Self-diffusion in Isotope Enriched Amorphous Silicon Nitride Multilayers

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Amorphous silicon nitride is a model system for a covalently bound amorphous solid with a low atomic mobility where reasonable values of self-diffusivities are still lacking. We used neutron reflectometry on isotope enriched $Si_3{}^{14}N_4/Si_3{}^{15}N_4$ multilayers to determine nitrogen self-diffusivities ranging from 10^{-24} to 10^{-21} m²/s between 950 and 1250 °C. The diffusivities follow an Arrhenius law with an activation enthalpy of 3.6 eV. The results are indicative for a direct diffusion mechanism without the involvement of thermal point defects.

Self-diffusion in metastable amorphous or glassy solids is a fundamental transport process, whose understanding is essential for the high temperature stability and the crystallization of these materials. While for metallic glasses and ionic oxide glasses there exist reliable diffusion data for the non-crystalline state, these data are still lacking for covalently bound amorphous solids. The lack of suitable radioactive tracers, the non-applicability of conventional tracer deposition methods, the existence of very small diffusivities also at high temperatures, and the metastability of the material complicated such experiments substantially.

During beam time at AMOR we demonstrated that it is possible to determine small nitrogen self-diffusivities down to 10^{-24} m²/s in amorphous silicon nitride (as a model system for a covalent amorphous solid) using neutron reflectometry on magnetron sputtered multilayers (e. g. $[Si_3{}^{14}N_4(19\text{ nm})/Si_3{}^{15}N_4(6\text{ nm})]_{20}$). The different bound coherent neutron scattering lengths for ^{14}N and ^{15}N of 9.37 and 6.44 fm, respectively, resulted in a significant contrast, and a Bragg peak due to isotopic periodicity was proven in the neutron reflectivity pattern (Fig. 1). It was observed that annealing of these amorphous multilayers in the temperature range between 950 and 1250 °C leads to a decrease of the Bragg peak intensity with increasing time (Fig.1) and the diffusivity was calculated using the relation:

$$\frac{d}{dt}\left[\ln\left(\frac{I(t)}{I_0}\right)\right] = -\frac{8\pi^2 n^2}{d^2} D(T) \qquad (1)$$

where I_0 is the intensity of the n^{th} order Bragg peak at time $t = 0$, D is the diffusivity at the annealing temperature T, and d is the bilayer periodicity. About 15 measurements were realized on quenched samples at different temperatures and times. The determined diffusivities show an Arrhenius behaviour as a function of reciprocal temperature with an activation enthalpy of about 3.6 eV (Fig. 2). The diffusivities are about 10 - 100 times higher than those in the polycrystalline state (Fig. 2), where an activation enthalpy of 4.9 eV is found by SIMS measurements at higher temperatures. In contrast to polycrystalline Si_3N_4, the results on amorphous Si_3N_4 are indicative for a direct diffusion mechanism without the involvement of thermal equilibrated point defects. The diffusing atoms may jump into a vacant neighbouring site, formed by frozen-in excess free volume. Consequently, the activation enthalpy is determined by the migration enthalpy alone.

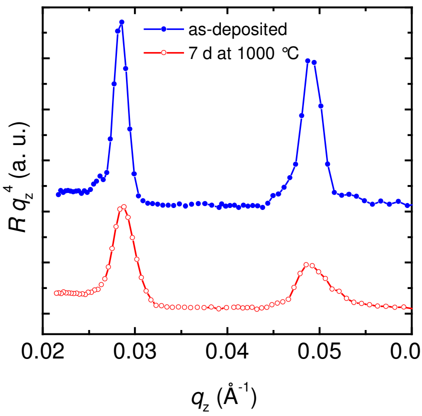

Figure 1: Neutron reflectivity patterns of a $[Si_3{}^{14}N_4(19\text{ nm})/Si_3{}^{15}N_4(6\text{ nm})]_{20}$ isotopic multilayer in the as-deposited state (shifted for clarity) and after annealing for 7 d at 1000 °C. The patterns are multiplied by q_z^4 in order to correct for the background.

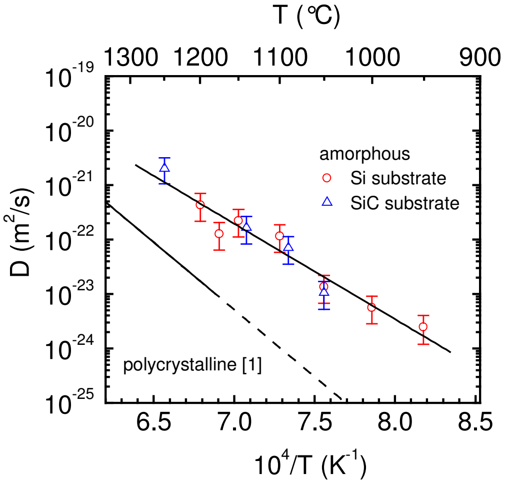

Figure 2: Nitrogen diffusivities in amorphous Si_3N_4 films as a function of reciprocal temperature. The dashed line is an extrapolation of the experimental data in polycrystalline Si_3N_4 films represented by the solid line [1].

[1] H. Schmidt et al., Appl. Phys. Lett. 85 (2004), 582.

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