First principles calculations of SiC polytypes including finite temperature effects

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SiC has been expected to be a next generation material for the power devices due to its superior physical properties. Among the many polytypes of SiC, 4H-SiC shows the widest band-gap, and the most expected candidate for the devices. The problem is its high cost of making single crystals of 4H-SiC. Very recently, Nishitani and Kaneko have reported a novel growth method, named Metastable Solvent Epitaxy (MSE) [1].
In MSE, the feed of polycrystalline 3C-SiC dissolves and crystalizes at the seed of single crystalline 4H-SiC at 1800 degC. The driving force of the MSE should be the difference of the solubilities between the coexisting phases of metastable 3C-SiC and stable 4H-SiC, which is speculated from the similar growth mechanism of the high pressure diamond synthesis.
A reported Si-C phase diagram, however, show that the stable phase should be 3C-SiC at the whole temperatures below the evaporation temperature. Experimental confirmations are very difficult due to i) small energy differences of these SiC polytypes, ii) contaminations especially nitrogen, and iii) high temperature-long time holdings for thermal equilibrium [2]. Therefore, we have performed the first principles calculations using Vienna ab initio package (VASP) and PHONON package for including finite temperature effects.
Small black spheres plotted in Fig. 1 show the calculated free energies of 4H-SiC at 1500 K for different a/a_0 and c/c_0 lattice parameters, where a_0 and c_0 are lattice parameters at the ground state. The energy surface was obtained by least square fit from all of 169 calculated values, and showed the minimum free energy (E_{min}) of -1.050 eV/SiC pair indicated by the gray sphere near $[a/a_0, c/c_0]=[1.01, 1.01]$ due to the thermal expansion. We have also performed the same method for the other temperatures to obtain the temperature dependency of the free energies of 3C and 4H-SiC phases at totally 71 points from 0 K to 3000 K. Fig. 2 shows the temperature dependency of the calculated free energy difference of the 3C-SiC phase against the 4H-SiC phase. The energy difference is quite small, but the result indicates the 4H-SiC phase is more stable than the 3C-SiC phase below 1000 K. The phase transition occurs at 1000K, and the 3C-SiC phase becomes stable above the critical temperature. These results are not consistent with the phase diagrams, but are consistent with the experimental results of MSE, the co-existence of stable and metastable phases of SiC.

Keywords: first principles calculation, SiC, polytype, vibration free energy, phonon

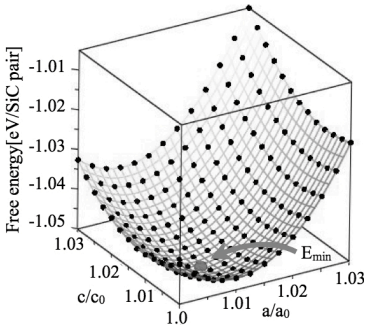

Fig. 1. The lattice parameter dependency of the free energy of 4H-SiC at 1500 K. The a_0 and c_0 mean lattice parameters of 4H-SiC at the ground state.

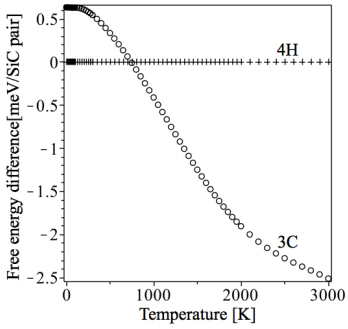

Fig. 2. The temperature dependency of the calculated free energy of 3C phase against 4H-SiC phase.

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