Structure of mixed-phase Si films studied by C-AFM and X-TEM

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Abstract. Thin Si films prepared by plasma enhanced chemical vapor deposition at low temperature and containing microcrystalline grains in amorphous tissue were studied by two complementary microscopy techniques. The conductive atomic force microscopy was performed in standard ambient conditions, whereas the presence of the surface oxide was overcome by more sensitive (pA) current detection. The cross-sectional transmission electron microscopy images of the amorphous phase revealed the columnar structure, which was successfully correlated with the bumpy surface detected by the atomic force microscope.

1. Introduction

Thin Si films with mixed-phase structure (or close to the microcrystalline/amorphous transition) seem to be the optimal material for thin film solar cells [1]. However their complicated inner structure, containing the mixture of microcrystalline (μc-Si:H) grains embedded in amorphous (a-Si:H) tissue, is strongly dependent on deposition conditions. This is one of the reasons why there are still many open questions concerning the electronic properties of these films. An intensive effort is devoted to making cheaper thin Si films e.g. by the reduction of the deposition temperature allowing to use a variety of low-loss substrates. These unusual conditions open new questions and bring new research challenges.

2. Experimental details

The samples presented in this work were prepared by plasma enhanced chemical vapor deposition (PECVD) [2] at very low deposition temperature of T_s=39°C (sample A and B), hydrogen dilution ratio r_H=[H_2]/[SiH_4]=40 and f_exc=50 MHz [3]. The sample C was prepared at r_H=[H_2]/[SiH_4]=32, f_exc=13.56 MHz and T_s=100°C [4]. The thickness of the deposited Si films was around 900 nm. The sample A was deposited on Corning 1737F glass, the samples B and C on Cr coated Corning glass - necessary for the conductive atomic force microscope (C-AFM) measurements. A part of the sample A was prepared [3] for the cross-sectional transmission electron microscopy (X-TEM) measurements.

The other part of the sample A was measured by the AFM in tapping mode, the samples B and C were measured in contact mode by C-AFM. The AFM (Veeco Dimension 3100) was equipped with the “tunneling AFM” option providing very sensitive current detection (pA range). For the tapping
mode measurements we used Si cantilevers with resonant frequency around 330 kHz. The contact mode was performed with PtIr coated Si cantilevers with resonant frequency ~13 kHz, keeping the low normal force (~25 nN, [5]) and low scanning speed of 500 nm/s to reduce the wear of the metal coating. With these quite conservative scanning parameters the influence of the topography on the local current measurement is minimized even on such rough surfaces as the mixed-phase Si films.

For the evaluation of the typical lateral dimension of the surface features we computed [6] the power spectral densities (PSD) [7] of the AFM images. AFM data were processed by the WSxM software [8]. The AFM topography images show the real signal obtained as the amplitude or the deflection of the cantilever in the tapping or contact mode, respectively. The “Z range” above each topography image shows the full height data scale of the inspected area. Similarly, the “I range” shows the full range of the detected currents, whereas the data ranges of the images are narrowed to improve their contrast.

3. Results and discussion

3.1. Structure of the samples
The AFM topographies in Figs. 1(a), and (b) indicate that the sample A is a typical mixed-phase Si sample containing μc-Si:H grains in a-Si:H tissue. The larger scale view in Fig. 1(a) reveals the arrangement of these grains into the interconnected network, just behind the percolation threshold. This is probably the reason for the best optoelectronic properties of this sample [9]. The sample A was, in fact, selected from the series of samples prepared with variable dilution rH, where the structure changed from fully amorphous to fully microcrystalline [9].

Fig. 1(b) reveals the surface of the sample A on a smaller scale, which can be compared with the X-TEM image (c) shown in the same scale. This comparison of two different microscopy methods used for one sample shows a very good agreement of the size of μc-Si:H grains. The conical shape of the μc-Si:H grain observed in Fig. 1(c) is in agreement with our simple model of growth of μc-Si:H [10].

However, there is something new and surprising in the X-TEM image – the bright horizontal lines in Fig. 1(c) indicate the columnar structure of a-Si:H, which has not yet been seen by the X-TEM [11] in a-Si:H films prepared without the use of either high power or Ar dilution [12]. The device quality a-Si:H is generally accepted to be isotropic and this is the first indication of some internal structural
arrangement. The a-Si:H columns in the X-TEM image in Fig. 1(c) seem to correspond to the small topography bumps in Fig. 1(b). This is confirmed by the PSD analysis of the X-TEM image revealing column width of 54 ±8 nm, while the AFM topography exhibits bumps with 51 ±3 nm in diameter.

3.2. Identification of the structure by C-AFM

The columnar structure of the a-Si:H motivated us for the further study. We employed C-AFM, which was demonstrated [13] to be a useful tool for a proper identification of different structures in Si films.

The deposition of the Si film was repeated, this time (sample B) on Cr coated glass to enable the C-AFM measurement. The topography in Fig. 2(a) fully corresponds to the topography of the sample A shown in Fig. 1(b). The PSD analysis of the a-Si:H part of the sample B reveals bumps with 52 ±3 nm in diameter. The local current map in Fig. 2(b) exhibits brighter spots corresponding to µc-Si:H grains with higher conductivity. The dark surrounding represents the a-Si:H with lower conductivity. The line profiles in Fig. 2(c) reveal a higher local current signal of µc-Si:H grains represented by larger bumps in local height. There is only one exception - a bump in local height indicated by the short arrows - which must be amorphous, since it has no corresponding local current signal.

Figure 2. C-AFM measurement of the sample B (39°C) showing (a) topography and (b) local current map measured simultaneously at U_{bias} = 2V. The part (c) shows the line profiles of the local height (z) and local current (I) along the longer arrows indicated in (a) and (b). The grey stripe in (c) represents the narrowed data range used for the local current map in (b).

Since our first work done in UHV [13] it has been supposed that the surface oxidation of the Si films is a major obstacle for the measurement in air. Here we firstly demonstrate that the C-AFM in air is feasible with a sensitive current detection. In the presence of the surface oxide, the detected pA currents are tunneling currents compared to the data in [14]. Due to other factors influencing the C-AFM measurement (normal force, scanning speed, tip condition, etc. [5]) the local current should be only considered as a qualitative characteristics of the electronic properties. If the absolute value of the local current or the resistivity is required, then the Scanning Spreading Resistance Microscopy (SSRM) is a good alternative. However, the higher normal forces used in SSRM (µN range [16]) require stiff cantilevers and the spatial resolution is typically reduced.

The low deposition temperature significantly changes the properties of the thin Si films [15]. Therefore we performed another comparative C-AFM measurement of the sample C prepared at slightly higher T_s=100°C. The structure of the sample C (Fig. 3(a)) is analogical to the samples A and B, i.e., µc-Si:H grain with a-Si:H surrounding. The local current map in Fig. 3(b) also reveals higher current values for the µc-Si:H grain compared to the a-Si:H surrounding. However, the grain boundary in the local current map in Fig. 3(b) is not so sharp as in the case of the sample B in Fig. 2(b). This is also clear when comparing the local current line profiles in Figs. 2(c) and 3(c).
3.3. Local electronic properties

In the case of the sample C, the local current is slowly decreasing as the distance from the \( \mu c\text{-Si:H} \) grain edge increases - see Fig. 3(b),(c). There is no significant correlation of this local current decay to the structure of the a-Si:H observed in Fig. 3(a), which indicates homogeneous electrical properties of the a-Si:H phase surrounding the \( \mu c\text{-Si:H} \) grain.

![Figure 3](image3.png)

**Figure 3.** C-AFM measurement of the sample C (100°C) showing (a) topography and (b) local current map measured simultaneously at \( U_{bias} = 3\text{V} \). The plots in (c) show the line profiles of the local height \( (z) \) and local current \( (I) \) line profiles along the arrows indicated in (a) and (b). The grey stripe in (c) represents the narrowed data range used for the local current map in (b).

However, the behaviour of the a-Si:H phase in the sample B \( (T_s = 39°C) \) is different! A selected area of 250 x 250 nm\(^2\) - see the grey squares in Fig. 2) was further inspected by the C-AFM. The part of the \( \mu c\text{-Si:H} \) grain and its edge can be easily recognized by the bright spot in the left half of the local current maps in Figs. 4(b),(c). The a-Si:H phase is again significantly less conductive with only one exception indicated by the arrows. This spot precisely corresponds to the topography bump in Fig. 4(a), which is nothing but the surface part of the a-Si:H column observed in the TEM image in Fig. 1(c). It seems that this particular a-Si:H column is in a good electrical contact with the more conductive \( \mu c\text{-Si:H} \) grain and allows the local current pass through the sample as shown in Fig. 5(a). In the case of the other a-Si:H columns in Fig. 4, the local current probably follows the same path. However, most of these columns show rather low local current signal, which means, they must be electrically separated (in the lateral direction) from the \( \mu c\text{-Si:H} \) grain and also from each other. This

![Figure 4](image4.png)

**Figure 4.** Small scale C-AFM measurement of the sample B showing (a) topography and local current maps of the same area measured at \( U_{bias} = 2\text{V} \) (b) and 4V (c). The arrows indicate more conductive amorphous column attached to the \( \mu c\text{-Si:H} \) grain.
could be due to hydrogen concentrated to the a-Si:H column boundaries [5] or simply by spaces between the columns. Both would give similar contrast in the X-TEM image (Fig. 5(b)).

Figure 5. Sketch of the cross-section of the sample (a) with expected path of the local current explaining the results in Fig. 4. X-TEM image (b) of a small area around the edge of the μc-Si:H grain with nicely visible columns in the a-Si:H phase.

4. Conclusions
We have observed a nanometer-size columnar structure of a-Si:H phase in the samples prepared from silane and hydrogen at low deposition temperatures. We have correlated the cross-sectional TEM and surface AFM observations of the same sample and identified both conical microcrystalline grains and amorphous columns. We have succeeded in the conductive AFM measurement of intrinsic Si films in ambient conditions utilizing very sensitive current detection. The C-AFM measurements of different samples helped us discover the local electronic properties of the a-Si:H phase, which should not be, in the low temperature case, considered structurally and electrically homogeneous material any more.

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