Electrical properties of the n-ZnO/c-Si heterojunction prepared by chemical spray pyrolysis

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Abstract

Electrical, structural and compositional properties of n-ZnO/c-Si heterojunctions prepared by chemical spray pyrolysis on single-crystal n-type and p-type monocrystalline silicon(1 0 0) substrates are examined with the C–V method and admittance spectroscopy at temperature ranges between 223 and 373 K. The n-ZnO/c-Si heterojunctions show a height barrier consistent with the difference in energy of the work functions of Si and ZnO; however, the n-ZnO:Al/c-Si heterojunctions present a more complex behavior due to the defects at or near the n-ZnO:Al/c-Si interface, causing a Fermi energy pinning.

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1. Introduction

Transparent conducting oxides (TCO) are of great interest in electronic and electro-optical applications. They are used as coatings in a variety of devices as large flat screens [1], thin film photovoltaic cells [2], antireflective coatings in conventional silicon solar cells [3], light-emitting diodes (LEDs) [4], etc. ZnO is an n-type wide-band gap semiconductor (3.3 eV) with a hexagonal wurtzite structure. Intrinsic zinc oxide films are highly resistive, but when commonly doped with Group III elements (Ga, In or Al), they become conducting. Thin films of Al-doped ZnO (ZnO:Al), AZO, are emerging as an alternative candidate to Sn-doped In2 O3 (ITO), due to features such as non-toxicity, low cost, material abundance, and a high level of stability with hydrogen plasma and heat cycling.

Spray pyrolysis is a useful alternative to the traditional methods for obtaining thin films of pure and doped 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 to allow sintering or crystallographic phase transformation.

The ITO/Si structure has been extensively studied during the past two decades, having been obtained by various deposition technologies for potential application in solar cell technologies. The conversion efficiencies achieved in solar cells from ITO/c-Si junctions were 10–15% when using spray pyrolysis[5–8] . However, little information is available in the literature on the ZnO/c-Si heterojunction [9–13] in spite of the interest in its potential use in solar cells and other electro-optic devices.

In this paper, we report the electrical, structural and compositional properties of the junctions of both pure and Al (1 at.% ) doped thin films of ZnO on p- and n-type silicon, as obtained by chemical spray pyrolysis.

2. Experimental

Pure and Al doped ZnO thin films were prepared from 4 × 10−3 M of zinc acetate dihydrate dissolved in ultra pure water. Compressed air was used to atomize the precursor solutions. All the films were deposited onto type p polished Si(1 0 0) n (9 Ω−1 cm) (Topsil, Denmark) and fused silica.
substrates. Substrate temperature was kept at 573 K with an accuracy of ±2 K. The solution flow rate and gas pressure was kept constant at 50 ml h⁻¹ and 3 kg cm⁻², respectively. The nozzle to substrate distance was 10 cm. Aluminium doping was achieved by adding aluminium trichloride to the starting solution. The doping level in the solution, defined by a 100 × [Al]/([Al] + [Zn]) atomic ratio, was of 1%, and the deposition time was 15 min. Film thickness was determined ex situ by means of XRF (Siemens, SRS 3000) and the attenuation of the Si Kα signal in films deposited on Si, with an accuracy of ±5 nm. After deposition, the films were allowed to cool down to room temperature and then removed for further characterization. A more detailed description of the method to obtain the thin films and the characteristics of the spray pyrolysis device used were reported in previous papers [14,15].

Film structure was characterized by the X-ray diffraction method using Cu Kα radiation in a conventional goniometer with a θ–2θ scanning mechanism. Surface, depth down composition, and electronic states of the ions of pure and doped ZnO films were studied by X-ray photoelectron spectroscopy (XPS). XPS spectra were obtained using a Physical Electronic model PHI 5700 X-ray photoelectron spectrometer with Mg Kα radiation (1253.6 eV) and Al Kα radiation (1486.6 eV) as excitation sources. The energy scale of the spectrometer was calibrated using Cu 2p₃/₂, Ag 3d₅/₂ and Au 4f⁷/₂ photoelectron lines at 932.7, 368.3 and 84.0 eV, respectively. A PHI ACCESS ESCA-V6.0 F software package was used for data acquisition and analysis. Atomic concentrations were determined from the photoelectron peak areas using Shirley background substraction [16] and sensitivity factors provided by the instrument manufacturer. All sample spectra were referred to the C1s line of the residual carbon set at 284.8 eV. Depth profiling was carried out using 4 keV Ar⁺ bombardment at a current density of ~3 μA cm⁻². A sputter rate of 0.5 nm min⁻¹ was assumed, as determined by Ta₂O₅ under the same sputter conditions.

Electrical properties were determined by admittance spectroscopy using a Broadband Dielectric Converter (BDC) from Novocontrol with a Solartron 1255 Frequency Response Analyzer (FRA) for a frequency range between 1 Hz and 1 MHz. The n-ZnO/p-Si heterojunction was placed in a Novocontrol sample holder modified in our laboratory; the ohmic contact with the p-Si substrate was performed with Al and with the n-Si with In–Ga. The temperature range was between 223 and 373 K, and was controlled by a Quatro temperature controller from Novocontrol.

3. Results and discussion

3.1. Structural properties

Fig. 1 shows a typical X-ray diffractogram obtained from a 150 nm thick film of pure ZnO on p-Si(0 0 1) and ZnO:Al (1 at.%). As we can see, the ZnO(0 0 2) and (1 0 1) peaks are observed at 2θ = 34.24 and 36.26° [JCPDS card 05-0664]. The XRD spectrum of pure ZnO shows a powder-like pattern with no preferred growth orientation; the lattice parameters, c and a, are estimated to be 5.24 and 3.24 Å, respectively. Similar values are observed in the ZnO:Al doped film. These results are in good agreement with those from previously published papers [14,15].

However, when the thickness of the films increases, e.g. to 300 nm, we can observe that the films grow preferentially along the c-axis orientation in a (0 0 2) orientation (Fig. 2),
and vertically to the substrate; the lattice parameter $c$ is estimated to be 5.24 Å. For the pure ZnO, the peak at 34.2° has more relative intensity than the peak at 36.25°, which is very small. The mean crystallite size of the sample is evaluated by means of the Scherrer formula [17]; the grain size has been estimated to be $\approx 255.12$ and 429 Å for 150 and 300 nm thicknesses, respectively; no significant difference can be observed with ZnO:Al doped films.

3.2. Compositional and chemical surface states

Fig. 3 shows the wide scan (0–1200 eV) XPS spectra in the binding energy range of 0–1200 eV for a ZnO thin film prepared at 573 K and sputtered in the spectrometer for 30 s with 4 keV Ar$^+$. An XPS atomic ratio of Zn/O of 1.02/1.00 ($\pm$2%) was determined using the integrated peak area and sensitivity factors. For the ZnO:Al (1 at.%) doped films (not shown), the Al 2p line consists of a highly symmetrical peak located at 74.27 eV. This value is close to that reported for Al$_2$O$_3$. A more detailed discussion about the XPS results of the Al doped ZnO thin films will be presented in another paper.

3.3. Optical properties

Fig. 4 shows the optical transmittance spectra of pure ZnO and ZnO:Al doped thin films as a function of the wavelength in the range 300–900 nm. The undoped film transmittance spectra exhibit an average transmittance over 95% in the visible range of the optical spectrum. Doped films prepared under the same conditions but with a longer deposition time, exhibit a slight reduction in their transmittance, to 70%, because the thickness is higher and the homogeneity is lower as observed from SEM pictures not shown here. Since the ZnO is a direct transition semiconductor, $\alpha$ is related to the optical energy band gap ($E_g$) by

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

(1)

where $\alpha$ is the optical absorption coefficient, $h\nu$ the energy of the incident photon and $\beta$ is the edge width parameter [18]. $E_g$ is determined by extrapolating the straight-line portion of (1) to $h\nu \alpha = 0$. The doped films present a larger band gap (3.315 eV) than the pure ZnO films (3.307 eV).

3.4. C–V characteristics: barrier height and donor carrier density

The potential barrier at the junction can be measured by small-signal capacitance–voltage (C–V) [19] characteristics. Fig. 5 presents the C–V characteristics in the reverse bias region at 300 K for the n-ZnO:Al/p-Si and n-ZnO/p-Si heterojunctions at 1 MHz. As can be seen, the capacitance of the heterojunction is decreased with an increase in the reverse bias with an approximately linear $C^2 - V_{bias}$

Fig. 5. C–V characteristics in the reverse bias region at 300 K for the n-ZnO:Al/p-Si and n-ZnO/p-Si heterojunctions at 1 MHz.
relationship (Fig. 6). This means that the depletion region in the vicinity of the heterojunction interface is expanded with an increase in the reverse bias. This C–V characteristic is also described by the conventional heterojunction theory:

\[
C^2 = \frac{qN_D N_A \varepsilon_1 \varepsilon_2}{2(N_A \varepsilon_1 + N_D \varepsilon_2)(V_D + V_b)} \tag{2}
\]

Here, \(N_D\) is the donor density in n-ZnO, \(N_A\) the acceptor density in p-Si, \(\varepsilon_1\) and \(\varepsilon_2\) are the dielectric constants of n-ZnO and p-Si, respectively, and \(V_b\) is the applied voltage. Using Eq. (2), we can determine the effective space charge density of the depletion region of both heterojunctions from the slope of the \(C^2(V_b)\) relationship. The values obtained are presented in Table 1 for \(N_D = 8\) and \(\varepsilon_1(Si) = 12\) [19]. The values obtained for \(N_D\) in n-ZnO:Al 1 at.% (9 \(\times\) 10^{23} m\(^{-3}\)) and n-ZnO (5 \(\times\) 10^{23} m\(^{-3}\)) are higher than for \(N_A\) in p-Si, where \(N_A\) is estimated to be about 8 \(\times\) 10^{20} m\(^{-3}\) from the resistivity of p-Si (9 \(\Omega\)-cm). These results indicate that the junction is an abrupt p–n\(^+\) type junction. The built-in potential \(V_b\), or diffusion potential, is estimated to be 0.66 and 0.7 eV for the ZnO:Al/p-Si and ZnO/p-Si junctions, respectively. This result is consistent with the energy difference between the work functions of Si and ZnO. The Fermi level below the vacuum level is 4.97 eV for p-Si, and 4.25 eV for n-ZnO. The difference between them is 0.72 eV. The results obtained for n-ZnO/n-Si are very similar (not shown here). The built-in potential is 0.56 eV for the n-ZnO/p-Si junction (1 at.%)/n-Si and 0.50 for the ZnO/n-Si.

The most likely reason for a more complex behavior (n-ZnO:Al/p-Si and n-ZnO:Al/n-Si), compared to the model of a simple p–n heterojunction, are the defects at or near the n-ZnO:Al/c-Si interface, which cause a Fermi energy pinning. The pinning effect makes the height of the energy barrier independent of the ZnO work function. As shown in the literature [19], the Fermi energy at metal/n-semiconductor interfaces is often pinned at about \(E_g/3\). In the case of Si (\(E_g = 1.12\) eV), this corresponds to 0.37 eV above the valence band edge. Making this assumption, the energy barrier at the interface seen by the free electrons in 9 \(\Omega\)-cm p-Si is 0.53 eV, which is quite consistent with our \(1/C^2 – V\) measurements (0.56 eV).

### Table 1

<table>
<thead>
<tr>
<th>Junction Type</th>
<th>(N_D) (\times 10^{23}) m(^{-3})</th>
<th>(V_b) (eV)</th>
<th>(W) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-ZnO:Al/p-Si</td>
<td>8</td>
<td>0.66</td>
<td>34</td>
</tr>
<tr>
<td>n-ZnO/p-Si</td>
<td>8</td>
<td>0.70</td>
<td>26</td>
</tr>
<tr>
<td>n-ZnO/n-Si</td>
<td>5</td>
<td>0.50</td>
<td>30</td>
</tr>
<tr>
<td>n-ZnO:Al/n-Si</td>
<td>5</td>
<td>0.56</td>
<td>24</td>
</tr>
</tbody>
</table>

3.5. Admittance spectroscopy

Thermal admittance spectroscopy is a technique which allows thermal emission rates of deep levels from the variation of capacitance and conductance of a junction as a function of temperature and frequency [20,21] to be determined. These variations are due to the change in frequency of the measuring signal with respect to the time constant of charge and discharge processes of the deep level around the point of the space charge region where both time constants are...
equal. Under dark conditions, this point coincides with the crossing point of the Fermi level with the deep level. We can model the n-ZnO:Al/p-Si as a p–n+ diode heterojunction having a single diode composed of a parallel combination of a capacitor, $C_D$, and a resistor, $R_D$, in parallel with series connected capacitance and resistance elements, $C_{ds}$ and $R_{ds}$, due to deep state responses to the in and out-of-phase applied oscillating signal [22]. $C_D$ capacitance represents the high-frequency capacitance due to the depletion region, and $R_D$ describes the leakage path that often accompanies heterojunction devices and can physically arise from generation-recombination current within the depletion region, local shunting out defects across the thin film, or leakage due to periphery effects. If $G_D > G_{ds}$ ($G_D = \frac{1}{R_D}$), then the parallel leakage can dominate the real part of the complex admittance across the device and render the contribution of the trap difficult to determine. This problem is especially troublesome if $G_D$ changes with temperature, as is often the case, because even a change in the conductance of the junction with temperature is difficult to interpret unambiguously, and it is necessary to eliminate the contribution of the parallel conductance to the admittance of the junction. We can eliminate the $G_D$ conductance by determining the elements of the equivalent circuit from a complex fitting method (LEVM from Macdonald) [23] and then subtracting the effect of the parallel conductance to the experimental data, or fitting the experimental capacitance and conductance to the corresponding values of capacitance and conductance of this model. The capacitance and conductance for this model are:

$$C_t = C_D + \frac{C_{ds}}{1 + (\omega \tau_{ds})^2}$$

$$G_t = G_D + \frac{G_{ds}(r_m^0)^2}{1 + (\omega \tau_{ds})^2}$$

where $\tau_{ds}$ is the time characteristic (inverse emission frequency) for the defect associated with the quantities $C_{ds}$ and $G_{ds}$, and $\omega$ is the angular frequency of the applied oscillating signal [18]. Both methods are in very good agreement. Interface states can be determined from admittance spectroscopy [18]. Using appropriate modeling, the measured conductance as a function of frequency can be associated to the density of the interface states ($D_{ds}$). The density of interface states and the capacitance due to the interface states are related by the equation

$$C_{ds} = qD_{ds}$$

where $C_{ds}$ is the capacitance, $D_{ds}$ the density of the interface states and $q$ is the electronic charge. The equation describing the measured parallel conductance versus the frequency relationship to the $D_{ds}$ used for this junction was obtained from Eq. (4):

$$G_{tot} = G_{ds} + \frac{qD_{ds}r_m^0}{1 + \omega^2 \tau_{ds}^2}$$

where $\tau_{ds}$ is the trap time constant. Fig. 8 presents the trap time constant for the n-ZnO:Al/p-Si and Fig. 9 shows the $(G_t - G_{ds})/\omega$ data as a function of the logarithm of the frequency and the fitting for Eq. (6) at different temperatures at zero bias voltage. The nature of these peaks suggests that they may be associated with narrow defect energy levels.

A characteristic frequency exists for each energy level in the band gap. The inverse characteristic frequency is the characteristic time associated with that energy position. This time is, in effect, the response time for that energy level. Therefore, if an oscillating signal is applied to the sample at a frequency greater than that of the characteristic frequency for a given defect level, that defect level will not be able to respond to the applied signal. This property establishes a demarcation energy associated with the applied signal such that defects with energy positions below this level (having higher response frequencies) will be able to respond to the signal, but those defects with energy positions above this
level (slower response time) will not be able to respond to the signal. The demarcation energy is \( E_{\omega} \), where

\[
E_{\omega} = kT\ln\left(\frac{2\nu \omega}{\nu_0 \omega}\right)
\]

Here \( \omega \) is the angular frequency of the applied oscillating signal. Defect states lying below the Fermi level will not contribute to the impedance measurements or admittance measurements as they will remain filled throughout the measuring process. However, defects positioned between the Fermi level and the demarcation energy \( E_{\omega} \) of the applied signal will be able to contribute to the measured admittance. Due to band bending, both the demarcation energy level and the defect levels and bands may cross the Fermi level within the depleted region. Again, states located below the Fermi level remain filled during the measurement process, and will not contribute to the measurements.

Fig. 10 presents the density of interface states versus \( E_{\omega} \) energy for the n-ZnO:Al/p-Si at different temperatures. In order to obtain the dependence of the density of the interface states on the bias \( V_b \), the fitting procedure described in the previous paragraph was repeated for various values of bias and temperature. In an n-type semiconductor, the energy of the interface states with respect to the bottom of the conduction band at the surface of the semiconductor, \( E_{ss} \), is given by:

\[
E_c - E_{ss} = q(\Phi_e - V)
\]

where \( E_c \) is the energy of the bottom of the conduction band, and \( \Phi_e \) is the effective barrier height. Results, illustrated in Fig. 11, show a variation of states from \( 1.2 \times 10^{15} \text{ cm}^{-2} \text{ eV}^{-1} \) near the Si Fermi level to \( 6.5 \times 10^{15} \text{ cm}^{-2} \text{ eV}^{-1} \) near the midgap. Due to the high interface state density, spacing between states, which has previously been stated to be close to \( 10^2 \text{ Å} \) [24] indicates that there will be significant communication between states. Consequently, the assumption of an isolated interface trap is not acceptable.

4. Conclusions

The \( C(V) \) characteristics for the n-ZnO:Si heterojunctions show height barriers consistent with the energy difference between the work functions Si and ZnO; however, the n-ZnO:Al:Si heterojunctions present a more complex behavior due to the defects at, or close to, the n-ZnO:Al:Si interface, causing a Fermi energy pinning.

The density of states measurements show the usual tail of states curve across the energy range used. From the nature of the \( (G - G_D)/\omega \) peaks we can conclude that they may be associated with narrow defect energy levels; moreover, due to the high interface density, significant communication between states can be assumed.

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