Density functional study on intrinsic and impurity defect formation in layered $SrTiN_2$

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[Introduction] $SrTiN_2$ (STN) has a layered crystal structure composed of alternating stacking of edge-shared pyramidal Ti-N layers and rocksalt-like SrN layers along the *c*-axis[1]. Band structure calculations suggest STN is a semiconductor with a bandgap of ~1.6 eV and a conduction band minimum consisting mainly of Ti $3d_{xy}$ orbitals[2]; therefore STN is expected to show unique semiconducting properties originating from the two dimensional TiN transport layers. However, highly pure STN has not been synthesized, and the low-purity STN exhibited almost degenerated conduction with high conductivity ~2000 S/cm[3]. Further, there has been no report on other physical properties until now. It is known that defect formation in a semiconductor significantly depends on the chemical condition of synthesis process. In this study, to know the way to control semiconducting properties in STN, we performed density functional theory (DFT) calculations on the chemical potential window, defect formation energies, and defect structures of STN.

[Computational details] DFT calculations were performed using a PAW method as implemented in a VASP code. The primitive cell of STN was employed for thermodynamic stability calculations, and the 256-atoms supercell with the relaxed structure was used to build defect models, where a defect was introduced and internal atomic positions were relaxed until all forces became less than 0.05 eV/Å with the fixed cell parameters. We considered native defects, and unintentionally introduced oxygen/hydrogen impurities.

[Result] The calculated chemical potential window revealed STN is thermodynamically stable and pure STN can be synthesized in wide chemical window from Sr-rich to N-rich conditions. Figure 1 shows defect formation enthalpies (ΔH) of native point defects in STN. It is found that, at the N-poor condition, N vacancy at the N1 site (V_{N1}) is easily formed and is the origin of intrinsic n-type conduction in pure STN. H^- is easily incorporated to the N1 site to form H_{N1}, which works as a donor. On the other hand, at the N-rich condition, V_N is hardly formed, while O^{2-} is incorporated into the apical N2 site of a (TiN_5) polyhedron (O_{N2}) because O is also in the rich condition, which is the origin of n-type conduction in low-purity STN. At the moderate condition, the formation enthalpies of all defects become larger, which prevents the unintentional doping in STN. This result indicates moderately N-rich conditions can suppress formation of V_N donors to control low residual carrier density. However, impurity defect calculations (not shown) indicated that O / H impurities are easily incorporate and form donors. Unexpectedly, their formations are easy at the end-member conditions, i.e., the N-poor and the N-rich conditions, but well suppressed at the N-moderate condition. This result gives an important insight to choose fabrication condition STN; (i) the preceding reports on the almost degenerated STN would suffer from the V_N defects or O / H impurities, and (ii) low carrier density semiconducting films can be obtained by tuning the N chemical potential in the vicinity of the N-moderate condition under the equilibrium with Sr_2N. More detailed mechanism about the above unexpected effects of impurity doping will be discussed at the Meeting.

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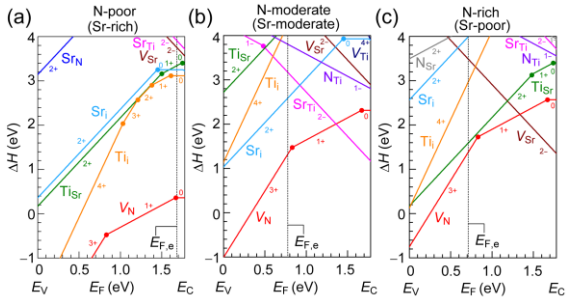

Fig. Defect formation enthalpies (ΔH) of native point defects in $SrTiN_2$ as a function of the Fermi level.