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Neutron Reflectometry – A Tool to Study Self-Diffusion on the (Sub)Nanometer Scale in Metastable Materials

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Self-diffusion is a fundamental point-defect mediated matter transport process in solids and self-diffusivities are a measure for the mobility of the constituting atoms in all kind of materials. Diffusion controls various kinetic processes in solids, which are important for a tailoring of materials properties and for thermal stability. Typical examples are mechanical deformation, grain growth, oxide layer growth, ion conductivity, crystallization and precipitation. Common methods which are generally used for the study of self-diffusion are radioactive or stable tracers combined with adequate depth profiling (SIMS, NRA), nuclear magnetic resonance (NMR), quasielastic neutron scattering (QENS) and Mößbauer spectroscopy [1]. Using these methods, self-diffusivities over 13 orders of magnitude in the range from 10^{-23} to 10^{-10} m²/s can be derived, which may serve as input parameters in various process simulations and models.

A method which can determine ultra-low diffusivities down to 10^{-26} m²/s and ultra-short diffusion lengths of 1 nm and below is neutron reflectometry applied to isotope multilayers [2-5]. The main advantage of this method is that the small detectable diffusion length allows the extensive characterization of solids, which are in a metastable or a non equilibrium state. Typical examples are amorphous materials and glasses, nano crystalline materials and also metastable chemical compounds.

For diffusion experiments, the samples have to be prepared in form of isotope multilayers. These are thin films deposited on a suitable substrate (*e.g.* a silicon wafer), which are composed of an alternating sequence of nanometer sized ⁿAB and ^mAB layers, where A and B are the components of a certain chemical compound and n and m are the mass numbers of different stable isotopes of A. This arrangement is chemically completely homogenous but isotope modulated (see Fig. 1(a)). If the two isotopes ⁿA and ^mA have sufficiently different coherent neutron scattering lengths, the isotope interfaces become sensitive to neutron scattering. During neutron reflectometry measurements a beam of cold neutrons is reflected at interfaces existing between the various isotope layers (see Fig. 1(a)). This gives rise to interference effects, which can be detected. In the reflectivity pattern, Bragg peaks are formed due to reflection at an artificial one-dimensional “isotope lattice” (see Fig. 1(b)). Annealing of such an arrangement at elevated temperatures leads to isotope interdiffusion without modifying chem-

ical composition and pure self-diffusion is measured. From the decay of the Bragg peak diffusivities can be calculated (Fig. 1(c)) [6].

Neutron reflectometry measurements were carried out at the Swiss spallation neutron source (SINQ) using the time-of-flight reflectometer AMOR and at the Geesthacht Neutron Facility (GeNF) using the monochromatic reflectometer PNR.

Up to now the described technique was successfully applied by our group to single crystalline germanium at very low temperatures [5], nanocrystalline Fe films [7], and amorphous silicon nitride semiconductors [4,8]. In the present contribution we focus on self-diffusion in silicon carbonitrides (Si-C-N), which are a new class of multifunctional high temperature materials [9]. We address the following items: (a) diffusion in different structural states (amorphous, crystalline), (b) diffusion in metastable chemical compounds and (c) correlation between diffusion and thermal stability.

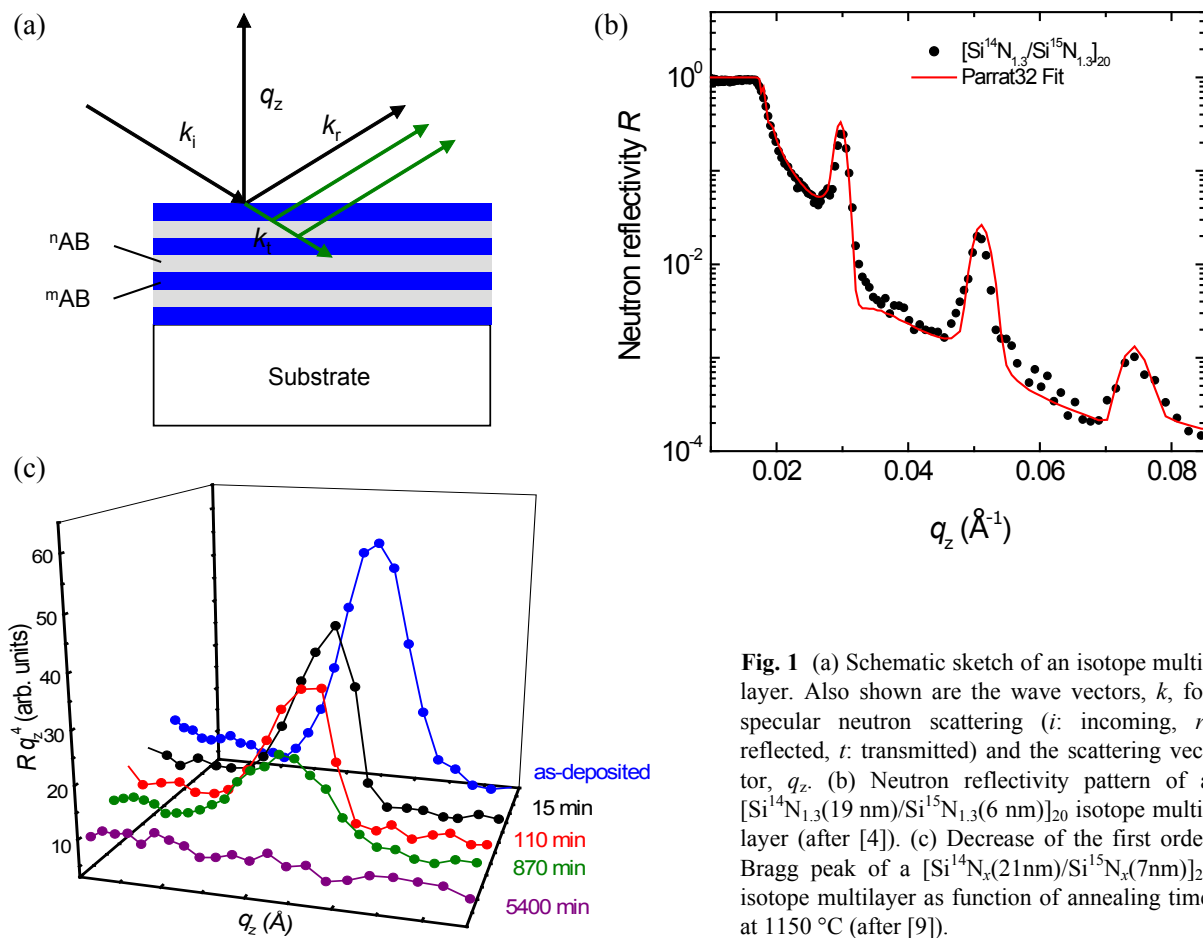


Fig. 1 (a) Schematic sketch of an isotope multilayer. Also shown are the wave vectors, k , for specular neutron scattering (i : incoming, r : reflected, t : transmitted) and the scattering vector, q_z . (b) Neutron reflectivity pattern of a $[\text{Si}^{14}\text{N}_{1.3}/\text{Si}^{15}\text{N}_{1.3}]_{20}$ isotope multilayer (after [4]). (c) Decrease of the first order Bragg peak of a $[\text{Si}^{14}\text{N}_x(21\text{nm})/\text{Si}^{15}\text{N}_x(7\text{nm})]_{20}$ isotope multilayer as function of annealing time at 1150 °C (after [9]).

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