Synthesis and optical properties of bismuth-based mixed-anion compounds epitaxial thin films

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Bismuth-based mixed-anion compounds (BMCs) are attracting much attention as photo-energy conversion materials because of their flexible bandgap and anisotropic layered structure. The conduction band bottom and the valence band top are mainly formed by Bi 6p orbital and the p orbitals of the constituent anions, respectively, which are sensitive to the local structure [1]. Therefore, it is essential to understand the relationship between the crystal structure and band gap to design BMCs with suitable optical properties for applications. We recently succeeded in synthesizing Bi_2OS_2 and $Bi_3O_2S_2Cl$ (Fig. 1) in the form of epitaxial thin film by mist chemical vapor deposition (CVD) [2]. In this study, we investigated the crystal structure and the optical properties for the Bi_2OS_2 and $Bi_3O_2S_2Cl$ thin films.

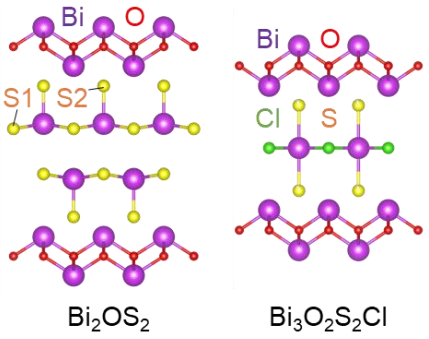

Figure 1. Crystal structures of Bi_2OS_2 and $Bi_3O_2S_2Cl$.

The Bi_2OS_2 and $Bi_3O_2S_2Cl$ thin films were selectively synthesized from N,N-dimethylformamide solutions of $BiCl_3$ and thiourea (CH_4N_2S) on $(LaAlO_3)_{0.3}(SrAl_{0.5}Ta_{0.5}O_3)_{0.7}$ (100) single crystal substrates by mist CVD with different setups. X-ray diffraction, energy dispersive X-ray spectroscopy, and X-ray photoemission spectroscopy confirmed epitaxial growth of these compounds without any impurity.

Figure 2 shows the Tauc plots of optical absorption spectra for (001)-oriented Bi_2OS_2 and $Bi_3O_2S_2Cl$ epitaxial thin films. $Bi_3O_2S_2Cl$ showed a significantly smaller bandgap of 0.6 eV than that of 1.0 eV for Bi_2OS_2 despite the formation of S 2p orbital at the valence band top in both the compounds. First-principles calculations indicated that the different local structures surrounding the Bi cations caused the reduction of bandgap in $Bi_3O_2S_2Cl$ [3].

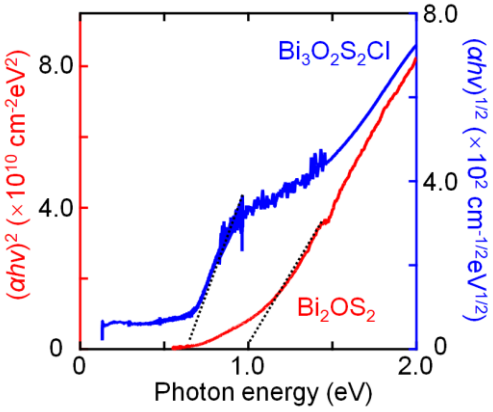

Figure 2. Tauc plots of absorption spectra for Bi_2OS_2 and $Bi_3O_2S_2Cl$ epitaxial thin films. Direct and indirect transitions were assumed for the former and latter.

References

[1] T. Li *et al.*, Adv. Mater. **33**, 2008574 (2021).

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