CONDUCTIVITY MEASUREMENT OF NANOCRYSTALLINE SILICON THIN FILMS GROWN BY LEPECVD FOR PHOTOVOLTAIC APPLICATIONS

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ABSTRACT: Low Energy Plasma-Enhanced Chemical Vapor Deposition (LEPECVD) is one of the new techniques available to grow hydrogenated microcrystalline silicon (μc-Si:H) at high growth rate. μc-Si:H is long known as a promising material for photovoltaic applications, however, more accurate correlations between growth conditions, microstructure and physical properties are to be found in order to exploit its full potential. In this framework, μc-Si:H i-layers grown at low silane dilution ($[SiH_4]/[SiH_4+H_2]$) were deposited on oxidized silicon wafers at different temperatures and dilutions and current voltage characteristics were measured in a 2 point configuration at various temperatures. At low voltage we extracted the activation energy and the conductivity at room and infinite temperature. At high voltage the conduction is due to Space Charge Limited Currents (SCLC) and excess carriers will fill the conduction bandtail traps and their distribution can then be determined around the Fermi level. The discovery of a Meyer-Neldel rule in these μc-Si:H layers seems to be consistent with a conduction mechanism involving the amorphous tissue. The study of SCLC is consistent with a widely distributed exponential conduction bandtail in correlation with the conduction in the amorphous tissue and low photogain performances.

Keywords: Microcrystalline Si, electrical properties, Meyer-Neldel rule, Space charge limited current

1 INTRODUCTION

Hydrogenated microcrystalline (or nanocrystalline) silicon is considered as one of the most promising materials for photovoltaic application mainly due to its potential in reducing the costs of solar cells [1].

In this framework, Low Energy Plasma-Enhanced Chemical Vapor Deposition (LEPECVD) [2], like HWCVD (Hot Wire CVD) and VHF(Very High Frequency)-PECVD, is one of the new techniques for growing μc- or nc-Si at high deposition rates, which is expected to lift one of the most important obstacles for its industrial application.

It is also widely known that the growth conditions of the film significantly affect its microstructural properties such as the crystalline fraction, the grain size and the amount of grain boundaries [3]. As the optical and electronic properties strongly depend on the structural features, it should be possible to modulate optical and electronic properties of μc-Si:H by proper control of the process parameters.

As LEPECVD is a new technique, suitable reactor parameters need to be found to achieve optimal growth conditions for photovoltaics. In order to identify basic electrical and optical features of the material some preliminary samples were grown using low silane dilution ratios ($d = \Phi(SiH_4)/[\Phi(SiH_4) + \Phi(H_2)]$). The purpose of the present paper is therefore:

1) the study of the conductivity at various temperatures with or without illumination which allows us to identify conduction mechanisms and to quantify them.

2) the study of the distribution of the conduction bandtail above the Fermi level.

Finally, we present a discussion on the validity of the present results and give some hints about the future direction of this study.

2 EXPERIMENTAL

2.1 Material

One micrometer thick μc-Si:H films were grown on oxidized crystalline silicon substrates using the LEPECVD process. The films were deposited at substrate temperatures in the range of 200–400°C, using SiH_4 and H_2 as precursor gases. The dilution ratio ranged between 1% and 10%, always well below the a-Si/μc-Si phase transition, which is expected to be at a values around 25%. The growth rate ranged between 0.5 and 1.3 nm/s [4].

The crystallinity fraction χc, according to Raman measurements [5], was around 70%. Further details relevant to the growth processes can be found in [4] and [5].

The 4 and 5 digit samples are grown in two different LEPECVD reactors.

2.2 Measurement device and procedure

Two rectangular contacts of aluminum are evaporated on the layer and annealed at 180°C in Ar atmosphere for 90 min.

We used a Keithley 617 electrometer in a 2 point configuration allowing a voltage sweep from -105 to 105 V. A temperature sweep between 80 and 340 K can be performed thanks to a helium heat pump. A window in the enclosure allows the illumination of the sample.

3 CONDUCTIVITY MEASUREMENT

We performed parallel conductivity measurements at temperatures ranging from 180 to 340 K between two coplanar electrodes. From this we derived the activation energy E_a in the intrinsic range, conductivity at room temperature (σ_{RT}) and infinite temperature (σ_0).

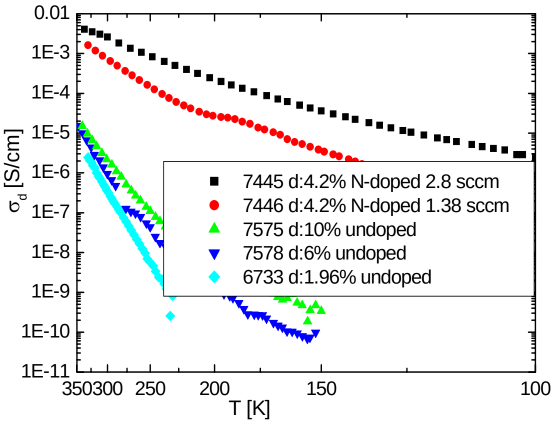

Figure 1: Arrhenius plot of the different samples.

Table I: Parameter extracted from the Arrhenius plot.

T > 250K	7578 I d:6% Ts:280K	7575 I d:10% Ts:280K	6733 I d:≈2% Ts:280K	7446 N d:≈2% Ts:210K	7445 N d:≈2% Ts:210K
E_a (eV)	0.52 ± 0.02	0.45 ± 0.02	0.50 ± 0.02	0.20 ± 0.02	0.12 ± 0.02
σ_0 (S/cm)	480	12	200	1.6	0.33
σ_{RT} (S/cm)	1.4 E-6	3 E-6	3.2 E-7	6.0 E-4	2.6 E-3

These values of activation energy are consistent with intrinsic or non intentionally doped µc-Si:H with high crystalline fraction. For doped samples E_a is significantly different in correlation with the doping level which seems to indicate that there is no Fermi level pinning as reported for a-Si. However, the activation energy, in correlation with the conductivity at room temperature indicates that these first n-doped samples are not doped high enough for use as n layer in PIN solar cells.

3.1 Meyer-Neldel Rule

For disordered semiconductors, a correlation can exist between the activation energy and σ_0 for different materials with the same microstructure but different doping levels according to theoretical thermodynamics considerations.

The relationships below can be obtained considering that the activation energy has a linear dependence with the temperature [6].

$$\sigma(T) = \sigma_0.\exp\left(-\frac{E_a}{kT}\right)$$

$$with\,\sigma_0 = \sigma_{00}\exp\left(\frac{E_a}{E_{NM}}\right) \qquad \text{(Eq. 1)}$$

$$\sigma(T) = \sigma_{00}\exp\left(\frac{E_a}{E_{NM}}\right).\exp\left(-\frac{E_a}{k.T}\right)$$

This is the so called Meyer-Neldel Rule.

By representing $\ln(\sigma_0)=f(E_a)$, σ_{00} and E_{MNR} (the Meyer-Neldel energy) can be extracted if the rule is valid. The values of σ_{00} and E_{MNR} are characteristic of a well defined conduction mechanism.

A good fit with σ_{00}=0.04 S/cm and E_{NMR}=57 meV (Figure 2) is obtained for samples with dilution ratios between 2 and 6%.

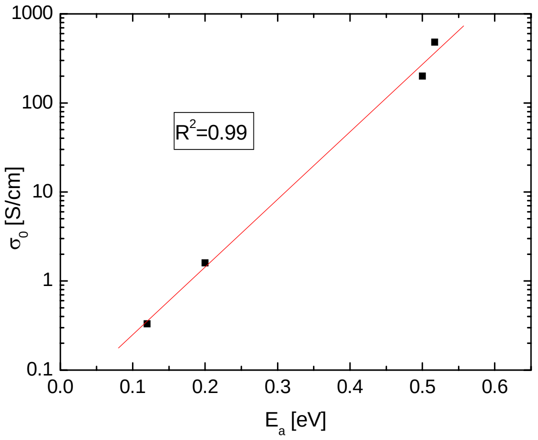

Figure 2: $\ln(\sigma_0)=f(E_a)$ plot showing a Meyer Neldel Rule for samples 7578,6733,7446,7445.

These values are in good agreement with one of the two MNR found by Lubianiker and Balberg for porous silicon (σ_{00}=0.007 S/cm and E_{NMR}=50 meV [6]). This MNR is close to the one found for a-Si and so is likely to correspond to conduction through the amorphous phase.

The presence of the MNR for samples grown at different temperature and different dilution (while remaining at low dilution) might indicate, in this range of temperature and dilution, that there is no significant difference between the microstructure of the different materials and, for temperatures between 250 and at least 340 K, that the conduction should occur through the amorphous tissue.

4 SPACE CHARGE LIMITED CURRENT

4.1 Introduction

In a biased material, the transit time (average time for the electron to move from one electrode to the other) is inversely proportional to the voltage applied. When the bias is low, the transit time is longer than the dielectric relaxation time and we are in the case of ohmic conduction. However, if we increase the bias, the transit time will become equal to the dielectric relaxation time and these two quantities will remain equal while decreasing with the bias. This will induce an increase of the number of charges in the material and the conduction will occur by Space Charge Limited Current (SCLC).

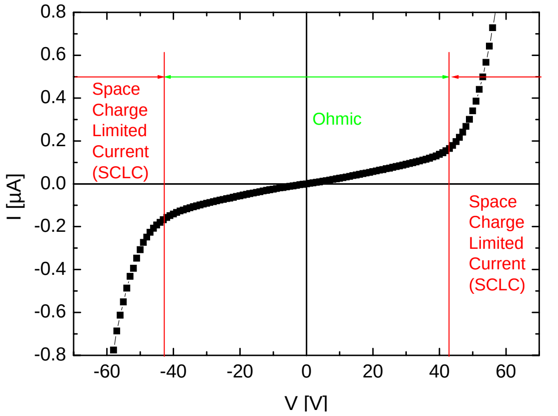

Figure 3: typical current voltage characteristic showing ohmic and SCLC conduction.

In the case of ohmic conduction the number of free carriers remains unchanged whatever is the voltage applied, the material is at thermal equilibrium and $I \propto V$ (Ohm's law).

In the case of SCLC, some of the electrons reach the anode without colliding with atoms and add to those already present in the material: the number of free carriers increases with the voltage. The material is no more at thermal equilibrium and, in the case of a trap-free material, it has been demonstrated that $I \propto V^2$ [7].

If we consider a material with an exponentially distributed conduction bandtail, the carriers injected in excess will fill the traps of the band tail located between the Fermi level and the quasi Fermi level. In this case, we can demonstrate that $I \propto V^{\gamma}$ with $\gamma=1+T_c/T$ in which T_c is the characteristic temperature of the band tail [7]. This law can be shown in a log(I)=f(log(V)) diagram for a measurement at $T<T_c$ and traps uniformly spatially distributed:

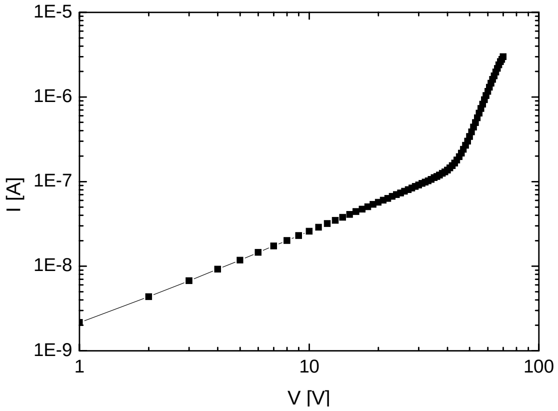

Figure 4: log log representation of a typical current voltage characteristic.

It appears that we have this conduction mechanism in some of our samples when the voltage exceeds ≈40 V (Figure 4).

Then from the power extracted in the SCLC region considering the temperature at which the measurement has been performed, we can extract the characteristic temperature of the conduction band tail (considering the material is slightly n type [8]).

The characteristic temperature of the bandtail gives only an indication of the relative energy distribution of the traps. Nevertheless, a widely distributed bandtail (high T_c) is representative of a material with a high recombination rate and so with a low photoconductivity.

4.2 Measurements

We observe in figure 5 that the fitting is accurate and the extracted values for T_c are almost the same for two different temperatures. (Here: Slope=16.3 at T=152 K ➔ T_c=2280 K and Slope=19 at T=126 K ➔ T_c=2330 K)

We have to notice here that the value is very large in comparison to the value commonly found in a-Si (around 400 K).

In order to check the influence of this wide bandtail on the photoconductivity, we carried out a measurement at room temperature on sample 56170 (Figure 5).

This measurement reveals a quite low photoconductivity and photogain (ratio of the illuminated conductivity over the dark conductivity around 1.5 at room temperature) which seems to be in correlation with the high T_c extracted.

Then further characteristic temperatures were extracted from previously studied samples (Table II).

The samples grown in the second reactor show a high T_c in correlation with poor photoconductivity performances.

We can remark that sample 6733 shows a value of T_c more close to the amorphous case which is in correlation with a higher sensitivity to light than the other samples.

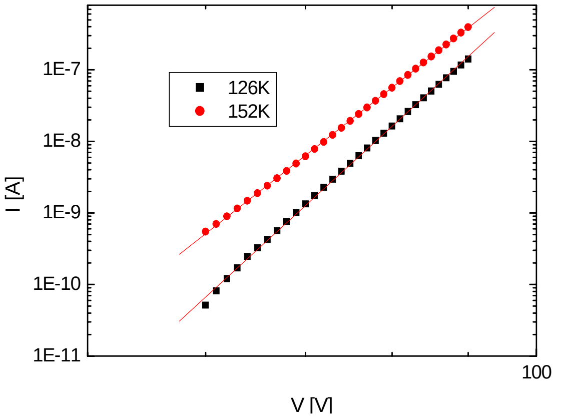

Figure 5: Evolution of the log log representation with temperature for sample 56173 in the SCLC region.

Table II: Summary of E_a, σ_{RT}, and T_c for different samples.

T > 250K	7578 I d:6% Ts:280K	7575 I d:10% Ts:280K	6733 I d:≈2% Ts:280K	56170 I d:10% Ts:280K	56173 I d:≈1% Ts:280K
E_a (eV)	0.52 ± 0.02	0.45 ± 0.02	0.50 ± 0.02	0.43 ± 0.02	0.47 ± 0.02
σ_{RT} (S/cm)	1.4 E-6	3 E-6	3.2 E-7	2.8 E-7	3.2 E-7
T_c (K)	1300	1000	470	1700	2140

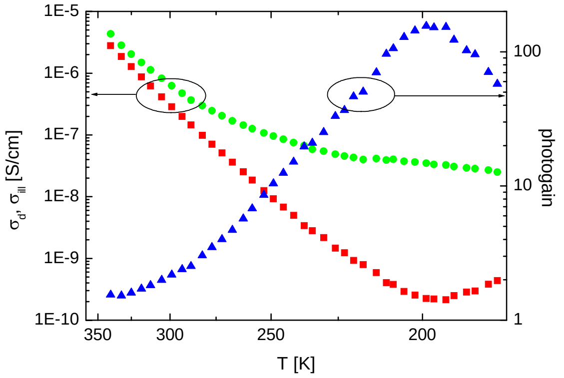

Figure 5: Illuminated, dark conductivity and photogain (σ_{ill}/σ_d) in an Arrhenius plot representation for sample 56170.

5 DISCUSSION

The NMR indicates an amorphous-like conduction type; however, the values of the activation are relatively low for a-Si which seems to indicate that the material contains a large quantity of unwanted impurities. It is however more likely that the conduction occurs through the crystalline grains by a thermoionic or tunnel effect at the grain boundary. This could be checked by looking for a change in the slope of the Arrhenius plot at higher temperature [9].

Considering SCLC, the information extracted in this paper is likely to be valid considering that the presence of the power law at higher voltage and its dependence on the temperature has been shown to follow the theoretical law. However, as the increase of the voltage induces an excess injection of the carriers in the material and therefore a shift of the Fermi level (quasi Fermi level), the energy range in which the DOS (Density Of States) are studied lies between the Fermi level and the quasi Fermi level. The evaluation of this range can be performed by integrating Eq. 2 applied to the IV curve

$$d\Delta E = kT\left(\frac{V}{I}\frac{dI}{dV}-1\right)\frac{dV}{V} \qquad \text{(Eq. 2)}$$

in which ΔE is the energy difference between the Fermi level and the quasi Fermi level in SCLC [10].

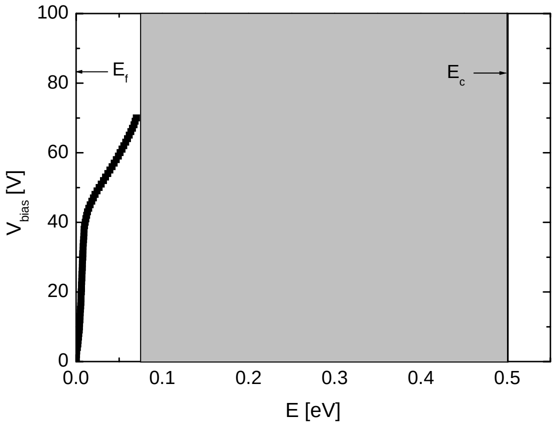

Figure 6: Energy level probed above the Fermi level as a function of the voltage applied to the sample.

We can then remark that at 70 V we have studied only up to 80 meV above the Fermi level and we cannot predict the shape of the DOS above this limit. The solution consisting in increasing the voltage to explore more of the DOS has not been implemented up to now due to the breakdown voltage of the insulating silicon oxide layer inside the sample.

Therefore, the usefulness of this method is limited by the fact that only a small portion of the DOS is probed and unseen recombination phenomena influencing the photogain can occur in the non probed DOS.

6 CONCLUSION

In this study of parallel conductivity, a Meyer-Neldel Rule has been found for samples with parameters close to a-Si. This seems to indicate that the conduction is likely to occur through the amorphous tissue for samples grown at d=2-6%. A SCLC study has shown the presence of a wide exponentially distributed conduction bandtail which seems to indicate bad quality of this amorphous tissue.

However, only few elements have been gathered by these methods concerning the correlation between the growth conditions and the electrical properties.

The defect study will be more accurately performed on a wider range of energy using optical methods.

7 ACKNOWLEDGEMENT

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