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Influence of the electro-optical properties of an α-Si:H single layer on the performances of a *pin* solar cell

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ABSTRACT

We analyze the results of an extensive characterization study involving electrical and optical measurements carried out on hydrogenated amorphous silicon (α-Si:H) thin film materials fabricated under a wide range of deposition conditions. By adjusting the synthesis parameters, we evidenced how conductivity, activation energy, electrical transport and optical absorption of an α-Si:H layer can be modified and optimized. We analyzed the activation energy and the pre-exponential factor of the dark conductivity by varying the dopant-to-silane gas flow ratio. Optical measurements allowed to extract the absorption spectra and the optical bandgap. Additionally, we report on the temperature dependence of the activation energy to satisfy the Meyer–Neldel rule. Finally, the influence of the individual films parameters upon the final performances of a single junction *pin* α-Si:H have been studied. The measurements show how a more than doubled enhancement in energy conversion efficiency can be obtained in an α-Si:H solar cell with a proper selection of synthesis conditions.

1. Introduction

Since the report of a hydrogenated amorphous silicon (α-Si:H) junction in 1976 [1], the α-Si:H material, with a large tailorable bandgap, easy dopability and high optical absorption coefficient, has attracted a great deal of worldwide interest for photovoltaic (PV) applications, also thanks to the chance of large areas deposition at very low cost, as required for PV market [2]. In the meantime, over the past decade, hydrogenated amorphous silicon has generated great interest as a key component in the development of next-generation multi-junction PV devices [3,4]. In fact, although the single-junction α-Si:H solar cell suffers from low conversion efficiency, α-Si:H based tandem cell is one of the most promising thin film candidates for the advancement of photovoltaic technology due to high attained efficiency and low materials costs. Thus, after years of research and technology development, there is still great interest in improving materials for stable high-performance α-Si:H solar cells [5–9].

In order to obtain solar cell as efficient as possible, there are many interdependent parameters to consider. Most importantly, each layer in the typical *pin* structure must have appropriate electrical and optical properties. This work presents and discusses a systematic investigation on the effects of synthesis parameters on the behavior of a homojunction α-Si:H *pin* solar cell under solar simulator and monochromatic illumination. The measurements show improved results as the hydrogen content in the intrinsic layer increases. In particular, a more than doubled enhancement in energy conversion efficiency (η) was observed in the solar cell in which the intrinsic layer has the highest hydrogen content.

Moreover, the paper outlines the temperature dependence of the average energy of the conduction electrons and the Fermi level in our amorphous films and contributes to a body of work analyzing the Meyer–Neldel (MN) correlation [10].

2. Sample preparation and experimental details

In order to optimize the *pin* diodes, a series of doped and undoped α-Si:H films were synthesized on soda-lime substrates (which are used in commercial solar cells) in a radio frequency plasma enhanced chemical vapor deposition (RF PECVD) system at 280 °C. The p layers were deposited using silane (SiH_4) and trimethylboron, $B(CH_3)_3$ (abbreviated as TMB), as gas sources with different flow ratios of [SiH_4/TMB] (5:1, 3:1, 2:1), and dilution ratio of [H_2/SiH_4] of 1:1.5. The n-doped films were synthesized using SiH_4 and phosphine, PH_3, as gas sources with different flow ratios of [SiH_4/PH_3] (6:1, 3:1, 2:1), and a fix [H_2/SiH_4] ratio of 1:0.6. The undoped α-Si:H layers were deposited by the decomposition of pure SiH_4 with flow rates of 12 and 100 sccm (sccm denotes standard cubic centimeters per minute) and dilution ratio of 10:1 to study the effect of

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silane flow. The H content of the deposited films was measured through Elastic Recoil Detection Analysis (ERDA). All the synthesized films are summarized in Table 1. Once α-Si:H films were deposited, their optical and electrical properties were characterized.

Optical analyses were done on samples with thin thickness (d) of 100 nm, by extracting transmittance (T) and reflectance (R) spectra in the 400–1000 nm wavelength range by using a Varian Cary 500 double beam scanning UV/Vis/NIR spectrophotometer equipped with a photomultiplier and a PbS detectors to measure in the spectral range between 175–800 and 800–3300 nm, respectively. More precisely, normal transmittance spectra were collected with a 100% baseline obtained mounting the sample holder without any sample, while the normal reflectance spectra have been detected using an integrating sphere accessory.

The electrical properties were characterized by temperature-dependent Van der Pauw resistivity measurements [11] on samples with d of 1 μm, square area of 5×5 mm^2 and coplanar Pd contacts deposited by sputtering on the corners of the square to form Ohmic contacts. The samples were mounted on a holder equipped with heating and cooling facilities in a vacuum chamber (under no illumination). The measurements were recorded in the temperature range 200–450 K by using a Keithley 236 to force a low stress current to two terminals of the sample and a Keithley 4200 with two source measure units, configured as high impedance voltmeters, to read the voltage on the other pair of electrodes.

After the thin films characterization, we chose the layers with proper electro-optical properties to conveniently fabricate the *pin* diodes listed in Table 2. More precisely, we selected the single layers in order to have diodes as different as possible from each other. Thus, we considered p films with different conductivity, since they exhibit the same E_{opt}, n films with different optical properties, since they show similar conductivity, and both the undoped layers. A 20 nm thick p-type α-Si:H, followed by 250 nm of intrinsic layer and 20 nm of n-doped were sequentially deposited by PECVD on transparent conducting oxide (TCO) coated glass substrates and terminated with a ZnO:Al (AZO) in order to provide a transparent contact on both sides for charge collection evaluations. The diodes have circular area of 6.4 mm diameter. The radiation source consists of a 30 W tungsten halogen lamp equipped with a CVI ¼ m Digikrom monochromator, an optical fiber and an objective, to focus light at different wavelength to the sample placed within a Karll Suss probe station. The electrical characterizations under irradiation were performed with an Agilent 4155 parameter analyzer. To obtain accurate results, the energy of the monochromatic radiation was monitored by an OPHIR Nova optometer. Spectral sensitivity expressed as quantum efficiency (QE), the ratio of the number of carriers collected by the solar cell to the number of photons of a given energy incident on the solar cell, were performed under zero electrical bias. Finally, a Newport-Oriel 91194 Solar Simulator was used in order to determine and compare the energy conversion efficiency of different cells when exposed to simulated sunlight (250 W/m^2) using an AM1.5G (ASTM E891) filter.

Table 1
Summary of the α-Si:H films synthesized by PECVD using different flow ratios of SiH_4/dopant and H_2/SiH_4, together with hydrogen content, as extracted by ERDA measurements, and optical bandgap, as derived from Tauc's approach.

Sample	SiH_4:TMB:PH_3	H_2: SiH_4	10^{21} H/cm^3	E_{opt} [eV]
p1	2:1:0	1:1.5	4.7 ± 0.5	1.82
p2	3:1:0	1:1.5	4.8 ± 0.8	1.82
p3	5:1:0	1:1.5	4.5 ± 0.5	1.81
n1	2:0:1	1:0.6	7.5 ± 0.7	1.87
n2	3:0:1	1:0.6	8.1 ± 0.8	1.90
n3	6:0:1	1:0.6	7.0 ± 0.7	1.88
u1	100 sccm:0:0	10:1	6.0 ± 1.0	1.85
u2	12 sccm:0:0	10:1	11.0 ± 2.0	1.92

Table 2
Set of *pin* diode conveniently selected.

Diode	*p*	*i*	*n*
d1	p1	u1	n2
d2	p1	u2	n2
d3	p3	u1	n2
d4	p3	u2	n2
d5	p1	u1	n1
d6	p1	u2	n1

3. Results and discussion

3.1. Thin film of α-Si:H

3.1.1. Electrical properties

The doping of α-Si:H was achieved by Spear and LeComber in 1975 [12]. It is well known that in an amorphous semiconductor the disorder creates tails of localized states extending from both bands into the energy gap. In addition to these tail states, one expects the existence of localized states of varying physical origin within the band gap [13]. The incorporation of dopants can move the Fermi level inside the forbidden gap. However, the introduction of high density of donors and acceptors creates defects states near midgap which limit the doping efficiency. It has been experimentally established that doping efficiency of amorphous materials is much lower than that of crystalline ones. For this reason, it is difficult to achieve the high conductivities required for doped layers in solar cells.

Fig. 1a and b presents the temperature dependence of the dc dark conductivity, σ, measured for various n and p doped samples, respectively. One immediately sees that use of phosphorus doping can produce films with high conductivity while boron doping is not so effective in moving the Fermi level close to the mobility edge due to dihedral-angle disorders at the top of the valence band [14,15]. In our experimental synthesis conditions, the changes, shown in Fig. 1, of the conductivity with hydrogen content and dopant levels are in agreement with those expected from literature [14].

The variation of dark conductivity with temperature follows the Arrhenius form:

$$\sigma(T)=\sigma_o exp\left(-\frac{E_\sigma}{kT}\right)=\sigma_o exp\left(-\frac{(E_{TR}-E_F)}{kT}\right) \quad (1)$$

where k denotes Boltzmann's constant, T the absolute temperature, σ_o the pre-exponential factor, and E_σ the activation energy given by the difference between the average energy of the conducting electrons, E_{TR}, and the Fermi energy, E_F. Thus, the conduction is a thermally activated process with a change of slope in Fig. 1, more evident in the n-doped curves, above and below the equilibration temperature, denoted by T_{eq}, that represents the temperature at which the defect structure comes into dynamic equilibrium. The equilibration of the structure is manifested in reversible changes of the material properties as the temperature is changed [14,16,17]. In our n-doped films the defect density is in thermal equilibrium at temperatures above 380 K. Also in the p-type films σ vs E_σ curves show a kink, although less pronounced, but at a lower T_{eq} around 315 K.

Based on Eq. (1), a measurement of $\sigma(T)$ immediately gives the activation energy and the pre-exponential conductivity factor below (green straight line fit) and above (fit in pink) the equilibration temperature. Fig. 2 collects all the extracted data and shows the correlation between our measured conductivity prefactor, that we denote by σ', and activation energy, E_σ. It is evident that the conductivity has larger E_σ and σ' above T_{eq} for both n and p doped α-Si:H thin films, and that in both equilibrium and frozen state regimes p-type samples have larger values respect to n ones. It is well known that