Crystal growth mechanism of zinc selenide semiconductor: Molecular dynamics simulations and theoretical calculations

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Abstract

Crystal nucleation and growth are fundamental natural processes and central phenomena in several technologies. Crystal nucleation relies on the emergence of a critical nucleus from an SCL that enables other atoms or molecules to join the system, starting crystal growth. According to classical theories, the crystal growth rate can be separated into thermodynamic and kinetic terms. Two main theoretical models have been proposed to describe the crystal growth mechanism and dynamics. In the first model, proposed by Wilson [1] and Frenkel [2] (WF), the addition rate of atoms or molecules to a crystal is proportional to the atomic diffusion coefficient; whereas in the second scenario, which Broughton-Gilmer-Jackson proposed (BGJ) [3], called collision-controlled crystal growth, the ordering kinetics are controlled by the thermal velocity of the particles. For each theoretical setting, two main growth models exist: one is the "Continuous" or "Normal" growth model (N-model), and the second is the "Screw Dislocation" model (SD-model). In the N-model, the crystal surface is atomically rough, and the degree of roughness is independent of temperature. In the SD model, the crystal/SCL interface is smooth on the atomic scale, and atomic or molecular addition to a growing crystal occur preferentially on screw dislocations. In this work, we applied molecular dynamics (MD) simulations of spontaneous and seeded growth to infer the crystallization kinetics in supercooled zinc selenide (ZnSe) liquid used as a model material for which an excellent interatomic potential already exists, which was proposed by one of us (J.P. Rino). ZnSe is a type II-VI semiconductor, which is very important in optics. Experimental attempts have been made to understand its structural evolution and crystallization from vapor and melt. Hence, knowledge about its crystal growth mechanism is significant for technology applications. In MD simulations, ZnSe can nucleate spontaneously on the MD time scale only at deep supercoolings, $T < 0.75$ T_{melt}. Hence, using the seeding method, we determined growth velocities at shallow supercooling and then, according to WF and BGJ theories, extrapolated them towards deep supercooling where MD could detect spontaneous nucleation and growth. **The results showed that the Normal Growth model is the most probable growth mechanism in this material**. Although the inserted seed had a zinc-blende structure, which is the most stable polymorph of ZnSe, during the growth process, layers with wurtzite structure also form, demonstrating that seeding with the desired crystalline structure (here, the ZB structure) does not always lead to the same crystalline structure. The final crystal structure in both approaches, seeded and spontaneous growth, at different supercoolings, was a mixture of the two most stable phases of this material, i.e., **zinc blende and wurtzite,** with a predominance of the latter. This double-crystal formation probably occurs because the difference in the thermodynamic stability of the two phases is relatively small. This work sheds light on the mechanism and structural details of crystal growth in this important semiconductor.

References

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