# ELECTRONIC AND OPTICAL PROPERTIES OF THIN SILICON FILMS

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#### ABSTRACT

We discuss the properties of thin silicon films that were deposited on glass by different techniques namely solid-phase crystallisation of amorphous silicon, plasma-enhanced chemical vapour deposition and hot-wire chemical vapour deposition. Values of the mobility-lifetime products for the majority and minority carriers of high-crystallinity material are comparable to those of hydrogenated amorphous silicon. It is possible to relate these properties to subgap absorption and the density of states that we derived from transient and modulated photoconductivity. Local electrical characterisation was performed with an atomic force microscope with conducting tip, revealing much smaller spatial structures as compared to the topographic image. As an alternative to atomic force microscopic determination surface-roughness evaluation is explored by optical means based on reflection data from the ultraviolet spectral range.

#### 1. Introduction

We studied the electronic and optical properties of thin film silicon on glass prepared by various deposition techniques. The films cover the range from amorphous silicon over nanocrystalline (nc) or so-called microcrystalline silicon ( $\mu$ c-Si) with nanometersized grains to polycrystalline silicon with grain sizes larger than 1000 Å. The latter films were prepared by solid-phase crystallisation (SPC) of amorphous silicon. Plasmaenhanced chemical vapour deposition (PECVD) and hot-wire chemical vapour deposition (HWCVD) were used for the microcrystalline and amorphous silicon samples. We also present structural information to indicate the crystalline character of the films.

The undoped thin-film Si samples were studied with respect to majority and minority carrier mobility-lifetime products from steady-state photoconductivity (SSPC) and photocarrier grating (SSPG) experiments together with the aspect of light-induced degradation. We relate the electronic properties to the profile of the sub-gap absorption coefficient detected with the constant photocurrent method (CPM). We applied transient photoconductivity (TPC) and modulated photoconductivity (MPC) as tools to determine the density of states (DOS) below the conduction band edge ( $E_c$ ). In addition, local electrical characterisation was performed with a homebuilt extension of an atomic-force microscope (AFM) Nanoscope III (Digital Instruments) devoted to electrical cartography. In combination with the AFM measurements for the characterisation of the RMS surface roughness an evaluation procedure of optical reflection measurements is explored.

# 2. Deposition and sample details

We characterised nominally undoped thin-film Si samples deposited on glass substrates at several laboratories and with different deposition techniques for which the references provide further details. We present results here on HWCVD  $\mu$ c-Si samples from Ecole Polytechnique, that were deposited in a high-vacuum deposition chamber [1,2] with a ratio *R*, defined as the silane to hydrogen flux *R* = [SiH<sub>4</sub>]/[H<sub>2</sub>], of 5 and 7 %. Hot-

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wire  $\mu$ c-Si samples were also deposited at Institut für Physikalische Elektronik (*ipe*), Universität Stuttgart, in a high-vacuum and in an ultra-high-vacuum deposition system [2-5]. PECVD samples were deposited at *ipe* at an excitation frequency of 66 MHz [6]. We studied SPC poly-Si samples crystallised at 600°C from Université de Rennes I [7] and *ipe* [8]. The amorphous silicon films for the crystallisation stem from low pressure chemical vapour deposition (LPCVD) at 550 °C or PECVD at high substrate temperatures. The samples were fitted with coplanar Al electrodes, which were 0.5 to 1 cm wide with gaps between 0.5 and 2 mm, that showed Ohmic current-voltage characteristics.

We applied an LED array or a HeNe laser for measuring photocurrents  $I_{\rm ph}$  to calculate the mobility-lifetime product  $\mu\tau$  representative of the majority-carrier properties. The ambipolar diffusion length  $L_d$  characteristic for the minority carriers was determined by the SSPG technique [9]. Samples were light-soaked under water-filtered strong "white" light illumination (500 mW/cm<sup>2</sup>) for more than one day, both at 25°C and at 80°C. These measurements were performed under atmospheric pressure. CPM [10] together with optical transmission and reflection provided details about optical absorption

in the thin films. Details of the MPC experiment which measures the phase and amplitude of the photocurrent under intensity-modulated photogeneration can be found in Ref. 11. In the TPC experiment we studied the time-dependent photocurrents after photoexcitation with a short laser pulse that are then converted into the DOS after Fourier transformation and use of appropriate equations [12].

The AFM measurements for the topographic and local resistance profiles were carried out in ambient air in contact mode with doped-diamond coated tips and an applied voltage of typically 1 V with respect to the tip.



**Figure 1**: Raman spectra for an amorphous silicon HWCVD sample (bottom curve) and three thin-film crystalline samples with high crystallinity.

# 3. Experimental results and discussion

#### 3.1. Structure

Figure 1 shows the Raman spectra for PECVD and HWCVD  $\mu$ c-Si films in comparison with results for hydrogenated amorphous silicon and SPC poly-Si. With caution [13], Raman spectroscopy serves as a tool to identify the crystalline volume fraction. Here we find the same high numbers for this fraction from fitting the spectra for the  $\mu$ c-Si PECVD and HWCVD samples, indicating that with adjustment of deposition parameters both PECVD and HWCVD techniques allow the deposition of films with high crystallinity. The SPC sample shows the typical Lorentzian shape as found for monocrystalline Si (c-Si) with no amorphous contribution and peaks at much lower wavenumbers.

# 3.2. Dark conductivity, majority/minority carriers and light-soaking

Concerning the majority carrier properties Fig. 2(a) summarises the dark conductivity  $\sigma_d$  values and  $\mu\tau$  products for PECVD, HWCVD and SPC samples, at a photon flux  $\phi$  of 10<sup>15</sup> cm<sup>-2</sup> s<sup>-1</sup>. The labels for the different samples will be used throughout the text. The minority carrier properties are displayed in Fig. 2(b) in terms of  $L_d$ , with the same abscissa scale. The  $L_d$  values of the PECVD and also of HWCVD  $\mu$ c-Si can be larger than 150 nm. Other HWCVD samples show quite low values of around 30 nm. SPC2 sample shows  $L_d$  larger than 500 nm.

For HWCVD and SPC crystalline samples light-soaking under intense illumination (500 mW/cm<sup>2</sup>) does neither lead to a deterioration of  $I_{ph}$  nor of the value for minority carrier property  $L_d$ , measured before and after light-soaking.



**Figure 2:** Mobility-lifetime products (a) and ambipolar diffusion lengths (b) vs. dark conductivity for a number of PECVD, HWCVD and SPC Si samples indicate the range of sample properties. The values for the  $\mu$ c-Si samples are in the range as those found in hydrogenated amorphous silicon.

#### 3.3. Optical absorption

Figure 3 compares the absorption coefficient  $\alpha$  of three  $\mu$ c-Si samples and one SPC sample. We plot here the measured and calibrated CPM signal together with  $\alpha$  determined from optical spectroscopy at high energies.

# **3.4.** Density of states from transient and modulated photoconductivity

The typical defect shoulder [14] in TPC-derived DOS for a-Si:H



**Figure 3:** CPM-derived absorption spectra for HWCVD (open symbols) with low and high subgap absorption, PECVD (line) and SPC (full symbols) samples

is found for HWCVD samples if the film is amorphous but is not present in the  $\mu$ c-Si DOS that exhibits exponential energy dependence [3]. This exponential shape of the DOS is also revealed in MPC-derived data as shown in Fig. 4 for a set of MPC data of the PECVD1 sample, taken at different temperatures *T* for which the overlap shows an expo-

nential increase towards the conduction band edge  $E_c$ . Additional data are shown for HWCVD2 and HWCVD3 samples, that also exhibit the exponential shape of the DOS. An exponentially increasing DOS towards  $E_c$  was also found for SPC poly-Si samples as displayed in Fig. 5. The energy variation in the set of MPC-derived DOS data is in good agreement with the TPC-derived DOS.



**Figure 4:** The set of MPC-derived DOS for PECVD1 sample (open symbols) exhibits an exponential increase towards the conduction band edge. The DOS of two HWCVD samples (full symbols) also show the same trend.



Figure 5: The set of MPC-derived DOS for an SPC sample, taken at different T exhibits exponential increase over a wide energy range in agreement with the TPC-derived DOS (line).

# **3.5.** Electronic properties: Discussion

We find a good correlation between transport properties, subgap absorption coefficient and densities of states. In Figs. 2 and 3, we observe that HWCVD2 sample with the *high* subgap absorption shows the *lower* values for  $\mu\tau$  and  $L_d$  while HWCVD1 with the *low* subgap absorption is comparable with the PECVD1 sample, not only from the absorption values but also as far as the *high*  $\mu\tau$  and  $L_d$  values are concerned. It is possible that HWCVD  $\mu$ c-Si samples show a pronounced shoulder in subgap absorption below 1.1 eV indicating higher values for subgap absorption in HWCVD as compared to PECVD  $\mu$ c-Si [4,6,15]. In Fig. 3 the best HWCVD sample shows low subgap absorption comparable to PECVD samples.

It should be pointed out that this correlation between transport properties and subgap absorption is not a general rule, but is also dependent on the Fermi-level position and to some degree on optical scattering. For highly conductive samples the Fermi-level position results in an increase in the electron lifetime by the filling of recombination centres with electrons, so that they may exhibit both a high  $\mu\tau$  product and a high subgap absorption, as with HWCVD2 and HWCVD4. However, in that case, as Fig. 2(b) shows, the transport properties of holes are very poor, with a very low  $L_d$ .

Optical scattering may also influence the CPM-derived absorption spectra [5,16,17], a point also discussed later in the paper. We find that the subgap absorption is still a good indicator for the photoelectronic properties in thinner samples where optical scattering is weak or negligible.

Comparing the transport properties (Fig. 2) and the DOS derived either from MPC or TPC (Figs. 4,5), we observe that a larger DOS is related to a lower  $\mu\tau$ .

No light degradation is found for the µc-Si thin films. This was already documented in the literature for PECVD samples [18], we note it here for HWCVD and SPC samples with light-soaking being performed at either 25°C or 80°C.

We find a pronounced shoulder in the subgap absorption for the SPC samples but which have quite large values for  $\mu\tau$  and  $L_d$ . As both mobility and lifetime determine the latter properties and by relating the shoulder to a relatively large density of recombination centres, determining  $\tau$ , we suggest that the free carrier mobility in the poly-Si SPC samples is larger as compared to the µc-Si films for both electrons and holes.

(right)

AFM

R



3.6. Atomic force microscopy

# 3.6.1. Topographic and electrical images

Figure 6 compares a topographic and an electrical AFM image, obtained with a so-called *Resiscope* [19], of a HWCVD µc-Si sample [20]. The electrical image is given in terms of resistance with +1 V applied to the tip. While the topography shows typical features with dimensions up to the µm range the typical spatial size of the features in the electrical image is much smaller, indicating substructures, not visible in the topography. A striking effect was observed when a given area is scanned in the contact mode several times. The successive images show that the topography is unchanged whereas the conductivity in the electrical images degrades. If a further scan is performed at a larger scale  $(say 20 \mu m)$  including the area  $(say 10 \mu m)$  explored before, the electrical image clearly shows that the resistance values have only increased in the smaller square previously scanned by the tip [20]. The evolution of local electrical measurements cannot be explained by a gradual oxidation of the whole sample surface, neither by a slow contamination of the tip apex. A similar effect was observed under a polarisation of -1V or with no voltage bias for the previous scans, respectively. This effect needs further investigation,

but we suggest that it is related to a contact-induced chemical change of the surface leading to the formation of a thin silicon-oxide layer that does not alter the topography.

#### 3.6.1. Topography and surface roughness

The topography shown in Fig. 6 is not unique for any  $\mu$ c-Si samples. In fact, it is known [17] that the size of the features and the surface roughness increase with increasing film thickness. Figure 7 illustrates this effect for a thickness series of HWCVD samples, deposited with the same parameters but different deposition time. The RMS surface roughness  $R_q$  varies from 8.5 nm for the thinnest film to 54 nm for the thickest in the figure. Films with higher H<sub>2</sub> dilution in the source gases show larger roughness at the same thickness, respectively. In contrast, SPC samples were found to be much smoother with a roughness of only 3 nm vs 40 nm for 2  $\mu$ m thick samples.



**Figure 7:** Height variations increase with increasing deposition time in HWCVD  $\mu$ c-Si with SiH<sub>4</sub>:H<sub>2</sub> ratio of 4:60. The corresponding thicknesses are 0.54, 2.5, 7.2  $\mu$ m.



**Figure 9:** Calibrated CPM-derived absorption coefficient for 3 samples of the series, showing the increase in sub-gap absorption with increasing thickness. The absorption coefficient for c-Si is shown for comparison.



**Figure 8:** Specular reflection *R* decreases with increasing thickness as optical scattering increases. The sample deposited with higher hydrogen dilution(SiH<sub>4</sub>:H<sub>2</sub> of 2:60) shows low *R*.



Figure 10: Good agreement in the comparison of the RMS surface-roughness  $(R_q)$  from AFM (abscissa) and from optical measurements (ordinate). The ordinate data are evaluated at 330 nm.

The increased  $R_q$  leads to increased optical scattering as can be seen in the reduction of the specular reflection R in Fig. 8. Here, a sample with higher H<sub>2</sub> dilution shows much smaller values for R which is related to the larger surface roughness.

We monitored optical scattering for the different film thicknesses by measuring the CPM signal. Figure 9 illustrates the increase in sub-gap absorption as the film thickness increases. While it is straightforward to make optical surface scattering, which increases with increasing  $R_q$ , responsible for the increase in the CPM signal there are indications from measurements with polished films [5] that optical volume scattering is also present in the HWCVD µc-Si.

With optical scattering theory [21,22] the surface scattering that influences the R values in the ultraviolet spectral range in Fig. 8 can be exploited for a determination of the RMS surface roughness, labelled  $R_s$ , from the expression  $R_s = \lambda/4\pi \times [\ln(R_{c-Si}/R)]^{1/2}$  where  $R_{c-Si}$  is the reflection of crystalline silicon. It is noted that for simplicity and to test its applicability we use the c-Si reflection rather than that of an ideally reflecting flat sample surface required by the theory. Fig. 10, where the diagonal represents the theory, summarises the range for which we found very good agreement between  $R_s$  and the values  $R_q$  deduced from the AFM.

For larger  $R_q$  on the one hand, as  $R_q$  approaches the wavelength of the radiation, the validity of the theory vanishes. Computed values for  $R_s$  become smaller than  $R_q$ . For smaller  $R_q$  on the other hand, the error introduced by applying the c-Si reflection data increases. We find that  $R_{c-Si}$  is larger than that for example of a polished surface of our samples. Thus,  $R_s$  values that are too large are then returned from the formula. Nevertheless in the large range shown in Fig. 10 the error that one makes when applying  $R_{c-Si}$  is minor and surface roughness determination by optical means, as also applied in Ref. 16, may provide an alternative if an AFM is not available.

# 5. Conclusions

The mobility-lifetime products and diffusion lengths of microcrystalline silicon from PECVD and HWCVD are in the range of those of a-Si:H. The diffusion length of SPC poly-Si can be much larger than that of  $\mu$ c-Si. Both MPC and TPC determine exponentially distributed DOS in the HWCVD and PECVD microcrystalline silicon and in the SPC polycrystalline silicon over a wide energy range. Any defect shoulder below the conducting band, prominent in a-Si:H, is absent. Subgap absorption may serve as an indicator for the photoelectronic properties. While PECVD and SPC samples do not degrade upon light-soaking we also find no light-induced degradation in HWCVD  $\mu$ c-Si for neither the majority nor the minority carrier properties. Conducting-tip AFM reveals profound differences between the topographic and electrical image suggesting substructures within the large features that form the surface. Optical scattering increases the absorption in the film. Its influence on the specular reflection in the UV can be exploited to determine the surface roughness by simple means without the need to rely on equipment like an AFM.

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