Al-induced layer exchange (AILLE) is an effective route to fabricate polycrystalline seed layers from amorphous Si (a-Si) for solar cell and transistor applications. The process utilizes the tuneable nucleation and growth of crystalline Si (c-Si) in nano-crystalline Al (Fig. 1). This means, heating a stack of a-Si/diffusion barrier/Al at a temperature of around 450 °C leads to the diffusion of Si into the Al layer followed by the sparse crystallization of Si at some Al grain boundaries and the subsequent in-plane growth of those crystallites. Thereby Al is replaced by Si (change of stacking order). This results in Si grain sizes up to several tens of micrometres. A crucial role for this reaction plays the barrier layer between Si and Al, which is intendedly induced in order to tailor the diffusion kinetics (larger Si grain sizes). Usually, the barrier layer is formed by oxidizing the surface of the Al prior to deposition of a-Si. Recently, it has been shown that with oxidized Ti as a barrier layer the resulting Si grain sizes can be increased up to 250 µm [1]. However the underlying mechanism is not clarified.

In our study, layers of Al (45 nm), Ti/TiOₓ (2-5 nm) and a-Si (85 nm) were subsequently deposited onto quartz glass using e-beam PVD. The Ti layer was either natively oxidized in air (Ti/native TiOₓ) or TiOₓ was directly deposited (PLD-TiOₓ). In situ heating light microscopy was performed in order to pre-characterize the process kinetics of the samples (growth of c-Si). For TEM studies a FEI TITAN³ 80-300 was used. In situ TEM heating experiments with a DENSsolutions heating holder were conducted to follow reaction-phase formation and Si crystallization. It turned out in our experiments that the complete oxidation of Ti is important to generate secondary-phase free c-Si layers. The in situ heating experiments further revealed that, in the case of only natively oxidized Ti (remaining metallic Ti in the vicinity of the Al layer), the metallic Ti forms secondary phases with Al and Si at grain boundaries of the Al layer (brighter crystallites in Fig. 2b). The most important result is, independent of the complete oxidation of the deposited Ti, that the TiOₓ is unintendedly reduced by the underlying Al during heat treatment. This causes the formation of aluminium oxide and metallic Ti, which can further react to secondary phases in the upper layer (Fig. 3b). EDXS and SAED show that the secondary phases exhibit TiAl₃-type structure and consist of Ti, Al and Si. Our results indicate that the Ti.Aille process is similar to a conventional AILLE process where native aluminium oxide is utilized as the barrier layer, simply due to the fact that such an oxide forms upon reduction of the TiOₓ.


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Fig. 1: TiAlILE process using a) native oxidized Ti and b) PLD-TiO₅: Starting at 350 °C, in case of a), the unoxidized Ti forms a secondary phase in the bottom layer (cf. 2b). In both cases, a) and b), later Al reduces TiOₓ, releasing Ti, which forms a secondary phase in the upper layer and Si crystallizes as in conventional AlILE.

Fig. 2: TiAlILE process with natively oxidized Ti: ADF-STEM planview images (the a-Si layer on top is not recognizable): a) before heat treatment (cf 1a) and b) after 30 min at 450 °C showing secondary phases (brighter crystallites) in the original Al layer containing Ti, Al and Si (preferentially formed at grain boundaries of Al).

Fig. 3: Reduction of TiOₓ by Al: ADF-STEM cross-sectional images of a) unreacted and b) reacted region of a sample with PLD-TiO₅ (30 min at 450 °C). While the TiOₓ layer is clearly discernable in a) (bright contrast), it has disappeared after reaction due to the reduction of the TiOₓ by Al. This causes the formation of secondary phases in the upper layer.