

## Diblock Copolymer Templated Si/Ge/C thin films

With high energy density, long lifespan, and environmental friendliness, lithium-ion batteries (LIBs) represent one of the most attractive energy storage devices and are playing increasing roles in modern society. This technology is already present in the portable electronics markets, electric vehicles, and small-scale energy storage systems. For higher performances, changing the anode material from graphite to silicon (Si) or germanium (Ge) could enhance the capacity multiple times. Si in particular, is a potential anode material due to environmentally friendly production, resource abundance, low cost and its outstanding high theoretical capacity of which is roughly ten times larger than the state-of-the-art graphite. Although Ge has non-negligible drawbacks as commodity price and abundance, it benchmarks Si and graphite in conductivity and  $\text{Li}^+$  diffusivity.

There are several different approaches to template inorganic semiconductor thin-films, such as lithography, molecular beam epitaxy, or chemical vapor deposition. However, these technologies have the significant disadvantage that the processes are comparatively expensive and time-consuming. Our concept is to synthesize porous SiGe thin-films in a sol-gel process via an amphiphilic diblock copolymer template as already well investigated with  $\text{TiO}_2$ . Contrary to former projects, where only Ge was templated with diblock copolymers, here also Si is present in the Zintl-phase.<sup>[1]</sup> These phases are polyanionic cages formed in intermetallic compounds between alkali or alkaline earth metals and p-block semimetals.<sup>[2]</sup> In this study, the non-oxide source of the two semiconductors is the precursor  $\text{K}_{12}\text{Si}_{17-x}\text{Ge}_x$ . With this concept, different SiGe ratios can be achieved by varying the content of Si in the synthesized precursor itself. For the sol-gel approach, polystyrene-b-polyethylene oxide (PS-b-PEO) is used as the structuring agent. Here the polymer solution is blended with the Si/Ge Zintl-phase dissolved in ethylenediamine (en). The solution is then spin-cast on pre-cleaned silicon substrates. As en is not an excellent solvent for the polymer, microphase separation of the polymer in the thin film can be enhanced by using dichloromethane as a highly selective solvent for the PEO. Here, an additional solvent vapor annealing (SVA) increases the PEO mobility again and leads to a film rearrangement. After removing the template with a temperature of 600 °C in vacuum (see Figure 1), the final porous structure can be observed.

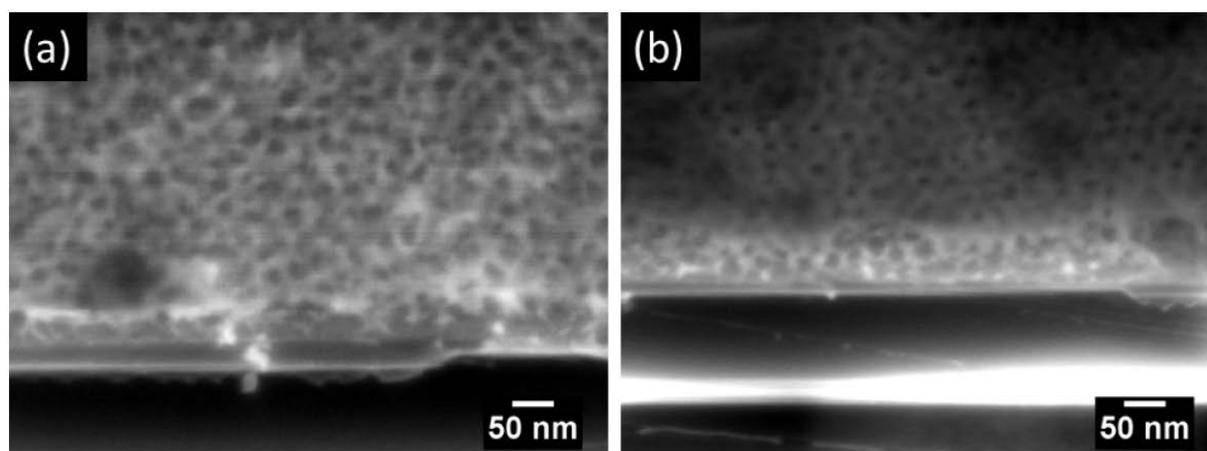


Figure 1: Scanning electron microscopy (SEM) cross-section images of pyrolyzed Si/Ge thin films without (a) and with solvent vapor annealing (b).

The SEM images reveal porous structures for the reference (a) and the SVA sample (b). Due to a high degree of order, especially in the SVA thin film (b), structural rearrangement could be

evidenced. In the cross-section array of the films, also a vertical alignment of the PS spheres is present. Here, the SVA thin film shows a spherical packing, whereas the formation in the reference follows no ordered structure. Additionally, the size of the voids for the reference sample shows more significant deviations than for the SVA thin film. The latest elemental investigations revealed oxygen residues in the thin-film, which will have a huge impact on the optoelectronic properties. Nevertheless, crystalline Ge could be observed in both films which is vital for a high conductivity in the thin film. Although the structures could be rearranged homogeneously with the SVA treatment, backfilling with a liquid electrolyte would still be challenging due to these small voids. Therefore, we are currently working on PS nano bead templates (see Figure 2) in the micrometer regime printed on copper anodes to gain a hierarchical structure by backfilling this with the polymer/precursor solution.

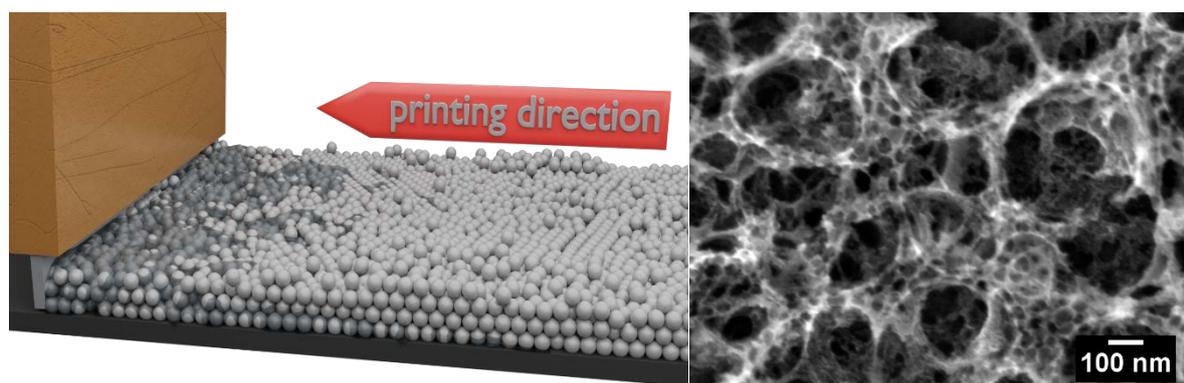


Figure 2: PS template printing with a slot-die printer and water as the solvent and a SEM image of the final thin film after removing the templating PS-spheres and the diblock-copolymer via pyrolysis.

After pyrolysis, the templating polymer and nano-spheres are removed. The SEM images show the hierarchical structure consisting of spherical voids with sizes of about 350 nm from the PS nano-sphere template and 30-40 nm voids from the diblock copolymer.

Several measurement techniques are applied within this project to study the thin film's surface morphology, inner structure, and elemental distribution. To depict the surface morphology of these thin films, techniques as SEM and atomic force microscopy are advantageous. On the other hand, setups as grazing-incidence small/wide-angle X-ray scattering (GISAXS/GIWAXS) can extract information about the inner morphology with higher statistical relevance.[3] Additionally, crystal size, orientation and lattice parameters can also be probed. With Raman spectroscopy, the presence of carbon bands can be proven. X-ray photoelectron spectroscopy provides the missing information about the oxidation states of Si and Ge in the thin film. Also, backfilling studies will be carried out via X-ray reflectometry to optimize the penetration depth of the liquid electrolyte in LIBs.

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