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Morphology studies of Si-SiO_2 nanocomposites using energy-filtered transmission electron microscopy

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Due to significant band gap widening by quantum confinement, Si nanosponge structures embedded in SiO_2 formed by spinodal decomposition of metastable silicon-rich silicon oxide are promising, advanced Si absorbers for 3rd generation solar cells. In thermodynamically metastable, silicon-rich oxide, i.e. SiO_x with $x < 2$, high-temperature annealing results in the formation of Si precipitations in a stoichiometric SiO_2 matrix. According to $SiO_x \rightarrow \frac{x}{2} SiO_2 + (1-\frac{x}{2}) Si$, phase separation of SiO_x films with $1.2 \leq x < 2$ (Si excess of up to 40 at.-%) leads to disconnected Si nanoclusters, whereas for $x < 1.2$ (Si excess larger than 40 at.-%) phase separation results in percolated Si nanostructures with a sponge-like morphology [1].

To reveal such a sponge-like morphology in sputter-deposited SiO_x films for $x \sim 1$ after activation by rapid thermal annealing (RTA), energy-filtered transmission electron microscopy (EFTEM) imaging as well as EFTEM tomography were carried out and the results were compared with kinetic Monte-Carlo (KMC) simulations. To this end, 200 nm thick SiO_x layers were prepared at room temperature on p-type (100) Si wafers by magnetron sputtering in Ar plasma from two simultaneously operating Si and SiO_2 targets. During subsequent RTA in Ar or Ar + 5 % H_2 ambient, samples were heated up to 1150 °C and annealed for 30 s. Sponge-like nanostructures were investigated by EFTEM imaging using an image-corrected FEI Titan 80-300 microscope equipped with a Gatan Imaging Filter 863. For EFTEM tomography, a tilt series between ±70° was acquired in steps of 2° in a Philips CM200 FEG microscope with Gatan Imaging Filter 678. The tilt series alignment, i.e. the correction of residual displacements, was carried out using the IMOD software [2], while the tomographic reconstruction of the Si 3D morphology was performed with the Weighted Simultaneous Iterative Reconstruction Technique [3].

The contrast in zero-loss filtered high-resolution TEM images such as Figure 1 is caused by the coherent superposition of unscattered and elastically scattered electrons within the thin TEM lamella, and hence, related to the projected atomic structure. Consequently, Bragg-oriented Si nanocrystals larger than a minimum size are visible in Figure 1 and indicate phase separation of the SiO_x film with subsequent crystallization during RTA. Since large amorphous Si precipitates crystallize preferably, high-resolution TEM images allow the determination of a maximum Si structure size. For small Si structures, however, phase separation is also possible without crystallization. Such amorphous precipitates as well as not Bragg-oriented Si nanocrystals cannot be observed with high-resolution electron microscopy, leading to an underestimation of the Si phase fraction. Therefore, EFTEM analysis is a suitable alternative for Si morphology studies. In particular, valence-band plasmon energy-loss imaging is an appropriate approach, since the Si plasmon peak is, except the zero-loss peak, the most intense feature in the electron energy-loss spectrum. It has a narrow energy distribution of a few eV, and thus, allows to distinguish the Si phase from the SiO_2 compound [4]. As shown in Figure 2, the expected sponge-like Si morphology in phase-separated SiO_x has been proven by Si plasmon imaging, which particularly shows that Si filaments have diameters of a few nanometers with a narrow size distribution. This finding is in excellent agreement with large-scale simulations based on KMC (Figure 3). Although Si plasmon EFTEM images can show the Si phase distribution in a planar projection, they do not provide three-dimensional information. For example, a superposition of Si nanodots cannot be distinguished from a sponge-like morphology in a 2D projection. Therefore, EFTEM tomography was applied, revealing that the separation of silicon into percolated nanostructures is not obvious (Figure 4). Coarsening of the Si sponge accompanied by a loss of percolation may be the reason. Indeed, longer annealing at 1100 °C for 3 h leads to separated non-spherical nanoclusters [5]. However, an underestimation of the thinnest, presumably amorphous, Si filaments cannot be excluded. Prolonged electron irradiation during acquisition of the EFTEM tilt series might have an influence on the sponge-like morphology, too.

1. T. Müller, K.-H. Heinig, W. Möller, C. Bonafos, H. Coffin, N. Cherkashin, G. Ben Assayag, S. Schamm, G. Zanchi and A. Claverie, Appl. Phys. Lett. 85 (2004), p. 12.
2. J. Kremer, D. N. Mastronarde and J. R. McIntosh, J. Struct. Biol. 116 (1996), p. 71.
3. D. Wolf, A. Lubk and H. Lichte, Ultramicroscopy (2013), submitted.
4. S. Schamm, C. Bonafos, H. Coffin, N. Cherkashin, M. Carradaa, G. Ben Assayag, A. Claverie, M. Tencé and C. Colliex, Ultramicroscopy 108 (2008), p. 346.
5. A. Yurtsever, M. Weyland and D. A. Muller, Appl. Phys. Let. 89 (2006), p. 151920.
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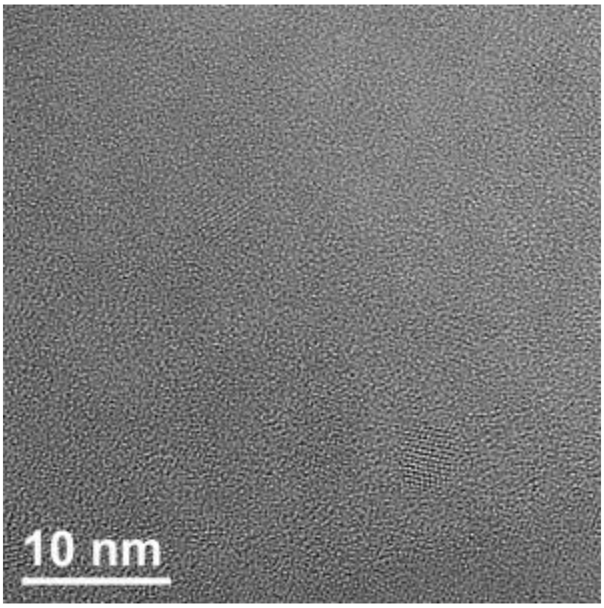

Figure 1. Cross-sectional zero-loss filtered high-resolution TEM image of a $SiO_{0.9}$ layer decomposed into Si and SiO_2 during annealing at 1100 °C for 30 s. Only Bragg-oriented Si nanocrystals can be clearly observed.

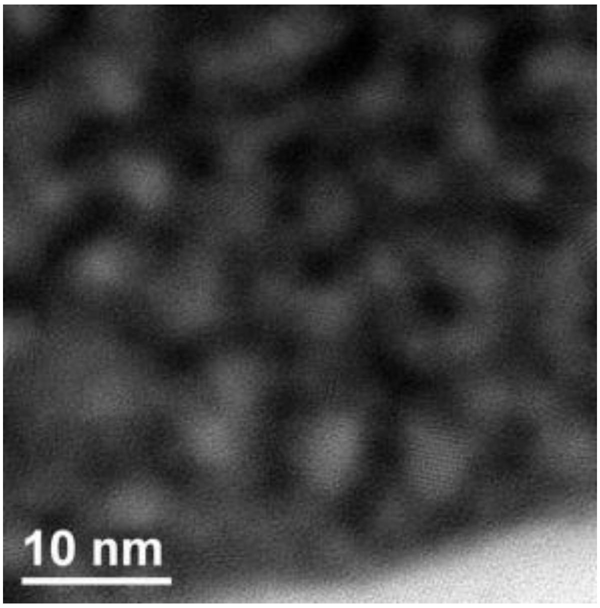

Figure 2. Cross-sectional Si plasmon EFTEM image of the same field of view as in Figure 1. Valence-band plasmon energy-loss imaging at E_{loss} = 17 eV allows to visualize both, crystalline as well as amorphous Si structures of various sizes.

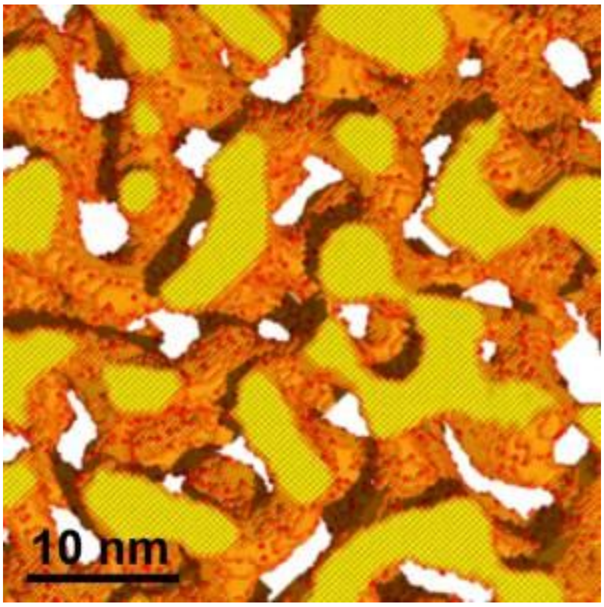

Figure 3. 3D morphology of an approximately 10 nm thick phase-separated $SiO_{0.9}$ film predicted by KMC simulation corresponding to annealing at 1100 °C for 30 s. The yellow areas represent a cut through silicon by slicing the simulation box, while the orange color visualizes the interface between Si and SiO_2, which is assumed to be transparent.

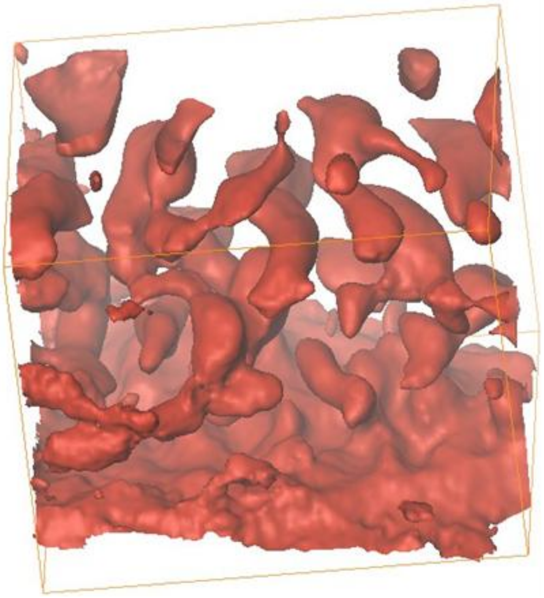

Figure 4. Si plasmon EFTEM tomography (E_{loss} = 17 eV) of phase-separated $SiO_{0.9}$ confirms a 3D sponge-like morphology as expected by spinodal decomposition. Si (red) and SiO_2 (transparent) are separated applying an intensity threshold resulting in ca. 30 vol.-% Si within a 28 x 31 x 24 nm^3 volume.