TEM analysis of multilayered nanostructures formed in the rapid thermal annealed silicon rich silicon oxide film

Authors: Hasan Ali (1), Ling Xie (1), Martijn van Sebille (2), Adele Fusi (2), Ren`e A C M M van Swaaij (2), Miro Zeman (2), Klaus Leifer (1)
1. Department of engineering sciences, Uppsala University, Uppsala, SWEDEN
2. Photovoltaic Materials and Devices, Delft University of Technology, Delft, NEDERLAND ANTILLES

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Corresponding email: hasan.ali@angstrom.uu.se
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Silicon (Si) nanoparticles (NPs) embedded in an ultrathin silicon rich silicon oxide (SRSO) film through the thermal annealing process has emerged as a highly absorbing layer for third-generation solar cells 1. The concept of using Si NPs is to achieve a band gap tunable absorber layer by controlling the size and structure of Si NPs because of the quantum confinement effect 2. In our study, a multilayer stack of silicon oxide with 35 periods of alternating layers of 1-nm thick near-stoichiometric and 3-nm thick Si-rich hydrogenated silicon oxide were deposited on fused quartz substrate by plasma-enhanced chemical vapor deposition (PECVD) method. Two samples were annealed using a rapid thermal annealing (RTA) furnace in forming gas atmosphere (90% N₂ + 10% H₂) for 210s and 270s respectively. From the Raman spectroscopy, a reduction in crystallinity of Si has been discovered from 210s annealed sample to 270s annealed sample (shown in Figure 2). The goal of transmission electron microscopy (TEM) analysis is to investigate the nanostructural change of Si in these two annealed samples and try to correlate the TEM observations to the Raman spectroscopy results.

As the dimension of the Si nanostructures formed in SRSO films is in nanometer-scale, the energy-filtered TEM (EFTEM) tomography technique using the low-loss signals in electron energy-loss spectroscopy (EELS) has been applied as a powerful technique to correlate the precipitated Si nanostructures to the phase transformation mechanisms in the thermally annealed SRSO films 3. In this case, EFTEM spectrum-imaging (SI) technique was applied to characterize the Si nanostructures formed in SRSO films by different annealing times. The EFTEM SI dataset was acquired from -4eV to 40eV using a 2eV energy slit and the reconstructed zero loss peak (ZLP) was used to calibrate the spectra shift. Si plasmon images were extracted by fitting a Gaussian into the low-loss region with a peak position at 16.7 eV 4 and FWHM of 4.5 eV. In order to analyze the multilayer structures at different annealing durations, the TEM samples were prepared in cross sectional geometry using the conventional polishing and ion milling methods.

Figure 1 shows the EFTEM images extracted from the Si plasmon peak, in these images Si appears as bright contrasts. For shorter annealing time, an alternating bright and dark contrast can be observed which indicates that the multilayer structure still remains whereas for longer annealing time, Si shows nanoparticles like contrast. The continuous layer like contrasts shown in Figure 1(a) indicates the overlapping of the contrasts generated by small Si crystallites in a very high density. After longer annealing time (Figure 1(b)), the small Si crystallites grow in size but may take overall less volume fraction due to the Ostwald ripening process. Therefore, it explains the reduction in crystallinity of Si discovered from 210s annealed sample to 270s annealed sample by Raman. However, such a reduction in Si crystallinity was not observed in nitrogen annealed SRSO films, this indicates that samples annealed in the forming gas environment follow a different crystallization mechanism and hydrogen must play a decisive role during the Si crystallization at the initial stage.

References:
Figure 1: Energy filtered TEM images of samples annealed in forming gas for (a) 210s (b) 270s extracted at 16.7eV for silicon plasmon. The bright contrast shows silicon.

Figure 2: Crystallinity of samples annealed in (a) nitrogen and (b) forming gas atmospheres determined using Raman spectroscopy.