Supporting Information

Band alignment of the CdS/$Cu_2Zn(Sn_{1-x}Ge_x)Se_4$ heterointerface and electronic properties at the $Cu_2Zn(Sn_{1-x}Ge_x)Se_4$ surface: x=0, 0.2, 0.4

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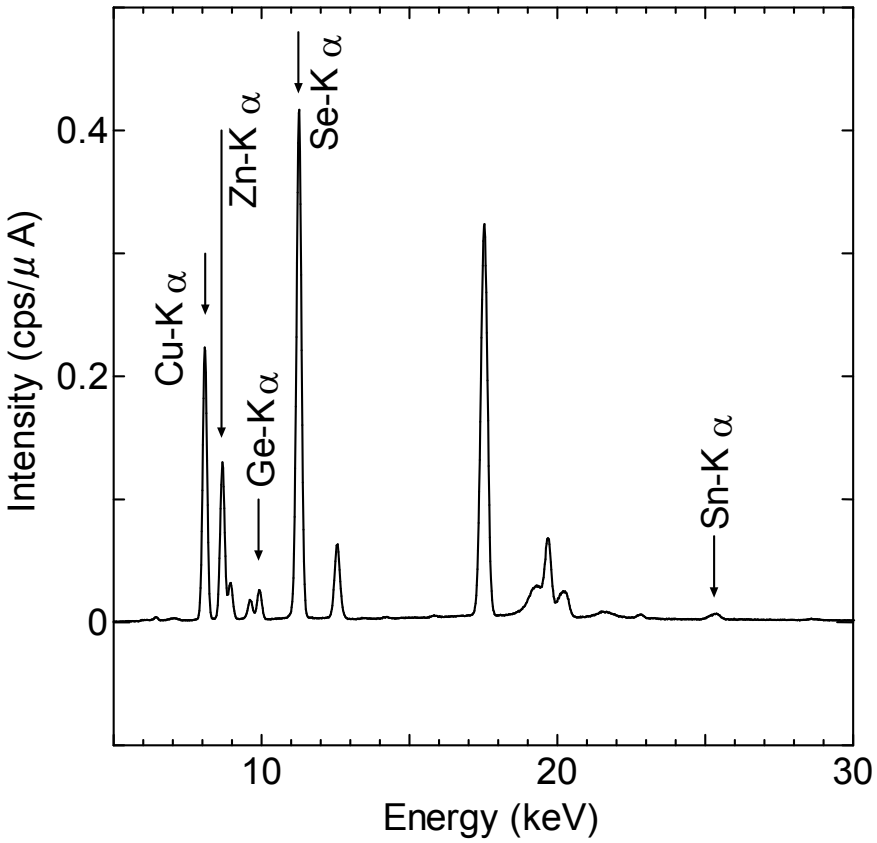

Figure S1. Representative XRF spectrum of CZTGSe with x = 0.2.

Figure S1 shows a representative XRF spectrum of CZTGSe with x = 0.2. The Ge composition, x = Ge/(Sn+Ge), was determined by integrating the Cu, Ge, Se, and Se XRF signals. Moreover, we report the XRD patterns of CZTGSe(112) as functions of Ge composition x.[29]

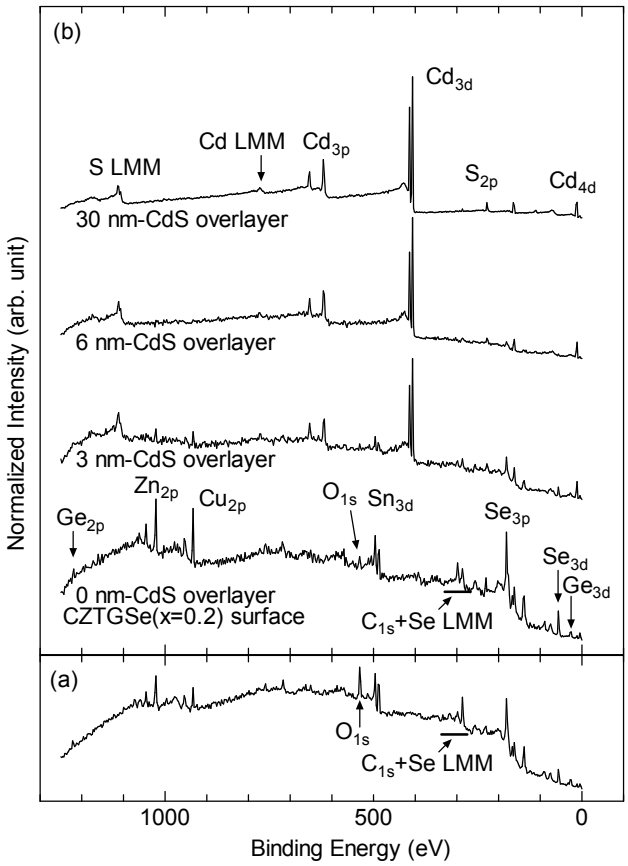

Figure S2. (a) Representative survey XPS spectra of CZTGSe (x=0.2) without NH_3 surface treatment. (b) Representative survey XPS spectra of CZTGSe (x = 0.2) after NH_3 treatment with 0–30-nm thick CdS overlayers.

Figure S2(a) shows representative survey Al K_α X-ray photoelectron spectra for 0-, 3-, 6-, and 30-nm-thick CdS overlayers on a CZTGSe bottom layer with a Ge composition (x) of 0.2 (a) prior to NH_3 treatment and (b) after NH_3 surface treatment. C and O were almost removed from the CZTGSe surface following NH_3 treatment and lamp annealing of the CZTGSe films, as shown in Fig. S2(a). XPS signals corresponding to Zn, Cu, Sn, Ge, and Se are clearly evident, while a small amount of O-related signals are observed at a binding energy of 532 eV. The intensity of the O-related signal decreased with increasing CdS-overlayer thickness, and the O and C signals were completely absent at a CdS-overlayer thickness of 30 nm, which suggests that we can suppress the additional attachment of C and O onto the CZTGSe surface during XPS, UPS, and IPES in our setup.

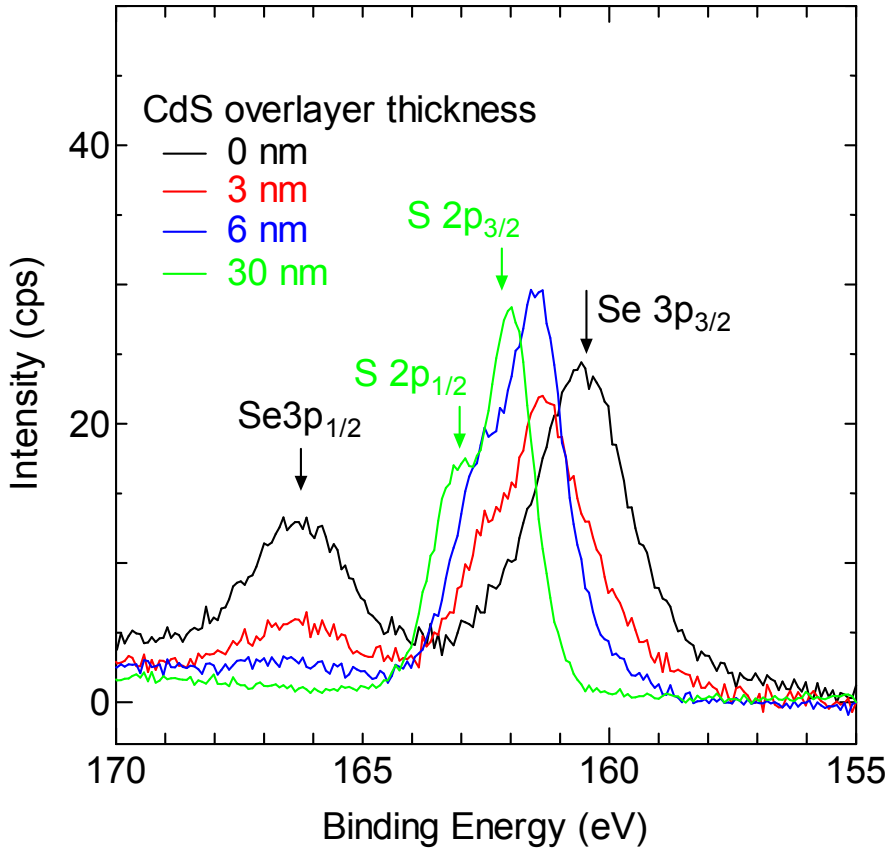

Figure S3. XPS signals originating from the S 2p and Se 3p signals as functions of CdS film thickness on the CZTGSe substrate. Black, blue, red and green correspond to CdS overlayer thicknesses of 0, 3, 6, and 30 nm, respectively.

Figure S3 shows representative survey Se 3p and S 2p XPS spectra of CZTGSe (x=0.2) with 0–30-nm thick CdS overlayers. The S 2p signals increasingly overlap with the Se 3p signals with increasing CdS film thickness; consequently, we only used the Cd core-level shift to discuss the iibb of the CdS overlayer.