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Synchrotron-radiation photoemission and O Kα emission study on (LnO)CuS (Ln = Ce, Pr, Nd)

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Abstract

Ln 4f partial densities of states (DOSs) in layered oxysulfide semiconductors (LnO)CuS (Ln = Ce, Pr, Nd) have been deduced by means of the Ln 4d–4f resonant photoemission spectroscopy. The Ce 4f DOS contributes just below the valence-band maximum (VBM) of (CeO)CuS, and on going from Ln = Ce to Pr, and to Nd, the 4f DOS shifts toward the deeper binding-energy side, leading no 4f contribution near VBM for Ln = Pr and Nd. The O 2p partial DOSs derived from O Kα emission spectra are almost unchanged with the Ln elements.

Keywords: Semiconductors; Electronic states; Photoelectron spectroscopies; Synchrotron radiation

1. Introduction

Layered oxysulfide (LaO)CuS is known to be one of few materials with a transparent p-type semiconductive property ($E_g \sim 3.1$ eV) and expected to be a candidate material for optoelectronic devices in ultraviolet and/or blue regions [1–3]. The crystal structure of (LaO)CuS is (LaO)AgS type and consists of LaO and CuS layers with OLa_4 and CuS_4 tetrahedra, respectively, alternately stacked along the *c*-axis. An interaction between the almost ionic LaO and covalent CuS layers is believed to be weak. The conductivity can be controlled by Sr- or Ca-substitutions of the La ion [2,4]. Furthermore, the photoemission studies confirmed that the valence bands of (LaO)CuS are composed of the hybridization bands between the Cu 3d and S 3p orbitals as well as the O 2p states, and in the Ca and Ni co-doped system $(La_{1-x}Ca_xO)Cu_{1-x}Ni_xS$ [5], the Ni 3d- and S 3p-derived new density of states (DOS) modifies the electronic properties of (LaO)CuS to be metallic [6].

By a replacement of the other lanthanide ions for the La ion, localized 4f electrons can be introduced to this material, and different electrical, optical and magnetic properties are expected. Recently, Ueda et al. investigated the valence-band electronic structure of (LnO)CuS (Ln = Ce, Pr, Nd) by means of photoemission spectroscopy (PES) using the He discharge lump (He II: $h\nu = 40.8$ eV) and reported that the basic features of the valence bands are similar to (LaO)CuS except for the Ln 4f bands [7]. However, the Ln 4f contribution to the valence bands is much less known. In this paper, we report the Ln 4f partial DOS in the valence bands of (LnO)CuS investigated by means of the Ln 4d–4f resonant PES using synchrotron radiation. We also present the O 2p partial DOS deduced by the O Kα soft X-ray emission spectroscopy (SXES).

2. Experimental

The Ln 4d–4f resonant PES experiments were carried out on the beamline BL7 at Hiroshima Synchrotron Radiation Center (HSRC). The synchrotron radiation from the storage

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ring, HiSOR, was monochromatized by the Doragon-type monochromator [8]. We used a hemispherical photoelectron analyzer (Gammadata Scienta SES100) to measure the spectra. The total energy resolution was set to ∼200 meV. The O Kα SXES experiments were performed on the undulator beamline BL19B of the Photon Factory at the High Energy Accelerator Research Organization (KEK-PF), equipped with the varied-line-spacing plane grating monochromator [9]. The SXES spectra were collected using a Rowland-type grazing-incidence monochromator and multichannel detector [10]. Total energy resolution was ∼1.4 eV and the accuracy of emitted photon energy was at most ±0.5 eV. For both experiments, clean surfaces were in situ obtained by scraping with a diamond file and all experiments were performed at room temperature.

Polycrystalline samples for the present experiments were prepared by the solid-state reaction. As starting materials, we used CeO_2, Ce_2S_3, CuO and Cu for (CeO)CuS, Pr, Pr_2S_3 and CuO for (PrO)CuS and Nd_2O_3, Nd_2S_3, Cu and S for (NdO)CuS. Stoichiometric amount of the starting materials were thoroughly mixed under an Ar atmosphere and the mixtures were sintered at ∼1100, 900 and 750–900 °C, respectively. The grown samples were characterized by the X-ray powder diffraction. No impurity phase was detected for (PrO)CuS and (NdO)CuS. As concerns (CeO)CuS, the CeO_2 impurity phase was slightly found, which is almost negligible for contribution to the PES spectra [11].

3. Results and discussion

Fig. 1 shows a series of valence-band PES spectra of (CeO)CuS in the Ce 4d–4f excitation region. Binding energy is referred to the Fermi level (E_F). The spectra have been normalized to the monochromator output. The feature of the spectrum measured at $h\nu = 114$ eV is similar to that of (LaO)CuS at $h\nu = 80$ eV [6]. Since the PES spectra in this energy region almost reflect the Cu 3d states [12], the similar feature indicates that the electronic structure of the CuS layer is almost unchanged by the Ce 4f electrons in the CeO layer, in consistent with the PES results at $h\nu = 40.8$ eV [7]. With increasing $h\nu$, the structure just below the valence-band maximum (VBM) shows a remarkable resonance enhancement. The intensity becomes a maximum at $h\nu = 122$ eV (on-resonance) and decreases with further increasing $h\nu$. The $h\nu$-dependence of the spectra indicates that the Ce 4f states dominantly contribute just below VBM. Since the 4f intensity is negligibly small at $h\nu = 114$ eV (off-resonance), the Ce 4f partial DOS is deduced by subtracting the off-resonance spectrum from on-resonance spectrum.

Fig. 2 shows the Ln 4f partial DOSs of (LnO)CuS by the procedure mentioned above. It should be noticed that the Ce 4f DOS largely contribute just below VBM, which is indicated by an arrow. On going from Ln = Ce to Pr, and to Nd, the center of gravity of the 4f DOS shifts toward deeper binding-energy side, which can be understood as a result of the lanthanide contraction. No 4f contribution near VBM for (PrO)CuS and (NdO)CuS is observed. Although VBM of (LnO)CuS is mainly composed of the hybridization bands between the Cu 3d and S 3p states as (LaO)CuS [3,6], the hole-doped (CeO)CuS system by Sr- or Ca-dopings and/or co-doping of the Ca and Ni ions instead of the Ce and Cu ions, respectively, is expected to have very large Ce 4f DOS at E_F

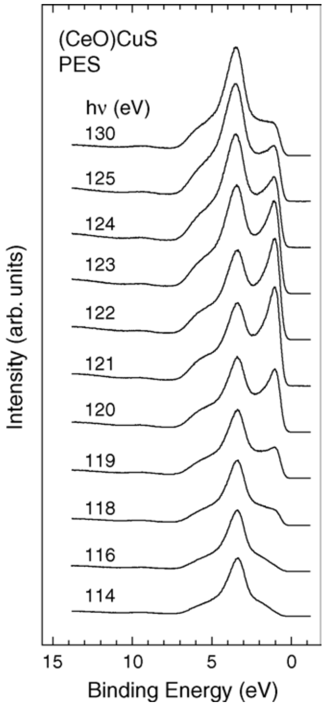

Fig. 1. A series of valence-band PES spectra of (CeO)CuS in the Ce 4d–4f excitation region.

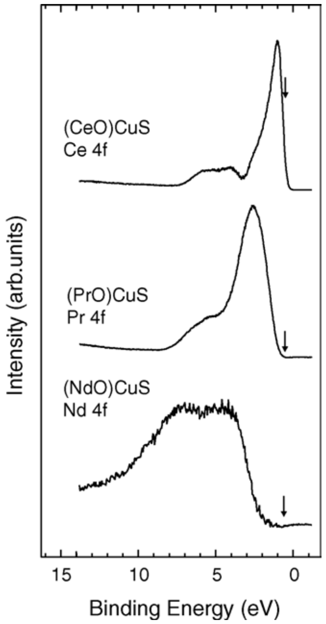

Fig. 2. Ln 4f partial DOSs of (LnO)CuS deduced from the Ln 4d–4f resonant PES spectra. Arrows denote VBM of respective samples.

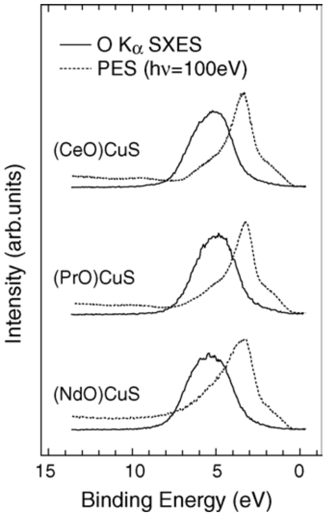

Fig. 3. O 2p partial DOSs of (LnO)CuS deduced from the O Kα SXES spectra (solid curves), in comparison with the PES spectra measured at $h\nu = 100$ eV (dashed curves).

just below VBM and show interesting physical properties, such as heavy fermion behavior.

All the Ln 4f partial DOSs exhibit a double-peak structure. The 4f DOS feature is similar to that of the insulating Ln trihalides [13] rather than the intermetallic compounds $LnCo_2$ and $LnNi_2$ [14], where the Ln 4f states hybridize with the conduction-band electrons and contribute to E_F still for Ln = Pr and Nd. The cluster analyses of the 4f spectra of the Ln trihalides confirm that the double-peak structure arises from the hybridization between the 4f states and ligand p orbitals [13]. Only the 4f DOS of (NdO)CuS is different from those of the other compounds with respect to relative intensities of the double-peak structure. Although this origin is not clear at present, the relative intensity would depend on the energy difference of the Ln 4f and O 2p levels and the 4f–2p hybridization strength. In order to investigate the 4f DOS feature more precisely, the Ln 3d–4f resonant PES experiments are planed.

Next, we move to the O Kα SXES experimental results. The feature of the several SXES spectra measured in the O 1s absorption region is independent of the excitation energy. This indicates that the SXES spectra originate from only the fluorescence component and reflect the O 2p partial DOS in the ground state. The O 2p DOSs of (LnO)CuS derived from the O Kα SXES spectra are shown in Fig. 3 by solid curves, where the excitation energy was set at 542 eV, around 10 eV above the O 1s absorption edge. For comparison, the PES spectra measured at $h\nu = 100$ eV, which reflect the electronic structure of the CuS layers and are almost unchanged with the Ln elements, are also represented by dashed curves. Here, the O Kα emission energy was converted to the binding energy using the O 1s PES spectrum measured in situ. For all compounds, the O 2p DOS locates at 3–8 eV region, in support of the previous assignment of the PES spectra [3,6]. Within the present experimental accuracy, we find no clear change in the O 2p DOS feature with the Ln elements. Thus, the 4f electrons do not change the electronic structure of (LnO)CuS so much. Further, O Kα SXES experiments with higher energy resolution and accuracy are required to reveal the slight change of the O 2p states hybridized with the Ln 4f states, as suggested by the double-peak structure of the Ln 4f DOS.

From the view points of fabrications of new materials using the 4f moment in the LnO layer, the hole-doped (CeO)CuS system can be advocated based on the present results as the most useful and promising candidate, since it has very large Ce 4f DOS in the valence band near or at E_F, which may be controlled by the amount of the doping.

4. Conclusion

We have deduced the Ln 4f and O 2p partial DOSs of (LnO)CuS by means of the Ln 4d–4f resonant PES and O Kα SXES, respectively. The Ln 4f DOS shifts toward deeper binding-energy side from Ln = Ce to Pr, and to Nd, reflecting the lanthanide contraction. In particular, the Ce 4f DOS contributes just below VBM of (CeO)CuS. Double-peak structure of the Ln 4f DOS suggests the Ln 4f–O 2p hybridization in comparison with those of the insulating Ln trihalides [13]. No clear changes of the PES spectra at $h\nu = 100$ eV and the O 2p DOS features with the Ln elements indicates that the 4f electrons do not change the electronic structure of (LnO)CuS.

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