DFT and MD Simulation of Self-Diffusion in Silicon: Study of Diffusion Vacancy Mechanism

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Summary: Computations of jump activation energy ΔH_j and diffusion jump frequency ν have been carried out using the Density Functional Theory (DFT) and Molecular Dynamics (MD) method for a single crystal of Si. These parameters define the rate of vacancy diffusion transport. It is shown that investigated vacancy configuration results in change of primary directions of atom diffusion jumps in Si.

Introduction

Modern molecular dynamics and quantum chemical simulation techniques offer a significant challenge for simulation of diffusion processes and determination of diffusion mechanisms in solids. A simulation method is developed to verify the bulk diffusion coefficient in solids as a function of temperature and vacancy concentration. As an example, here we consider the eigen atom diffusion in the Si lattice and the di-vacancy diffusion.

The so-called "size effects", or dependence of solids on crystal size at sequential decrease of crystals, have been in focus of extensive studies over the last decade. The concentration of defects is known to increase considerably in the neighborhood of a crystal solid. The highly defective layer, whose characteristic thickness can be 1÷2 nm, can occupy a considerable part of volume in nanowires (nanocrystals) or lie along the whole interface [1]. Thus, the total volume of nanowire is often noted for extremely high defectiveness. The existence of metastable structural modifications with high atomic mobility is typical of nanowires, while in bulk materials it is observed only at high temperatures.

The work performed allows us to proceed to diffusion coefficient computations in single crystals with different types of point defects, in polycrystal materials and, finally, in materials with a high concentration of defects (nanowires).

Results and Discussion

Molecular dynamics and quantum chemical computations of a Si atom jump to the neighboring single vacancy show that the jump should be for the most part in the [111] direction with ν= 1.31´ 1013 s^{-1} , ΔH_j @0.74 eV, and the jump in the [101] direction is energetically forbidden, ΔH_j @19.8 eV. However, the experimental value is much larger than 0.74 eV (ΔH_j^{exp} ~ 1.8 eV [2]). Thus, it can be expected that vacancy diffusion in Si is more complicated than just an atom jump to the neighboring single vacancy. We assume that at a certain vacancy concentration (or at a certain temperature), the [111] direction, which is energetically favorable for diffusion, is blocked. In this case, vacancy interaction is an important factor affecting the diffusion.

Molecular dynamics and quantum chemical computations of a Si atom jump to the neighboring vacancy were carried out to check this hypothesis for the case when two neighbor atoms are removed simultaneously. The simulation results suggest that there is a change in the primary directions of atom diffusion jumps in Si for the vacancy configuration of interest. Whereas the [111] atom jump direction is primary for the case of single vacancy, the [101] direction is primary for the di-vacancy configuration of

interest, and the [111] direction is energetically unfavorable for diffusion. The experimental value of activation energy for the diffusion vacancy mechanism of ΔH_j^{exp} ~ 1.8 eV [2] agrees with the calculated value of $\Delta H_j^{[101]}$ =1.6 eV. Thus, a conclusion may be drawn on the key role of vacancy interaction for atom diffusion transport in Si. Diffusion in Si cannot be explained within the framework of representation of atom jumps on single noninteracting vacancies.

Conclusions

According to the given results it follows that vacancy diffusion in Si is more complicated than just an atom jump to the neighboring single vacancy. The vacancy configuration under consideration is shown to result in a change in the primary directions of atom diffusion jumps in Si. Whereas the [111] atom jump direction is primary for the case of single vacancy, the [101] direction is primary for the di-vacancy configuration of interest, and the [111] direction is energetically unfavorable for diffusion.

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References

[1] B.S. Bokstein, A.B. Yaroslavtsev, *Atom and Ion Diffusion in Solids* (Moscow, MISIS, 2005) p. 362.

[2] H. Bracht, N.A. Stolwijk, H. Mehrer, Properties of intrinsic point defects in silicon determined by zinc diffusion experiments under nonequilibrium conditions, *Phys. Rev.* B 52, 16542 (1995).