

Effect of pressure on the band gap and the Seebeck coefficient of silicon

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Many physical properties of semiconductors and insulators are characterized by their band gap energy, which is the energy difference between the valence band minimum (VBM) and the conduction band maximum (CBM). The pressure dependence of the band gap energy of Si is unique among the group 14 elements, which form the diamond-type crystal structure. The other three semiconductors (C, Ge and Sn) have positive pressure coefficient of the band gap energy, i.e. the band gap energy increases with increasing pressure whereas Si has negative pressure coefficient (Wei & Zunger, 1999; Angilella et al., 2008). The Seebeck coefficient is one of the important physical properties that closely related with the band gap energy (Goldsmid & Sharp, 1999; Ricci et al., 2017). However, measurements of the Seebeck coefficient under high pressure are very limited for both metallic (e.g. Getting & Kennedy 1970; Nishihara et al., 2019) and non-metallic (Yoshino et al., submitted) samples. Therefore, we conducted first-principles calculations of Si-I (diamond structure) by using the Quantum ESPRESSO package. The structure relaxation was performed at 0, 5 and 10 GPa pressures with PBE-PAW potential. To calibrate the bandgap, we also computed the quasi-particle self-consistent GW (QSGW) calculation with the ecalj package. The calculated bandgap values are $E_{g,PBE} = 0.609$ and $E_{g,GW} = 1.465$ eV for PBE-PAW and QSGW, respectively at 0 GPa, whereas the literature value is 1.11 eV. The bandgap energy decreases with increasing pressure. Note that most of the exchange correlation functionals such as PBE underestimate the bandgap energy, whereas the GW approximation tends to overestimate it. Because the Seebeck coefficient critically depends on the bandgap energy, we empirically corrected it as $E_g = 0.4 * E_{g,PBE} + 0.6 * E_{g,GW}$. The Seebeck coefficient was calculated by using the BoltzTraP package. The effect of impurity is represented within the rigid band model. The absolute value of the Seebeck coefficient decreases with carrier (impurity) concentration. Our calculation at 0 GPa and 300 K underestimated the literature values with the impurity concentration lower than $\sim 10^{19}$ (cm³). This is due to the phonon drag effect (Weber and Gmelin, 1991). Our calculation considered the diffusion term only, but the actual Seebeck coefficient should be sum of the diffusion term and phonon drag term. Note that the phonon drag becomes negligible at high temperature and/or high carrier concentration. The absolute value of the Seebeck coefficient decreases with increasing pressure, because the bandgap decreases with pressure. Similarly, it decreases with decreasing carrier concentration at high temperature. Therefore, pressure (and hence the bandgap energy) and impurity concentration have competing effects on the Seebeck coefficient of Si.

Keywords: band gap, Seebeck coefficient, silicon, GW approximation