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Capacitance study of thin film SnO$_2$:F/p-type a-Si:H heterojunctions

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Abstract

We characterized SnO$_2$:F/p-type a-Si:H heterojunctions by current-voltage (I-V) and capacitance-voltage (C-V) measurements at room temperature to determine the junction parameters. Samples with circular geometry and different diameters were characterized. The current scales with the junction area, and the current density $J$ as a function of the voltage $V$ is a slightly asymmetric curve with a super-linear behaviour (cubic law) for high voltages. Using a transmission line model valid for devices with circular geometry, we studied the effects of the SnO$_2$:F resistivity on the measured capacitance when the SnO$_2$:F layer works as an electrical contact. The measured C-V curve allows us to determine junction parameters as doping of p-type a-Si:H, built-in potential and depletion width for the heterojunction with the smallest diameters, demonstrating that for these samples the TCO effects can be neglected. We compared theoretical and measured data to explain qualitatively the transport mechanism in this heterojunction.

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Keywords: amorphous silicon, TCO, SnO$_2$:F, capacitance, heterojunction;

1. Introduction

The thin-film hydrogenated amorphous silicon (a-Si:H) solar cells are attractive for photovoltaic applications and for cheap productions because amorphous silicon is a low cost material. In an a-Si:H p-i-n solar cell a transparent conductive oxide (TCO) is used as electrical contact on the top and bottom of the solar cell. The TCOs are usually degenerate n-type semiconductors and the most used are SnO$_2$ and ZnO. In a solar cell there are two critical interfaces that are TCO/p-type and n-type/TCO, but the most critical one is the former because it is the window layer. Many authors have studied experimentally [1,2] and by computer modelling [3,4], the TCO/p-type a-Si:H interface, but the transport mechanism and the band diagram are not well modeled and understood. Usually, this interface is treated as a Schottky or ohmic contact. Moreover, in capacitance studies the impact of the TCO on the measured admittance is usually neglected, because it is treated as a perfect conductor. The impact of the TCO in a

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solar cell was studied in [5], where it is shown that the losses in the TCO layer influence the measured capacitance of the pin solar cells due to the distributed resistance of the TCO.

In this work we investigate the SnO$_2$:F/p-type a-Si:H heterojunction with the final goal of understanding the transport mechanism and the energy band diagram of the heterojunction. We performed electrical characterization by measuring the J-V curves to investigate the transport mechanism and the C-V curves to extract some junction parameters. We propose a transmission line model to take into account the impact of distributed resistance of the SnO$_2$:F layer on the measured admittance. The measured admittance depends on the resistivity of the TCO layer and on the heterojunction admittance. This model, valid for devices with circular geometry as those we characterized, allows us to validate the correct values of the measured capacitance and to extract correctly the junction parameters of the heterojunction.

2. Materials and Methods

We characterized SnO$_2$:F/p-type a-Si:H heterojunction devices realized by STMicroelectronics (Catania, Italy) by plasma-enhanced chemical vapour deposition (PECVD) of SiH$_4$ and TMB with a ratio B/SiH$_4$=1% at low temperature onto an AGC ASAHI GLASS substrate consisting in a 1 mm thick glass covered with an 800 nm thick SnO$_2$:F film. The geometries were circles, with the following diameters: 200, 400, 800, 1600, 3200, 6400 μm. An 800 nm thick molybdenum metallization was deposited by sputtering on a 20 nm thick p-type a-Si:H layer. The structure is shown in the inset of Fig.1.

To extract the sheet resistance of the p-type a-Si:H material ad hoc samples were realized. In particular, 1000, 100, and 20 nm thick p-type a-Si:H films were deposited on silicon substrates covered with a 0.9 μm SiO$_2$ layer.

The sheet resistance of the p-type a-Si:H was measured using the four-point probe technique under vacuum, in dark and at different temperature (300 to 600 K). The temperature dependence of the sheet resistance $R_s$ was measured for constant rates ($dT/dt$). During the measurement the temperature was controlled and monitored by using a MMR K-20 temperature controller and a Joule-Thompson refrigerator, and the sample temperature was measured by a thermocouple in direct contact to the sample backside.

3. The impact of the TCO on the capacitance measurements

In a solar cell the resistivity of the TCO layer, which is about two orders of magnitude higher than that of a metal, can affect the capacitance measurements performed on the solar cell, when the metallization used for the electrical contact does not cover the whole area of the device. In [5] it was shown this effect in pin a-Si:H thin film solar cells and a transmission-line model was proposed, valid for solar cells with strip geometry. This model allows to estimate
the critical geometrical size of solar cells over which the capacitance measurements are sensitive to the TCO resistivity and its relation with the probe frequency, the TCO resistivity and the lumped parasitic series resistance. Usually, the impact of the TCO increases when both the length of the TCO strip and the frequency of the AC signal used for the capacitance measurements increase.

In our case, the heterojunction has a metal contact on one side and the TCO on the other side, thus when the devices are contacted by the probe tips on the TCO, the resistivity losses in the TCO layer can alter the value of the measured junction capacitance. Therefore, in order to quantify the effect of the TCO on the capacitance devices are contacted by the probe tips on the TCO, the resistivity losses in the TCO layer can alter the value of the measured junction capacitance. Therefore, in order to quantify the effect of the TCO on the capacitance measurements in the investigated devices, we propose an analytical model that is valid for devices with a circular geometry. We model the circular structure as a cylinder of radius $b$ composed by the TCO layer of height $t$ and sheet resistance $R_{s\theta}$ and by the heterojunction with admittance $Y_j (S/cm^2)$. The metal circle (the probe tip) of radius $a$, covers the top of the TCO layer. The elementary cell of the transmission line is the cylinder of internal and external radius $r$ and $r+dr$ respectively, and it is modeled with the series resistance per length unit $R_s/2\pi r (\Omega/cm)$, due the TCO layer, and the parallel conductance per length unit $Y_j 2\pi r (S/cm)$ of the heterojunction.

By solving Telegrapher’s equations we obtain the differential equation for the voltage $V/r$ along the TCO layer $V^2 + V'/r - \gamma^2 V = 0$, where $\gamma = \sqrt{Y_j R_s} (cm^{-1})$, under appropriate boundary conditions. In the investigated structures we can consider the lateral current density $J_l$ flowing into the TCO and the transverse current $J_t$ flowing into heterojunction. It is the lateral current which causes the voltage drop along the direction $r$ due to the TCO resistivity, $dV/dr = -\rho_{tc} J_t$. Along the metal circle of radius $a$ the voltage is constant and equal to the voltage of LCR meter $V_s$. The lateral current at $r=b$ is null. Hence, the boundary conditions for the differential equation are $V(a)=V(0)$ and $dV/dr|_{r=a}=0$. In order to calculate the measured admittance $Y_{meas}$ we consider that the whole current $I_s$ going from the LCR to the probe is the sum of the transverse current flowing into the circle of radius $a$ and the lateral current $J_l$, i.e. $I_s = I_l (a/2\pi a + J_t a^2)$, with $J_t = Y_j V_s$.

By combining the solutions of the differential equation with the previous conditions we obtain the following expression of the measured admittance of the heterojunction with circular structure:

$$ Y_{meas} = Y_j \left( \frac{a}{b} \right)^2 + \frac{2a}{b^{\gamma}} \frac{I_j(b)K_k(a) - I_j(a)K_k(b)}{I_j(a)K_k(a) + I_j(b)K_k(b)} $$(eq. 1)

where $I_j$ and $K_k$ are the modified Bessel functions and $a \neq b$. It is immediate to prove that when the metal contact covers the whole area of the TCO layer, i.e. $a=b$, it results $Y_{meas} = Y_j$. When $y b < 1$, i.e. the width of the devices is less than the characteristic length $1/\gamma$, the term in square brackets of eq.1 approaches to 1, and the measured admittance is equal to that of the heterojunction. Conversely, when $b > 1/\gamma$ this term is lower than 1 and approaches to zero when $yb$ increases. If the heterojunction is a capacitance $C_j$ without losses the characteristic length is $\sqrt{1/\alpha C_j R_{s\theta}}$, which decreases with the frequency and the resistivity of the TCO layer. Thus, when $b > 1/\gamma$ the measured capacitance drops comparing to that of the junction, due to the TCO working as an electrode. With this model we can estimate the effect on the measured capacitance caused by the resistivity of the TCO layers.

4. Measurements and Results

Firstly, we performed sheet resistance measurements of the SnO$_2$:F material with the four-point probe method. The sheet resistance of the SnO$_2$:F is above 8.8 $\Omega/m$). To determine the doping density we used the relation $N_d = 1/(\mu R_s a t)$ and assuming a value of 30 $cm^2/Vs$ for the electron mobility [3], we obtained $N_d = 2.9 \cdot 10^{10} cm^{-3}$. Furthermore, we extracted the resistivity activation energy of the p-type a-Si:H material. The sheet resistance $R_{s\theta}$ of the samples evolves as a function of the temperature $T$ according to $R_{s\theta} = R_s \exp(E_s/kT)$. Where $R_s$ is the measured resistance at 300 $K$ and $k$ is the Boltzmann constant. The measured activation energy of the p-type a-Si:H was 0.38 eV for all thicknesses used and the resistivity at room temperature was $2 \cdot 10^4 \Omega cm$. 
The J-V curves of the SnO$_2$:F/p-type a-Si:H heterojunction at 30°C are slightly asymmetrical and follow a cubic law: $J = aV^3 + bV$, as shown in Fig.1. In this structure there are two junctions: Mo/p-type a-Si:H and p-type a-Si:H/SnO$_2$:F. The Mo/p-type a-Si:H junction can be considered as an ohmic contact, because the current for positive bias voltage is slightly greater than that for negative bias. The equivalent diode is also shown in Fig.1.

We verified that the J-V curves do not change with the radius for the devices with diameter less than 800 $\mu$m. For a sample with a diameter of 1600 $\mu$m, the effects of the leakage and of the TCO resistivity become relevant. In order to investigate the small signal behaviour of the investigated heterojunctions, we performed impedance measurements. The analysis of the impedance was necessary to correctly implement the C-V intercept method, which we used to determine the built in voltage $V_{bi}$, the depletion width $W$ and the semiconductor doping $N_A$.

In Fig. 2 the modulus and the phase of the impedance versus frequencies at $V=0V$ and at different diameters are shown. The impedance shows the same trend in the linear region of the J-V curve that is an increase of the resistance (decreasing of the phase with the diameters). The equivalent circuit of the heterojunction at fixed voltage consists on a parallel conductance $G$ and a capacitance $C_j$. The capacitance of the heterojunction was measured at 1 MHz and for different radius $b$ of the heterojunctions. In Fig. 3 the values of the measured capacitance (circle) at 1 MHz and at different diameters of the devices under test are shown. We have chosen to measure the C-V at 1 MHz because at a such high frequency the traps do not respond to the AC signal, hence the contribution of traps and interface states to the capacitance can be neglected. Moreover, at 1 MHz the capacitance could be extracted with more precision respect to that at lower frequency. But at this high frequency the impact of the TCO could be significant in the capacitance measurements. Thus it was necessary to test the impact of the TCO on the admittance measurements using the transmission line model previously presented. Therefore, we measured the capacitance of the devices with different radii and simulated the results by using eq. 1. In the admittance measurements we used the four-point probe (Kelvin) connection, thus the voltage drop between the force and sense terminal due to the contact resistances with the tips were eliminated. The use of the Kelvin connection damps the impact of the TCO, because it increases the value of the radius $a$, which is approximately equal to the distance between the probes (about one a hundred microns). In Fig. 3 the comparison between the measured (circle) and the modeled (continuous line) capacitance at zero bias voltage, at 30°C and for different diameters is shown. We note that the value of the measured capacitance drops when the diameter of the device increases, and the model in eq.1 predicts this behaviour as seen in continuous line in Fig. 3. In fact, when the diameters of the circular pad is 800 $\mu$m the capacitance begins to decrease.
The transmission line model ensures that the measured values of capacitance are not affected by the resistivity of the TCO for diameters less than the characteristic length $1/\gamma \approx 500 \ \mu m$. Therefore, using the samples with diameter of 200 $\mu m$ for capacitance measurements, the TCO effects are negligible and the measured capacitance coincides with that of the junction. After testing the TCO effect in the capacitance measurements, we were able to perform the C-V intercept method at zero bias voltages because the capacitance was governed by junction capacitance.

In fig. 4 the C-V curve in the linear region for samples with 200 $\mu m$ diameter and at room temperature is shown. If the interface charge influences the heterojunction, the C-V curve decreases with the bias voltage [5]. In our case, the C-V curves increase monotonically, hence the contribution of the interface charges in C-V curves can be neglected.

In fig. 5 an example of the $C^2-V$ is shown. It has a linear behaviour so the deep traps do not play an important role in this heterojunction [6]. In this case the intercept voltage $V_{int}$ of $C^2-V$ plot is equal to the total built-in potential $V_{bi}$ of the heterojunction when the doping level is known, if the Gummel-Scharfetter correction [7] can be neglected: $V_{int} = V_{bi} = V_{bi} = V_{bi}$ and for abrupt heterojunctions. By linear fitting of the $C^2-V$ curves, we can extract the intercept voltage $V_{int}$, the doping of p-type a-Si:H layer $N_A$ and the depletion width $W$ [8]. The built-in potential is close to the difference between the work functions of SnO$_2$:F (4.8 eV) and of the p-type a-Si:H film. The latter is equal to the sum of the a-Si:H affinity (3.9 eV) and the distance between conduction band and Fermi level (difference between energy gap and measured activation energy: 1.87-0.38=1.49 V). This implies an expected $V_{bi}$ of 0.59 V. The measured $V_{bi}$ is 0.66 eV, that is, quite close to the expected value (0.59 eV). The difference between extracted and expected value can depend on the interface traps, probably acceptor interface charges [4]. The depletion width is 11.7 nm and the doping of p-type a-Si:H is $6.4 \times 10^{18} \ cm^{-3}$. The found values are consistent and allow to describe the heterojunction between SnO$_2$:F and a-Si:H.

5. Discussions and conclusions

This work is a preliminary study of the J-V and C-V curves at room temperature for the SnO$_2$:F/p-type a-Si:H heterojunction to extract the junction parameters. In literature there were some experimental studies on similar heterojunctions, [1,2], but in both works the heterojunction was considered as a Schottky contact governed by thermionic emission, without considering other possible transport mechanisms. They also used different measurement methods as J-V under illumination and the pulsed laser-induced transient photopotential technique. In this work we performed direct electrical measurements as C-V and J-V to determine the junction parameters and we demonstrated that the investigated heterojunction is not a Schottky contact, because the J-V curve is slightly
asymmetrical and it is not rectifying. Moreover, the J-V curves do not follow exponential law in any range of voltage bias, thus we can also rule out diffusion and recombination as possible principal transport mechanisms. By using the expressions valid for abrupt heterojunction without interface traps and by using the extracted doping of the SnO2:F and p-type a-Si:H i.e. \( N_n = 2.9 \times 10^{16} \text{cm}^{-3} \) and \( N_p = 6.4 \times 10^{18} \text{cm}^{-3} \) respectively, we can estimate the depletion width \( W \) and the barrier height \( V_b \) in both materials [9], indicating with 1 the parameters of the SnO2:F and with 2 of the p-type a-Si:H:

\[
W_i = \left[ \frac{2 \varepsilon \varepsilon_r V_i}{q} \left( \frac{N_n}{N_n + N_p \varepsilon_r} \right) \right]^{1/2} \quad W_i = \left[ \frac{2 \varepsilon \varepsilon_r V_i}{q} \left( \frac{N_p}{N_n + N_p \varepsilon_r} \right) \right]^{1/2} \quad (eq. 2)
\]

where \( \varepsilon \) is the dielectric constant and \( q \) is the electronic charge. Therefore, we can estimate the band bending and the depletion width in both semiconductors: \( V_{bi} = 0.07 \text{eV} \) and \( W_i = 1 \text{nm} \) in SnO2:F, and \( V_{bi} = 0.60 \) and \( W_i = 10.7 \text{nm} \) in the a-Si:H. Hence, the barrier seen by the holes in the p-type a-Si:H is quite high and tunnel via localized states in the p-type a-Si:H and subsequent recombination [10] could explain the transport through this interface. We are currently performing further analysis on these aspects.

In conclusion, we determined a sheet resistance of the SnO2:F of 8.8 \( \Omega/\square \) and an activation energy of p-type a-Si:H of 0.38 eV. We modelled the effect of the TCO considering a circular geometry for the devices under test. We demonstrated that for diameters greater than the characteristic length (500 \( \mu \text{m} \)) the effect of the TCO became important in the measured capacitance at zero voltage bias and 1 \( \text{MHz} \). We performed measurements only for diameters less than 500 \( \mu \text{m} \) to neglect the TCO effect in the devices under test. We performed also J-V and C-V measurements at room temperature to extract the junction parameters of the devices and we demonstrated that the measured curves depended mainly on the SnO2:F/p-type a-Si:H heterojunction. The data were reproducible and we characterized the junction using the C-V intercept method. We found a depletion width of the junction of 11.7 nm, a built in potential of 0.66 eV similar to expected value of 0.59 eV and a p-type a-Si:H doping of \( 6.4 \times 10^{18} \text{cm}^{-3} \). We estimated the depletion width and the band bending in both semiconductors. We are now performing further experimental analyses to better clarify the charge transport mechanisms.

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