doi:10.1017/S1431927622008819
Microsc. Microanal. 28 (Suppl 1), 2022

New Insights into the Mechanisms of Ag-induced Layer Exchange from Multimodal *In situ* Studies in SEM and TEM

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The metal-induced layer exchange (MILE) process has been studied intensively over the last decades due to its promising application in the field of thin film semiconductors. It offers an attractive way to produce large-grained polycrystalline semiconductor films (e.g. Si, Ge) on cheap substrates (glass, polymer) by lowering the necessary crystallization temperature [1]. Especially, in solar cells application crystalline semiconductors show increased efficiency compared to their amorphous counterpart. In addition, single crystalline semiconductors demonstrate even higher efficiencies by eliminating the detrimental influence of grain boundaries [2].

A typical sample composition of a MILE process comprises a metal layer prepared on an appropriate substrate, an oxide layer acting as a barrier and an amorphous semiconductor top layer. During annealing, both layers (metal and semiconductor) change their positions and the amorphous semiconductor crystalizes. Figure 1a illustrates the layer exchange (LE) process for the investigated Ag-Si (AgILE) system. Several combinations of metals (e.g. Al, Ag, Au) with group IV semiconductors (Si, Ge) are possible, which showcase the great potential of this phenomenon.

The current model divides the LE process into four steps (summarized in Figure 1f [1]). During annealing, the amorphous semiconductor diffuses through the oxide layer in the metal layer. Once a critical supersaturation is reached, nucleation starts (mainly at grain boundaries) and the ongoing lateral growth of the semiconductor pushes the metal into the top layer. In the end, both layers have changed their position, and the semiconductor is present in crystalline state.

The LE process has been known for a long time, however, the underlying mechanisms of this complex phenomenon, in particular regarding the early stages, are still under debate [3],[4]. To gain further insight into the underlying mechanisms, we utilized advanced *in situ* electron microscopy techniques which allowed us to directly monitor the key elementary processes of the LE, namely material transport, nucleation and crystal growth.

Pre-characterization experiments are performed to determine the optimum sample properties together with the necessary heating parameters by *in situ* light microscopy and ex-situ electron microscopy (see Figure 1b-c).

In scanning electron microscopy (SEM), we used a novel *in situ* chip-based heating stage in tandem with our low-energy nanodiffraction (LEND) setup [5] which offers simultaneous acquisition of real and reciprocal space information (Figure 1d). The combination of *in situ* transmission imaging, diffraction analysis and analytical modes of the SEM enables dedicated investigations of thin film phenomena like

AgILE. Especially, scanning transmission electron microscopy (STEM) facilitates the analysis of material transport and LE, because High Angle Annular Dark-Field (HAADF) imaging offers Z-contrast, which is perfectly suited for the Ag-Si system with its large atomic number (Z) difference (see Figure 1c). In addition, the extended field-of-view, large microscope chamber, easy access to the sample and strong STEM contrast (due to lower acceleration voltage compared to TEM) are beneficial for *in situ* experiments. Furthermore, the implemented DENSsolutions heating chips support ultra-fast and precise heating and cooling of the sample.

To analyze the ongoing processes in more detail, additional *in situ* experiments are performed in the transmission electron microscope (TEM). Moreover, we combine our TEM investigations with electron tomography, which is a non-destructive technique to gain 3D information on the sample's inner structure (see Figure 1e). Here, we recorded tilt series of an interrupted and final sample state. Afterwards, state-of-art reconstruction algorithms compute a 3D tomogram of the sample from the acquired 2D image stack.

In situ heating experiments in SEM reveal additional phenomena before the actual LE starts. Figure 2a depicts different states of the observed processes during heating, with all images acquired in HAADF mode. In addition, all observed events are illustrated schematically in Figure 2b. First, several Ag push-ups appear on the sample already after a short annealing time. Within those Ag push-ups, a second reaction starts with a dark contrast, indicating the precipitation of Si. This crystalline phase grows continuously until the original Ag push-ups are almost completely replaced by Si while the Ag is pushed sideways. After a certain time, one of these Si islands acts as nucleation site for the actual LE process, which is revealed by a darker contrast compared to the contrast of the initial layer stack.

Additionally, energy dispersive X-ray analysis (EDX) of bulk and lift-out samples supports the observed reactions (Figure 2c). Especially the performed lift-out reveals the crystalline structure of the Si-phase in the bottom layer, whereas the top layer comprises primarily a-Si and pushed-up Ag grains.

In situ TEM analysis displays similar behavior regarding the appearance of Ag push-ups followed by precipitation and growth of Si. As previously observed in SEM, the LE starts at one of those appeared push-ups. In addition, electron tomography (ET) is performed to reveal the three-dimensional distribution of the elements Ag and Si in the layer stack. Figure 2d depicts both computed reconstructions of an interrupted and final sample state. Corresponding slices through the sample enable a detailed view into the samples morphology. The reconstruction of the interrupted state supports the observation of the Ag push-ups within the upper Si-layer (Figure 2d). Several Ag push-ups emerging out of the original Ag-layer are visible in the 3D tomogram as well as in individual cross-sections. The final sample state consists of several pure Si crystals (black contrast) surrounded by the completed LE stack, in accordance with the SEM results.

Based on our detailed microscopic study of the AgILE process by advanced *in situ* electron microscopy we are able to propose a refined model that comprises new mechanisms which are active in the early stages, finally leading to the initiation of the LE process (Figure 2b). By combining *in situ* heating experiments with electron tomography, detailed analysis of such complex reactions can be performed in temporal and spatial resolution, which enables the description and understanding of the occurring phenomena [6].

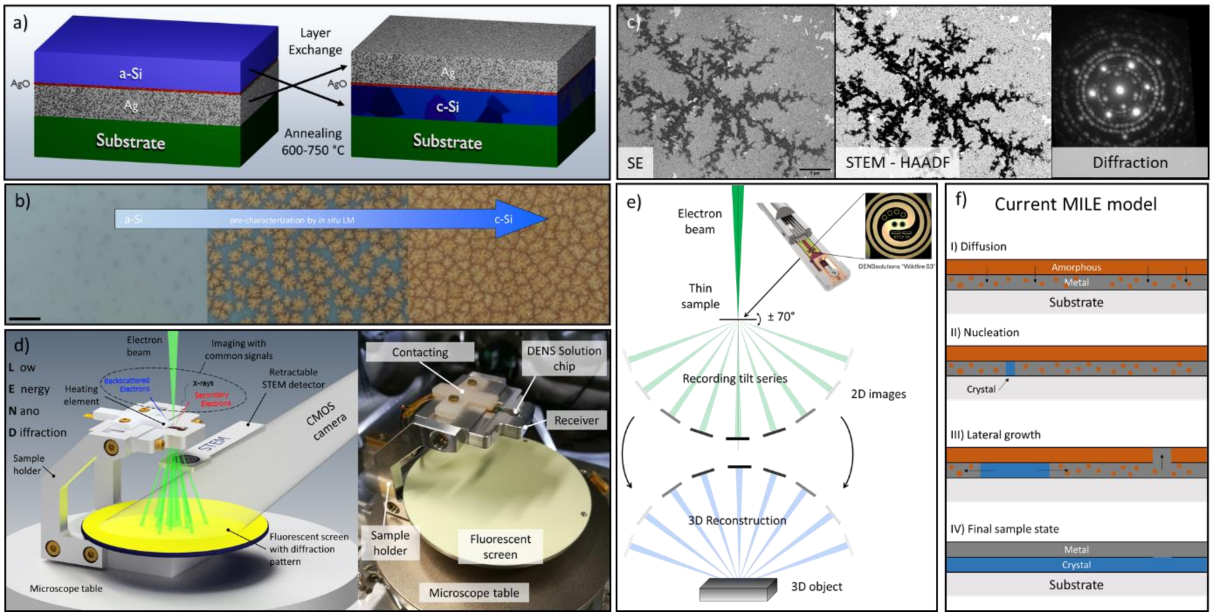

Figure 1. Overview of the Ag-induced LE process. a) During annealing, the initial sample stack (Ag / a-Si) changes their position (c-Si/Ag) and Si starts to crystalize. Pre-characterization of AgILE samples by *in situ* light microscopy (b) and ex-situ SEM (c) reveal the dendritic growth and crystalline structure of Si. d) Self-constructed chip-based *in situ* heating stage in SEM offers transmission and diffraction analysis. e) Non-destructive electron tomography enables the reconstruction of a 3D object by acquiring tilt-series and using reconstruction algorithm. f) Current model of MILE. It starts with diffusion and nucleation of the a-Semiconductor within the metal layer. The Semiconductor starts to crystalize and grow laterally, which pushes the metal layer into the top layer [1].

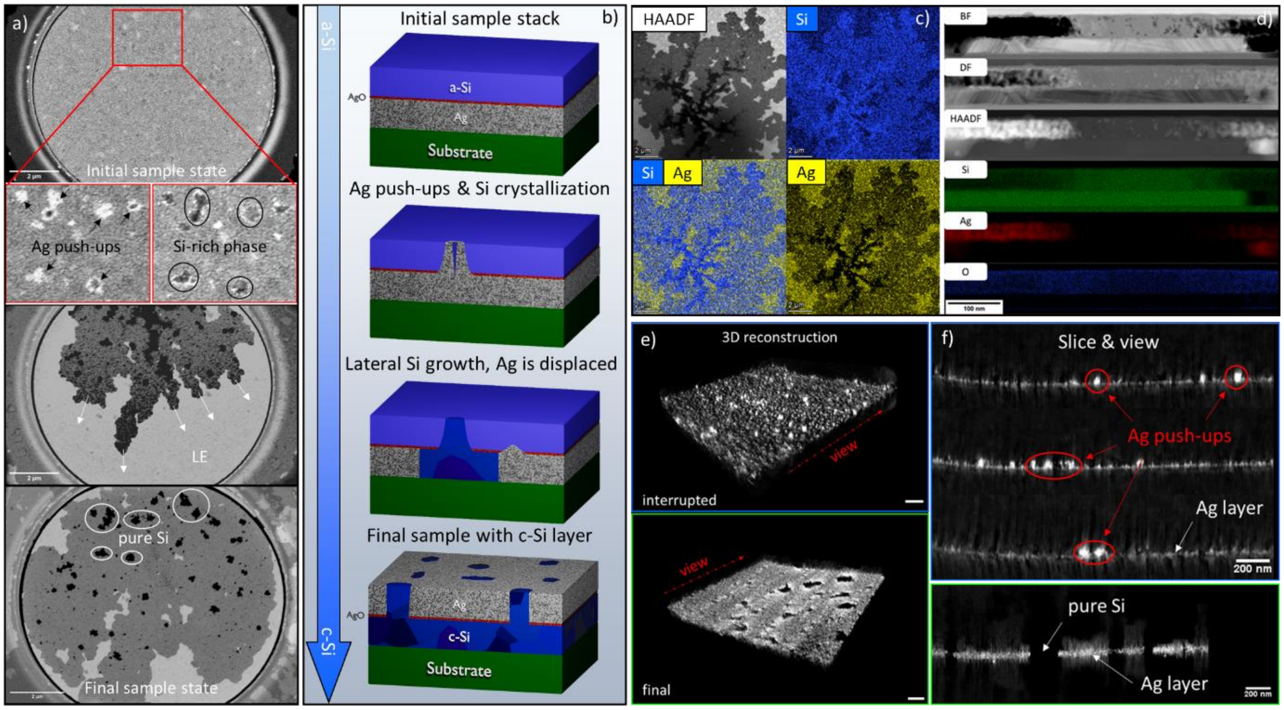

Figure 2. *In situ* experiments to reveal the underlying mechanism of AgILE process. a) *In situ* heating experiments in SEM reveal new phenomena in the early phases (HAADF). Ag push-ups appear (bright contrast – heaver element) with a following growth of a Si-rich phase within those push-ups (darker contrast – lighter element). The LE starts at one observed push-up (not shown) and grows through the whole sample with a darker contrast, indicating a higher concentration of Si. The final state consists of pure Si crystals (black), completed LE (darker contrast) and the initial sample stack in the outer region (brighter contrast). b) Schematic description of the observed processes. c) Top view EDX analysis uncover the elemental composition. Pure Si within the dendrite (black contrast), higher Si concentration within the completed LE area compared to the unreacted, outer region. d) Performed lift-out analysis enables detailed investigations of the inner sample structure. The present sample was extracted from a sample region showing almost complete LE: Apart from the most right side c-Si has already replaced Ag in the bottom layer. The top layer is composed of pushed-up Ag, but also contains excess Si islands (cf. plan-view HAADF image at the bottom of figure part a)). e) Electron tomography reconstruction of an interrupted and final state of the LE. f) Single slices through the reconstructed sample support the observations of Ag push-ups emerging in the upper Si layer.

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