Marc Amkreutz, *Modelling and structure determination of precursor-derived amorphous Si-C-N ceramics on the atomic scale*.
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Abstract

Based on the existing experimental results, the structure of amorphous Si-C-N precursor-derived ceramics is modelled in this work using a density-functional-based tight-binding scheme, DFTB. Possible models for the real structure of the amorphous ceramics have been generated that give direct insight into the structure and characteristics on the atomic scale.

The precursors used for producing the ceramics are first investigated, leading to the result that because of the few available data no concrete structural model can be determined. Therefore, it was not possible to obtain detailed information about possible starting structures for the generation of the amorphous ceramics.

A molecular dynamics procedure, adjusted to the experimentally used pyrolysis conditions, has been developed that proved to give good results compared with experimental findings. Concerning the starting structures, it was found that not the precursor-like ones, but instead an α-Si_3N_4 structure decorated with carbon, corresponding to the given stoichiometry of the ceramic, is to be favoured. Starting from this, amorphous models of various precursor ceramics with different stoichiometry and density, derived from different precursors, could be generated in very good agreement with experimental findings. Therefore, these models represent structural models for the real atomic structure of the amorphous ceramics. Characteristic of these structures is a phase separation into amorphous carbon and amorphous Si_3N_4 on a small scale and interconnecting silicon carbide bonds. The appearance of mixed silicon tetrahedra $Si(C,N)_4$, almost only sp^2-like bonded carbon, and voids within the structure at the edges of the amorphous phases are also characteristic. Thus, the density of the remaining structure without the voids is much larger than the microscopic density determined in the experiment.

These properties may also explain the high temperature resistance of the ceramics. The phase separation and the voids are thought to retard the crystallisation process by hindering the thermal diffusion of the atoms upon annealing. This may result in a much higher temperature up to which the crystalline ceramic is stable.

The developed simulated pyrolysis method makes it possible to generate amorphous ceramics by using a universal starting structure – with modification of the stoichiometry and density – regardless of the used precursor. Thus, a method has been found that is very simple and universal. The precursor used for preparing the amorphous ceramic is not so important, as it only has influence in an indirect way. The structure and characteristics rather depend on the stoichiometry and density, and therefore on the position of the ceramic in the Si-C-N phase diagram.

Keywords

DFTB-Method, molecular dynamics, structure modelling, X-ray diffraction, neutron diffraction, structure factors, precursor, pyrolysis, amorphous ceramic, phase separation, voids, silicon, nitrogen, carbon