Vibrational dynamics of hydrogen in *a*-Si: An atomistic approach

The study of vibrational properties of amorphous solids is important both from fundamental and technological points of view. The presence of topological disorder in amorphous solids makes the problem very difficult and interesting as the conventional analysis developed for the crystalline state, based on extended Bloech functions, is no longer valid in the amorphous state and the presence of localized vibrational modes in the vibrational energy spectrum introduces additional difficulty. Local vibrational amplitudes of the atoms in the amorphous matrix vary significantly, which often leads to a larger sampling of the anharmonic part of the inter atomic potential. This can affect the lifetime of the high-frequency excited modes upon photo illumination, or otherwise. The complex relationship between the degree of disorder in an amorphous network, the strength of anharmonic interaction and the nature of vibrational-energy decay upon excitation by itself are outstanding problems of fundamental interest. The problem is equally important from a technological point of view too; for example, the dynamics of H and D atoms in silicon play an important role in photo-degradation of *a*-Si:H or *a*-Si:D. We addressed the problem of vibrational-energy decay in realistic models of *a*-Si:H and *a*-Si:D, using first principles molecular dynamics, and compared the results obtained from femtosecond laser spectroscopy in *a*-Si:H and *a*-Si:D.

We study the vibrational relaxation of high-frequency stretching modes in *a*-Si:H and *a*-Si:D using first-principles density functional theory (DFT) with particular emphasis on the decay of the vibrational energy of stretching modes and the temperature dependence of the lifetime of the vibrational-population decay. For *a*-Si:H, the time evolution of the vibrational energy of the system appears to be largely bi- or multi-exponential in nature, whereas an almost mono exponential decay has been observed in *a*-Si:D at low temperature. The average lifetimes of the Si-H and Si-D stretching vibrations have been found to be approximately 51-78 ps and 57-70 ps, respectively, which approximately agree with experimental data in the temperature range of 25-200 K. In agreement with the experimental data from infrared transient-grating measurements, the simulated decay rates in *a*-Si:H and *a*-Si:D show a minor increase at elevated temperatures, which can be attributed to an increase of anharmonic coupling and the presence of stimulated emissions at high temperature.