective mass of the electron. The mechanism for electron conducting in the conduction band in a polycrystalline semiconductor can be considered similar to the mechanism for a metal-semiconductor Schottky barrier. In this case, for a semiconductor at high temperature or in a low doping range where $kT>E_0$, the mobility is limited by the thermionic emission of electrons over the grain-boundary barrier. However, if the semiconductor is at low temperature or in a high doping range where $kT<E_0$ the mobility is limited by the thermo field emission of electrons through the grain-boundary barrier. We consider an electron concentration of $5 \times 10^{23}$ m$^{-3}$, where $m^*=0.27$ m [27] and $\varepsilon=8.5$ and we obtain an $E_0$ much high than $kT$, and we can assume that the mobility is limited by the thermal field emission of electrons at the grain-boundary barriers.

3.5. Dielectric properties

The study of the dielectric properties is another important characteristic in a thin film; we can determine the electrical and dipolar relaxation time and its activation energy, but the analysis of dielectric dispersion data becomes difficult in the absence of a well-defined dielectric loss $\varepsilon''(\omega)$ peak, (Fig. 9) [28].

It has been suggested by Moynihan, Boese and Laberage [29,30] that in the absence of a well-defined $\varepsilon''(\omega)$ peak, information about the relaxation mechanism can be obtained from the dielectric modulus representation, which is defined as the reciprocal of the dielectric permittivity. The electric modulus formalism for analysis of data from a.c. impedance was originally developed by Macedo et al. [31] to allow the time/frequency-dependent electrical response of the conducting glasses to be treated as a relaxation process analogous to mechanical shear stress relaxation in a liquid. The
modulus representation suppresses the unwanted effects of extrinsic relaxation and is often used in the analysis of the dynamic conductivity of solids. In this formalism, for a pure conduction process a relaxation peak is observed in the spectrum of the imaginary part of \( M^* (\omega) \); while no peak is present in the corresponding plot of \( e^* (\omega) \). For a dielectric relaxation process, however, relaxation peaks are obtained in both the \( M^* (\omega) \) and \( e^* (\omega) \) representation with the peak position in the two representations related by the ratio \( \frac{\varepsilon_r}{\varepsilon_{\infty}} \), where \( \varepsilon_r \) is the dielectric static constant [32]. A comparison of the experimental data in the \( M^* (\omega) \) and \( e^* (\omega) \) representation is very useful to distinguish long-range conduction processes from localized dielectric relaxation [33]. Fortunately, the conduction and dielectric processes are decoupled; therefore, they are separable processes so that the linear superposition principle is valid and we can separate the different contributions to the electrical modulus \( M^* (\omega) \) or to dielectric permittivity \( e^* (\omega) \). In this procedure, we can assume a distribution of relaxation time \( \tau_\sigma \) in the conductivity part of \( M^* (\omega) \) and a distribution of dipolar relaxation time \( \tau_{dp} \) in the dielectric relaxation part of \( M^* (\omega) \) [34].

Table 2

<table>
<thead>
<tr>
<th>( T (K) )</th>
<th>( \Delta \varepsilon_r )</th>
<th>( \tau_r (\times 10^{-6}) )</th>
<th>( a )</th>
<th>( b )</th>
<th>( \beta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>373</td>
<td>0.266</td>
<td>2.16</td>
<td>0.925</td>
<td>0.230</td>
<td>0.507</td>
</tr>
<tr>
<td>348</td>
<td>0.222</td>
<td>4.5</td>
<td>0.893</td>
<td>0.315</td>
<td>0.5</td>
</tr>
<tr>
<td>323</td>
<td>0.209</td>
<td>10.8</td>
<td>0.862</td>
<td>0.365</td>
<td>0.495</td>
</tr>
<tr>
<td>298</td>
<td>0.202</td>
<td>32.3</td>
<td>0.841</td>
<td>0.387</td>
<td>0.475</td>
</tr>
<tr>
<td>273</td>
<td>0.199</td>
<td>120</td>
<td>0.819</td>
<td>0.397</td>
<td>0.467</td>
</tr>
<tr>
<td>248</td>
<td>0.197</td>
<td>625</td>
<td>0.796</td>
<td>0.390</td>
<td>0.432</td>
</tr>
<tr>
<td>223</td>
<td>0.203</td>
<td>4500</td>
<td>0.722</td>
<td>0.230</td>
<td>0.422</td>
</tr>
</tbody>
</table>

The relaxation time \( \tau_\sigma \) shows the Arrhenius behavior with activation energy of 0.37 eV, which corresponds to the hopping rates processes. Fig. 11 presents the Arrhenius plot of the frequency relaxation from \( M^* (\omega) \).

Fig. 9. \( \varepsilon^*(\omega) \) vs. frequency for different temperatures.

Fig. 10. Bode plot for the imaginary part of the electric modulus for different temperatures normalized at \( M^* \) maximum for 233 K.

Fig. 11. Arrhenius plot for the maximum frequency of \( M^* (\omega) \) and the inflection frequency of the electronic transition.
To analyze the dipolar contribution to the total dielectric permittivity it is necessary to separate the dispersive contribution arising from the independent conductivity process. No peak in $\varepsilon''(\omega)$ is observed in the experimental data, Fig. 9. However, by removing the contribution of the d.c. conductivity a peak in $\varepsilon''(\omega)$ can be observed. Fig. 12 shows $\varepsilon''(\omega) - \sigma_{dc}/(\omega\varepsilon_0)$ for different temperatures. These data can be fitted to the imaginary part of the HN distribution function. The fits are shown as the solid line in Fig. 12 and the fitted HN parameters given in Table 3. The relaxation times can be fitted to an Arrhenius plot with an activation energy of 0.22 eV (Fig. 13).

3.6. $C$–$V$ characteristic

The capacitance–voltage ($C$–$V$) measurements to obtain the barrier height $\phi$ values were performed for a frequency of 0.1 MHz. The barrier height is given by the following equation [36]:

$$\phi = V_{dc} + \xi$$

with

$$\xi = \frac{kT}{q} \ln \left( \frac{N_s}{N_d} \right)$$

The diffusion voltage at zero bias, $V_{dc}$, is equal to $V_{bi} + kT/q$, where $V_{bi}$ is the built-in voltage, while $\xi$ represents the depth of the Fermi level below the conduction band in the neutral region of the semiconductor. $N_c$ and $N_d$ represent the effective density of states (DOS) in the conduction band and the donor carrier density of the semiconductor material, respectively, and $q$ is the elementary charge (Table 1). It can be seen that the slope of $1/C^2$ vs. $V$ plots decreases with an increase in temperature (Fig. 14). This indicates that the value of the density of ionized acceptor atoms increases with temperature leading to a decrease in the depletion layer with the increase in temperature, $w = 31$ nm at 300 K. This observation is consistent with the
theory of the depletion layer in the Schottky barrier device. It is also observed that the potential barrier height decreases with an increase in temperature. From the $1/C^2$ plot it is evident that the capacitance is voltage dependent at low frequencies but independent at higher frequencies. In general, the main cause for the frequency-dependent capacitance is the trapping of an electron by surface states. Such electron transfer may be very slow, particularly for a small barrier. Therefore, when the capacitance is measured with an a.c. voltage of low frequency, the surface states can change their charge during this period and, thus, the capacitance under the influence of surface states is measured. The capacitance at higher frequency is independent on voltage, indicating that the capacitance at higher frequency is not the result of change in the surface charges but rather due to the dielectric polarization of the ZnO layer. The main features of the C-V plots are simply attributable to an extremely slow charge transport within our system. In our device, below a given frequency which is temperature dependent (Fig. 15), the capacitance is mainly derived from the existing depletion layer such that the charge carrier drifting responds to voltage change.

### 3.7. Admittance spectroscopy

Admittance spectroscopy can be used to investigate the frequency and temperature dependence of the capacitance $C(\omega, T)$ of a junction. This implies that the test frequency $\omega$ is small compared to the inverse dielectric relaxation time. The junction capacitance, in the simplest cases, is given by the space charge region capacitance ($C_{\text{SCR}}$). For a Schottky contact on semiconductor material, the equation per unit area, is given by

$$C_{\text{SCR}} = \frac{\varepsilon_r N_d}{w} \left(\frac{q\varepsilon_r N_d}{2V_{\text{bi}}}\right)^2$$

where $w$ is the space charge width, $N_d$ the donor concentration, $\varepsilon_r$ the semiconductor’s dielectric constant, and $V_{\text{bi}}$ the built-in voltage [37].

Electronically active traps in the SCR contribute to the capacitance spectrum at lower frequencies and higher temperatures. The contribution of a single majority carrier trap to the junction capacitance is [38]

$$C(\omega) = C_{\text{SCR}} + \frac{C_{\text{it}} - C_{\text{SCR}}}{1 + \omega^2 \tau^2}$$

where the low frequency capacitance $C_{\text{it}}$ depends on the trap density $N_T$ and the donor density in the case of an n-type semiconductor. The time constant $\tau$ is a function of $N_T, N_d$, and the width of the SCR [39]. In the limit of a small trap concentration, $N_T \ll N_d$, the time constant $\tau$ approaches the inverse of the inflection frequency of the electronic transition obtained from the plot of $dC/d(\omega) = 2\pi f$, $\tau = 1/\omega$, where $\xi_0$ is a temperature independent emission parameter, $E_T$ is the trap energy, and $kT$ the thermal energy [39]. In the case of an n-type semiconductor, electron traps within the space charge region having an energetic distance of $E_T - E_C$ to the conduction band can be charged and discharged at frequencies of $\omega < \omega_0$. Fig. 11 shows the Arrhenius plot of $\omega_0/T^2$ with an activation energy $E_a$ of 0.3 eV.

$$\omega_0 = \xi_0 T^2 \exp\left(-\frac{E_T - E_C}{kT}\right)$$

We assume an energetically continuous and spatially homogeneous distribution of bulk defects and we can apply the method from Walter et al. [38] to determine the defect spectra for different temperatures. Note, however, that the absolute values of the DOS are based on
assumptions about junction parameters. The necessary values are the space charge width, the diffusion voltage at zero bias and others were determined from the preceding C(V) measurements. Fig. 16 shows the DOS for different energies from the conduction band. The spectra in Fig. 16 exhibits a maximum at approximately 0.44 eV. To check where the traps are located in the junction, admittance measurements under different bias were carried out and we can determine that the position in the band gap does not change under bias [39]. Assuming that the Fermi level is not pinned at the surface, this hints at spatial homogeneity i.e. bulk defects.

4. Conclusions

Spray pyrolysis is a suitable technique for obtaining films of ZnO with very similar properties to the films obtain by methods employing a high vacuum environment, Table 4. Thin films with a flat surface without defects can be obtained. The activation energy for d.c. conductivity and the relaxation time of electrical conductivity, obtained from $M''(\omega)$, are very similar and we can conclude that both processes arise from the same conduction mechanism in this temperature range. The average grain size is smaller than those obtained by other methods [22,40] and, since electrons are transported in the conduction band in this ZnO film, a potential barrier around the grain-boundary is created by band bending, and the mobility is thermally activated. On the other hand, the electron concentration is high and the mobility of charge carriers is limited by the thermal field emission of electrons at the grain-boundary.

No peak is observed in the dielectric loss due to the free charge carriers, but by removing the contribution of the d.c. conductivity, a peak in $\varepsilon'(\omega)$ can be observed; the dielectric relaxation time obtained from $\varepsilon'(\omega) - \sigma_{dc}/\varepsilon_{0}$ shows an Arrhenius behavior with an activation energy lower than the d.c., the relaxation time from $M''(\omega)$ and a low characteristic frequency.

The behavior of the density of ionized acceptor atoms, $N_a$, and the width of the space charge, $w$, are consistent with the theory of the depletion layer in the Schottky barrier device. $N_a$ increases, and $w$ decreases, with an increase in temperature. Moreover, the capacitance is voltage dependent at low frequencies but independent at high frequencies because at high frequency the change in the capacity is due to the dielectric polarization of the ZnO layer and not due to a change in the space charge region. Above a certain frequency, that is temperature dependent, the capacitance is due to polarization processes in the bulk material; the low values obtained for these frequencies are simply attributable to an extremely slow charge transport within our device, which is in agreement with the low values obtained for the conductivity and the dipolar frequency relaxation.

The inflection frequency of the electronic transition obtained from the plot of $\omega dc/\omega_0$ shows an Arrhenius plot with an activation energy in good agreement with the activation energy of time relaxation conductivity. The densities of states are seen as wide, shallow spectra, which only exhibit a maximum at approximately 0.44 eV, which is very similar to the values obtain for $\tau_c$ and $\omega_c$; moreover, its position in the band gap does not change under bias, and assuming that the Fermi level is not pinned at the surface, this suggests spatial homogeneity i.e. bulk defects.

Acknowledgments

The authors are grateful to the European Union and CICYT (Spain) (grant IFD97-0839-CO3-01) for financial support and to ISOFOTON S.A. and SCAI of Málaga University for their collaboration. The bursary holder, R. Ayuochi, wishes to thank to the Junta de Andalucía (FQM192) and one of the authors (E.D.) gives thanks to Malaga University for the financial support for his stay.

References