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Single-atomic-layered quantum wells built in wide-gap semiconductors LnCuOCh (Ln=lanthanide, Ch=chalcogen)

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LnCuOCh (Ln=lanthanide, Ch=chalcogen) layered oxychalcogenides are wide-gap p-type semiconductors composed of alternately stacked $(Ln_2O_2)^{2+}$ oxide layers and $(Cu_2Ch_2)^{2-}$ chalcogenide layers. Energy band calculations revealed that Cu-Ch hybridized bands only spread in the $(Cu_2Ch_2)^{2-}$ layers, which suggests that hole carriers in these bands are confined by the potential barriers formed by the $(Ln_2O_2)^{2+}$ layers. Stepwise absorption spectra of a series of LnCuOCh experimentally verified that an exciton in the $(Cu_2Ch_2)^{2-}$ layers shows a two-dimensional behavior. These theoretical and experimental results indicate that LnCuOCh has "natural multiple quantum wells" built into its layered structure.

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Novel and useful electronic functions have resulted from the confinement of carriers or excitons in artificial quantum wells (QWs) of compound semiconductors.[1] Techniques for confining carriers/excitons in multiple quantum wells (MQWs) have been practically applied to quantum devices such as high electron mobility transistors and QW lasers.[2] The QWs, which are usually several nm wide, are artificially fabricated by alternating vapor phase epitaxy with the deposition of thin layers on single crystal substrates. Despite significant progress in film growth technology, the size of the QWs is still difficult to control precisely on an atomic scale. In contrast to artificial MQWs, there are many layered materials, which self-organize into periodically aligned atomic layers. If the width and energy level of each layer are properly selected, then a QW structure will form in the crystals on the atomic scale. Therefore, examining the quantum confinement effects in natural MQW layered crystals is important, and the results will provide a new viewpoint for finding and utilizing novel functions in layered materials.

Here we report two-dimensional carrier/exciton confinement effects for a series of layered oxychalcogenides, LnCuOCh (Ln=La, Pr and Nd, Ch=S, Se and Te). Hole carriers or excitons that are confined to chalcogenide layers typically show two-dimensional characteristics such as a stepwise shape of the optical absorption spectra similar to semiconductor artificial MQWs.[3] These results indicate that these compounds are natural MQWs as well as transparent p-type semiconductors with light emitting features.[4,5]

The crystal structure of LnCuOCh is characterized by alternately stacked $(Ln_2O_2)^{2+}$ oxide and $(Cu_2Ch_2)^{2-}$ chalcogenide layers along the c axis, as shown in Fig. 1.[6,7,8] Since Ln_2O_3 are typical electrical insulators, it is reasonable that the $(Ln_2O_2)^{2+}$ layer acts as a blocking barrier for carrier transport. On the other hand, the $(Cu_2Ch_2)^{2-}$ layer is a charged I-VI semiconductor in which the Cu^+ ions are coordinated to four Ch ions, forming a tetrahedral structure similar to those in III-V and II-VI semiconductors. As previously suggested in the wide-gap p-type oxide semiconductor studies,[9] the top of the valence band in LnCuOCh is composed of a highly covalent and dispersed Cu $3d-Ch$ p hybridized band. Therefore, $(Cu_2Ch_2)^{2-}$ layers work as hole-conduction paths sandwiched between insulating $(Ln_2O_2)^{2+}$ layers.

An energy band structure and a total or partial density of states of LaCuOS using a first principle pseudopotential method supports this view [Fig. 2(a)]. The energy band structure shows that both the conduction band minimum (CBM) and the valence band maximum (VBM) are located at the Γ point, which forms a direct band gap structure, and Cu 3d and S 3p orbitals form the VBM and Cu 4s orbitals primarily form the CBM. The orbitals related to the $(La_2O_2)^{2+}$ layer have negligible density of states in the energy range from -1.5 eV to the VBM (0.0 eV). Figure 2(b) shows a contour map of electron density at around the VBM on the (400) plane. The orbitals at the VBM have a node between Cu and S ions, indicating that the formation of an antibonding Cu $3d-$S $3p$ hybridized band at the VBM. It is noteworthy

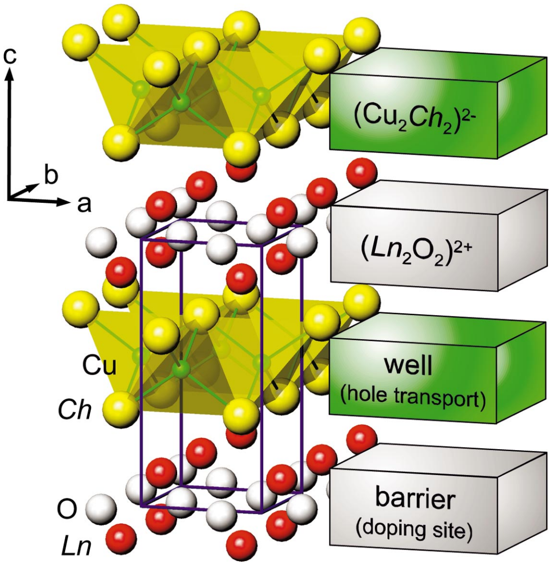

FIG. 1. (Color) Crystal structure of LnCuOCh (space group: P4/nmm). $(Ln_2O_2)^{2+}$ layers and $(Cu_2Ch_2)^{2-}$ layers are alternately stacked along the c axis, forming a MQW structure.

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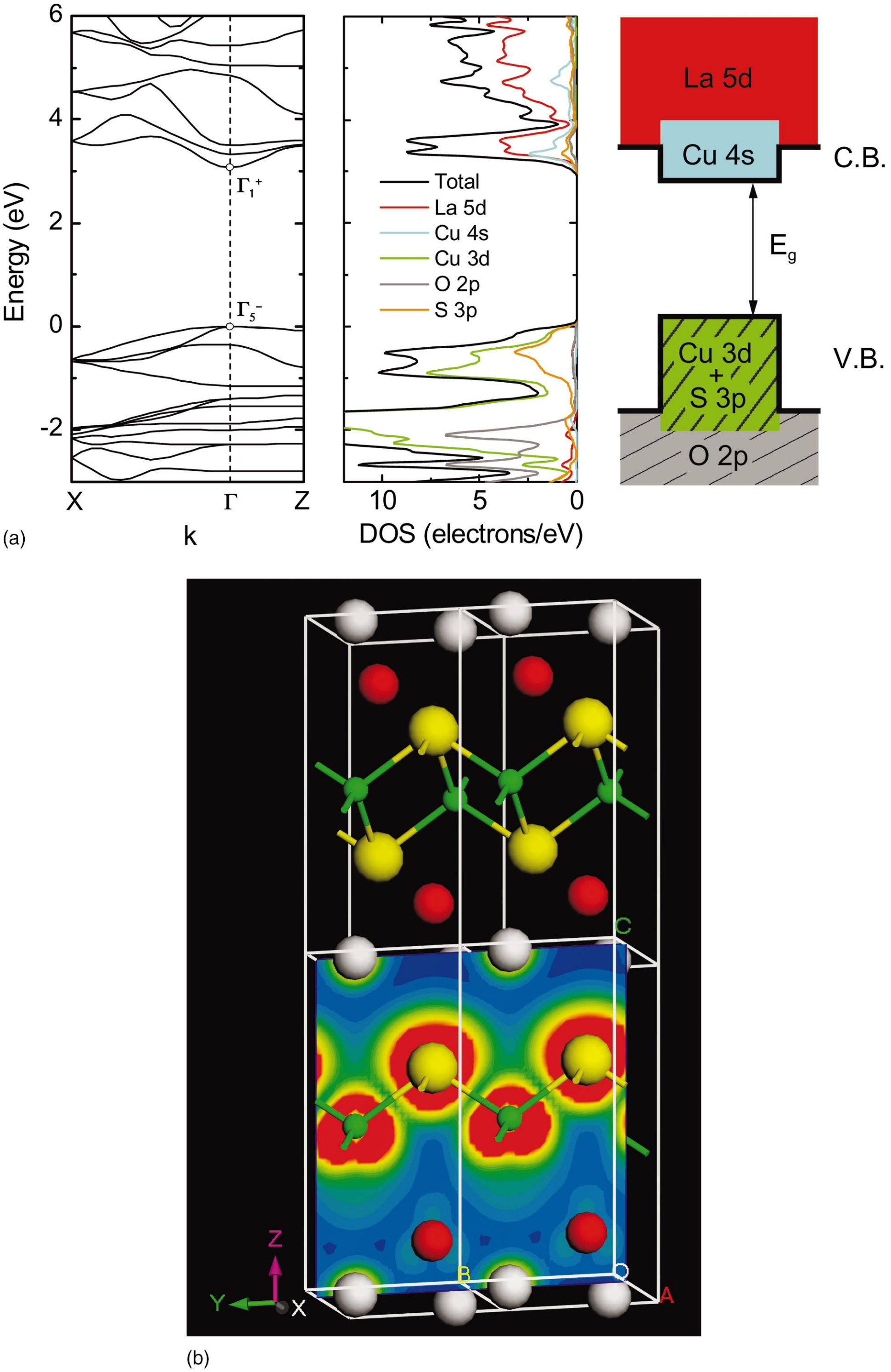

FIG. 2. (Color) (a) Energy band diagram and total/partial DOS of LaCuOS, along with a schematic illustration of the QW structure. (b) Contour plot of the electron density at the energies of around VBM ($-1.5\ \mathrm{eV} \leqslant E \leqslant 0\ \mathrm{eV}$), which shows the shape of Cu-S hybridized orbitals.

that the VBM orbitals only spread in the $(Cu_2S_2)^{2-}$ layers, which is consistent with the theory that holes are both spatially and energetically confined in the $(Cu_2S_2)^{2-}$ layers. These results demonstrate that the $(Cu_2S_2)^{2-}$ layer works as a well and the $(La_2O_2)^{2+}$ layer serves as a barrier for hole carriers due to the large offset energy at the valence band, forming a QW structure in LaCuOS.

This picture of the MQW structure was experimentally confirmed by optical absorption spectra measured on high-quality epitaxial thin films of $LaCuOS_{1-x}Se_x$ and LnCuOS (Ln=La, Pr, and Nd). The 150-nm-thick epitaxial films were grown on MgO single crystal substrates by reactive solid-phase epitaxy.[10] Measurements were conducted at 10 K using a conventional spectrometer with a cryostat, and unpolarized incidence light directed normal to the film surface. Absorption coefficients were obtained by dividing the optical absorption by the film thickness, neglecting reflections at the film surface. Figure 3(a) shows the optical absorption spectra

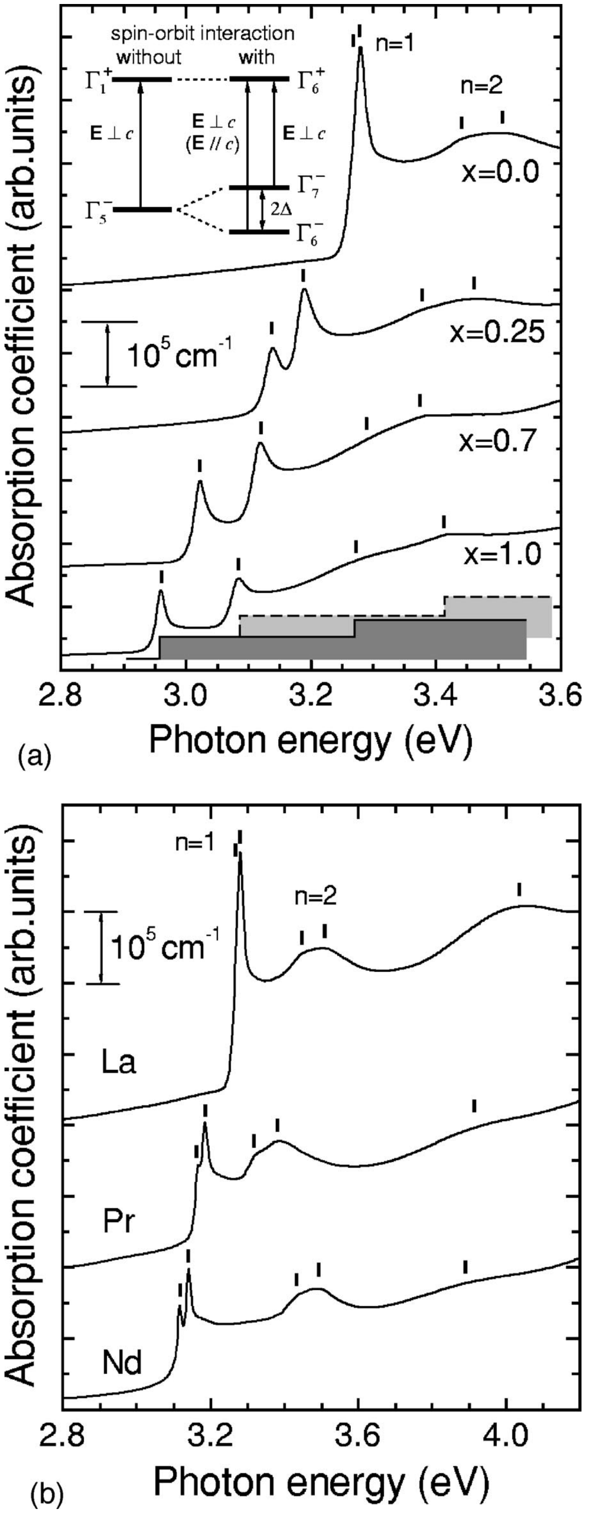

FIG. 3. Optical absorption spectra of (a) $\mathrm{LaCuOS}_{1-x}\mathrm{Se}_x$ $(0 \leqslant x \leqslant 1)$ and (b) LnCuOS (Ln=La, Pr, and Nd) at 10 K. Symmetries of the VBM and CBM at Γ point are shown in the inset when the influence of spin-orbit interactions is considered.

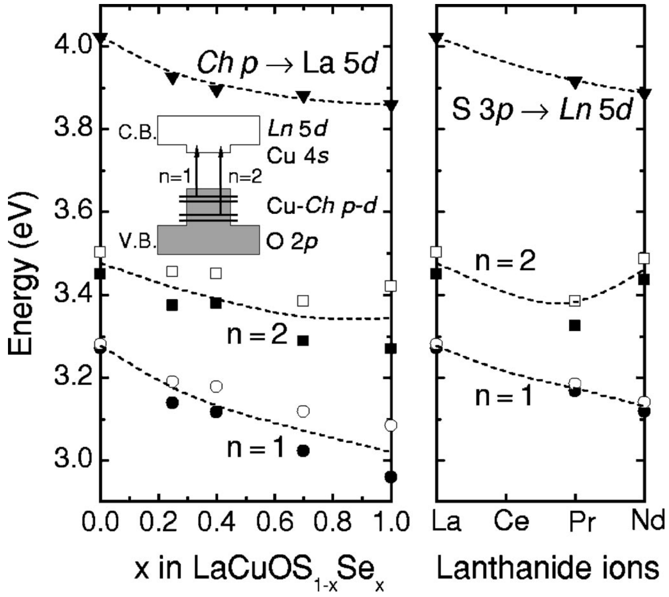

FIG. 4. Absorption peak energies near the band gap edge in (a) $\mathrm{LaCuOS}_{1-x}\mathrm{Se}_x$ $(0 \leqslant x \leqslant 1)$ and (b) LnCuOS (Ln=La, Pr, and Nd) at 10 K. The central positions between a pair of peaks (open and closed symbols) split by spin-orbit interactions are shown by dashed lines for $n=1$ and 2. The inset illustrates energy transitions for $n=1$ and 2.

of $\mathrm{LaCuOS}_{1-x}\mathrm{Se}_x$ $(0 \leqslant x \leqslant 1)$ above the fundamental absorption edges. A pair of sharp absorption peaks $(n=1)$ assigned as excitons is observed at the absorption edge in each film. The energy spacing between the peak pairs increases as the Se content increases, and a maximum splitting of 125 meV is reached for LaCuOSe $(x=1)$. Te anions further enhanced the peak splitting up to 220 meV in $\mathrm{LaCuOSe}_{0.6}\mathrm{Te}_{0.4}$. The symmetry of the VBM at the Γ point in the D_{4h} group is assigned as Γ_5^-, which is doubly degenerated without spin-orbit interactions. When the spin-orbit interactions are considered, the degenerated state (Γ_5^-) splits into two states $(\Gamma_6^-$ and $\Gamma_7^-)$ and the transitions from these two states to the CBM (Γ_6^+) are symmetry allowed. The increase in the splitting with atomic number of Ch ions and the symmetry analysis of the VBM lead to the conclusion that the splitting results from the spin-orbit interaction of Ch ions.[11]

This spin-orbit splitting at the VBM enabled clear stepwise shapes to be observed in optical absorption spectra, especially for LaCuOSe. This stepwise absorption confirms that these compounds have a two-dimensional density of states (DOS).[12] Therefore, the stepwise increase in the absorption spectra of LnCuOCh reflects overlapping two stepwise DOSs split by the spin-orbit interaction as illustrated in Fig. 3(a) for LaCuOSe. A sharp exciton peak at the step edge accompanies each step structure. These features are similar to those observed in artificial MQWs fabricated from III-V or II-VI compound semiconductors. However, the absorption bands for $n=2$ are much broader than those for $n=1$ and the stepwise shape becomes unclear for $n=2$, indicating that, as n increases, the confinement effect becomes weaker.

In addition to the Ch ions, lanthanide ions also cause splitting due to spin-orbit interactions, as shown in Fig. 3(b). Although the splitting by Ln ions is very small compared to that of the Ch ions, the splitting increases with the number of $4f$ electrons. The small energy splitting by the Ln ions may suggest that mixing of $4f$ orbitals with the Cu $3d$–Ch p hybridized orbitals is very small due to the spatial separation of these two orbitals.[13]

Another important feature for the observed confinement effects in the absorption spectra is that the energy separation between $n=1$ and 2 increases with Se content in $LaCuOS_{1-x}Se_x$ or as La ions are substituted for by Pr or Nd ions (Fig. 4). This increase in the energy separation between $n=1$ and 2 originates from an increase in the confinement effects due to an increase in the barrier height by the compositional change. Since the energy level of Se $4p$ is higher than that of S $3p$, the VBM becomes higher and the QWs of the holes become deeper as the Se content increases. In the case of Ln substitution, the VBM shifts to higher energy because the interaction at the VBM increases as the ionic size or lattice constants decrease in the Ln series. These shifts of the VBM are responsible for the decrease in the band gap in the compounds with the Se or Ln substitutions.

The observed two-dimensional features of the stepwise shape with multilevel excitons in the optical absorption are very unique for LnCuOCh. The stepwise exciton absorption has not been observed in other naturally layered crystals that we have surveyed such as GaSe, $CdCl_2$, and $(C_nH_{2n+1}NH_3)PbI_4$.[14–16] A relative dielectric constant (ε_r) measured by ellipsometry is 6–7 for LaCuOS at a photon energy of ~2 eV. A simple hydrogenlike model and the averaged reduced effective mass ($\mu^*/m_0=0.25$) of an electron-hole pair[17] yield a radius of excitons in LaCuOS of 12–15 Å without accounting for the anisotropy of these parameters. This radius of excitons is much larger than the thickness of the $(Cu_2S_2)^{2-}$ layers, 2–3 times larger than the size of a unit cell ($a=3.996$ Å, $c=8.517$ Å). Therefore, it is reasonable that the excitons can "feel" the two-dimensional environment in the $(Cu_2S_2)^{2-}$ layers.

The features of the excitons in LnCuOCh are not identical to those in artificial MQWs of semiconductors due to their crystal and electronic structure. Since the band dispersion at the VBM differs in the Γ-Z and Γ-X directions [Fig. 2(a)], the hole effective mass along the z axis (m^*_{zz}) is much larger than that along the x axis (m^*_{xx}), indicating that holes are strongly confined in the $(Cu_2Ch_2)^{2-}$ layers. In contrast, the band dispersion at the CBM does not display a large anisotropy, which suggests that electrons are not thoroughly confined by the $(Ln_2O_2)^{2+}$ barrier layers. In addition, it is expected that local dielectric constant or local electronic polarizability is different between the $(Cu_2Ch_2)^{2-}$ and $(Ln_2O_2)^{2+}$ layers, and may affect the size or shape of the excitons in a similar manner to the anisotropy of effective mass. Although a detailed quantitative discussion of the excitons is presently difficult, all the theoretical and experimental results to date indicate that a hole constituting the exciton is tightly confined by the barrier of the $(Ln_2O_2)^{2+}$ layers and is accompanied by its electron partner near the hole.

The energy band calculations and experimental observation of electronic and optical properties indicate that the layered LnCuOCh compounds should be treated like natural MQWs with large barrier heights that can be controlled by component ions. This paper demonstrates that built-in QWs on the atomic scale can be formed in layered compounds and that in the future the technology established for artificial QWs may be extended or applied to these natural MQWs.

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