Thin Films and Coatings

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In situ and analytical transmission electron microscopy: mechanism of material transport and crystallization during the metal induced layer exchange (MILE)

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When an a-Si/metal/glass stack is heated at a temperature of 400-500 °C diffusion of Si into the metal layer followed by metal induced crystallization takes place eventually resulting in a new stacking order of type (metal+Si)/c-Si/glass with Si grain size up to 250 µm. This surprising phenomenon is called metal induced layer exchange (MILE) and can be exploited for fabrication of polycrystalline semiconductor thin films with great potential for applications in thin film solar cells and transistors. In this work *in situ* analytical electron microscopy is used for the improved understanding of the microscopic mechanism of material transport during MILE.

In our experiments Al or Ag (~50 nm) and a-Si (~100 nm) layers were subsequently deposited on quartz glass using thermal evaporation and electron beam evaporation, respectively [1]. For the TEM studies a CM30 (Philips) and a TITAN^3 80-300 (FEI) equipped with an EDXS detector (EDAX) were used. *In situ* heating of the plan view samples was carried out during light and electron microscopy.

A reflection light microscopy (LM) image of a typical a-Si/Al/glass stack annealed to 10 % layer exchange is depicted in Fig. 1(a). In the LM image primary crystalline Si grains appear dark and dendritic. The sizes of the primary Si grains in the samples range between 5 µm and 50 µm. An Al-K_α STEM EDXS elemental map around a 6 µm large crystalline Si grain marked by a box in Fig. 1 (a) is shown in Fig. 1(b). For various regions marked in Fig. 1(b) the vertical stacking of Al and Si is schematically illustrated on the right of the image. The non-reacted region, marked by the top most box in the right, has the geometry of the starting stack. The box below has the darkest contrast and is therefore almost devoid of Al. It indicates that this region consists of Si in the top layer, as well as in the bottom layer which initially consisted of Al. The third box from the top depicts a region consisting of crystalline Si in the bottom layer and a mixture of Si and nanocrystalline Al in the top layer. In total it can be concluded that the region comprising this early stage Si grain primarily contains Si and is thus severely depleted of Al. The lowest box, which like the topmost box lies in the non-reacted region, depicts an area consisting of Al layer in the bottom layer and Al in the top layer, which we named “push up” Al [1]. Such a push up Al/Al geometry with an epitaxial relationship was confirmed by diffraction contrast microscopy and HRTEM in cross section geometry [1,2].

The influence of a Ti barrier layer between a-Si and Al has been investigated, as it results in Si grain size enhancement up to 250 µm [3]. It was observed that during annealing first the Ti wets some of the Al grain boundaries and forms Ti rich phases there. As a consequence nucleation of Si crystallites is suppressed, which in turn leads to enhanced Si grain size.

In particular Ag metal layer was used to directly visualize the material transport by Z contrast imaging in STEM due to the large difference in atomic numbers of Ag and Si. Figure 2 shows the development of a Si nucleus in plan view HAADF STEM during an *in situ* experiment. Due to the large difference in the atomic number Ag appears bright and Si dark. Like in Al induced crystallization, Si grains are nucleated in the original Ag layer and grow dendritically as the smaller Ag grains were preferentially replaced by Si. In the red boxes of figure 2, it can be seen, that push up Ag appears in the direct vicinity of the Si nucleus and inhibits further growth of the Si nucleus in the radial direction. The radial growth of the c-Si grains takes place predominantly at places where the push up Ag is absent as can be seen in the blue box marked in figure 2. The replaced Ag was observed to concentrate over the larger Ag grains replacing the a-Si which appears to migrate towards the Si crystallites enabling them to grow primarily in the lateral direction. These processes which lead to incomplete layer exchange of the Ag and Si layers were found to depend on the annealing

temperature as well as the grain size distribution in the Ag layer. Lower annealing temperature of 500 °C lead to a more complete layer exchange in comparison to 550 °C annealing temperature.

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3. T Antesberger et al., Journal Of Applied Physics 112, 123509 (2012).

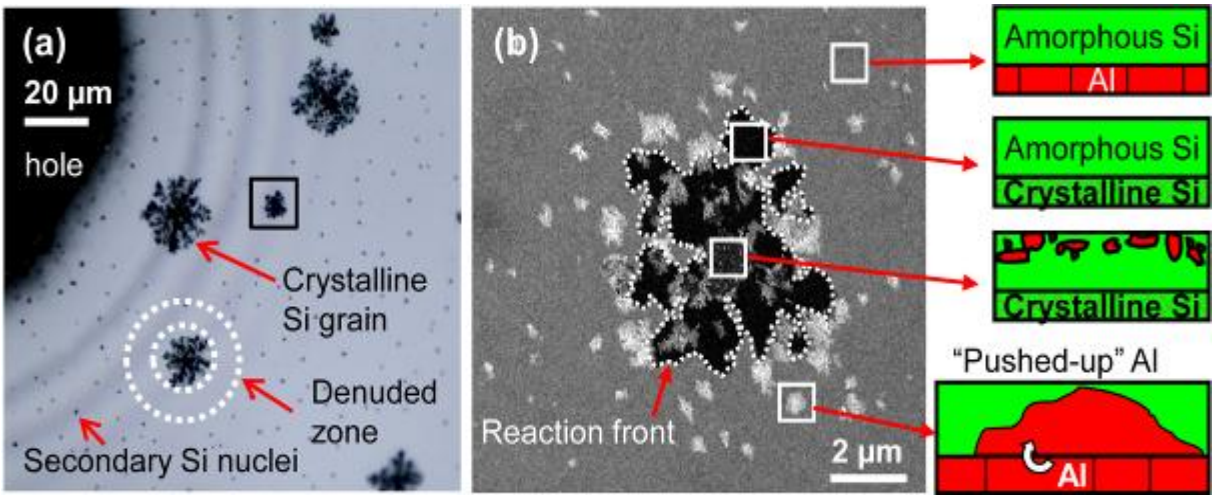

Figure 1.(a) LM image (reflection mode) of a 10 % ex situ reacted plan view TEM sample as viewed from the quartz substrate side. (b) Al K_α STEM EDXS elemental map of the region marked by a box in (a). The schematics of cross-section geometries corresponding to the various regions marked in Fig. 1(b) are shown on the right.

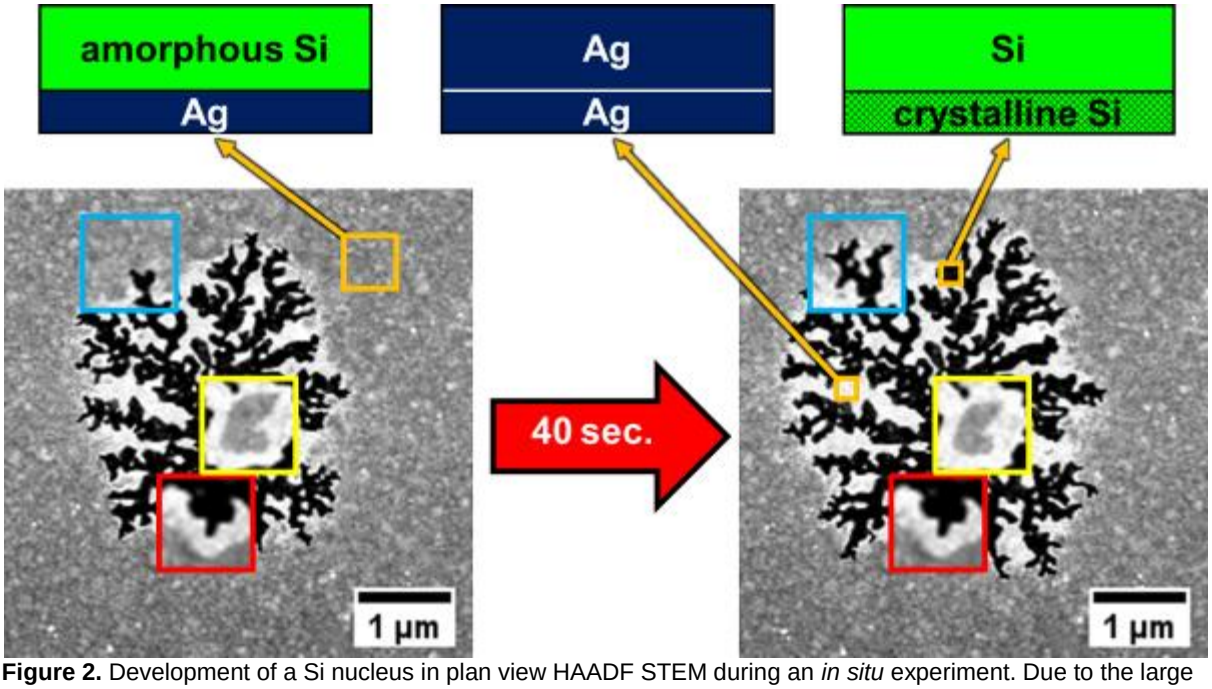

Figure 2. Development of a Si nucleus in plan view HAADF STEM during an *in situ* experiment. Due to the large difference in the atomic number Ag appears bright and Si dark. The red, blue and yellow boxes show enlarged regions indicating different effects during the growth of the Si nucleus.