Cupper nitride (Cu$_3$N) is a promising photovoltaic material with a desirable electronic band structure, a high absorption coefficient, and dopability into both $p$- and $n$-type [1,2]. Electronically benign behavior of native point defects has been suggested theoretically, which is advantageous in the practical application of Cu$_3$N as an absorber of thin-film photovoltaic cells [2]. Regarding carrier generation, the Cu vacancy and interstitial are predicted to be a major native acceptor and donor, respectively [2,3]. In this study, the electronic levels and formation energies of native point defects in Cu$_3$N are investigated using first-principles calculations to discuss their contributions to carrier generation.

The calculations were performed using the projector augmented-wave method [4] as implemented in the VASP code [5,6]. The Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA) [7] with a Hubbard $U$ correction [8] to the Cu-3$d$ states ($U = 5$ eV) [2] and the Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional [9,10] were employed. Point defects were modeled using supercells containing 32 atoms and a defect. Artificial interdefect electrostatic interactions in the supercell approach were corrected to accurately predict the properties of point defects at the dilute limit [11,12].

Figure 1 shows the calculated electronic band structure and density of states for Cu$_3$N. It exhibits an indirect-type band structure with a minimum band gap of 1.0 eV. This value is close to a previously reported value of 1.0 eV via a $GW$ calculation with a local potential correction [2].

The calculated formation energies of native point defects are shown in Fig. 2. A Cu-rich condition is considered here, where equilibrium between Cu$_3$N and Cu metal is assumed. The Cu vacancy shows a low formation energy and a shallow acceptor level. The Cu interstitial is a dominant donor-type defect whose donor level is located almost at the conduction band minimum. These results are qualitatively consistent with previous theoretical studies [2,3]. Because of the dominance of the Cu interstitial, $n$-type behavior is expected under the Cu-rich condition. However, the carrier type would be converted into $p$-type as the chemical potentials are controlled toward Cu-poorer conditions: this leads to the decrease in the formation energy of the acceptor-type Cu vacancy and the increase in the formation energies of the donor-type Cu interstitial and N vacancy.

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References


FIG. 1. Electronic band structure and density of states for Cu$_3$N obtained using the HSE06 hybrid functional. The origin of the energy is set at the valence band maximum.

FIG. 2. Formation energies of native point defects in Cu$_3$N as a function of the Fermi level. PBE-GGA+$U$ total energies in combination with band edges determined using the HSE06 hybrid functional were used. The origin of the Fermi level is set at the valence band maximum.