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Degenerate p-type conductivity in wide-gap LaCuOS$_{1-x}$Se$_x$ ($x=0–1$) epitaxial films

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Epitaxial films of LaCuOS$_{1-x}$Se$_x$ ($x=0–1$) solid solution were grown on MgO (001) substrates and their electrical and optical properties were examined. Sharp emission due to room-temperature exciton with binding energy of ~50 meV is observed for all x values. Hall mobility becomes large with an increase in the Se content and it reaches 8.0 cm$^2$V$^{-1}$s$^{-1}$ in LaCuOSe, a comparable value to that of p-type GaN:Mg. Doping of Mg$^{2+}$ ions at La$^{3+}$ sites enhances a hole concentration up to 2.2×10$^{20}$ cm$^{-3}$, while maintaining the Hall mobility as large as 4.0 cm$^2$V$^{-1}$s$^{-1}$. Consequently, a degenerate p-type electrical conduction with a conductivity of 140 S cm$^{-1}$ was achieved. © 2003 American Institute of Physics. [DOI: 10.1063/1.1544643]

P-type wide-gap semiconductors are crucial components in the fabrication of such p–n junction devices as UV light-emitting diodes (LEDs). We have reported on several p-type electrical conducting wide-gap oxides, including CuMO$_2$ ($M=Al$, Ga, and In) and SrCuO$_2$. P-type conductivity has been explored by a guiding principle on the basis of chemical bonding structure of the valence bond maximum in oxides. We have extended this idea to oxychalcogenides, leading to the discovery of LaCuOCh (Ch=S and Se) with a layered structure exhibiting p-type electrical conduction. These materials are direct-transition semiconductors and exhibit excitonic photoluminescence (PL), which are the characteristics that have not been observed for other p-type wide-gap oxides reported to date. In addition, highly conductive p-type thin films are required to fabricate LEDs featuring the excitonic PL properties.

LaCuOS$_{1-x}$Se$_x$ ($x=0–1$) has a layered structure in which (La$_2$O$_3$)$_{2+}$ and (Cu$_5$S$_{1-x}$Se$_x$)$_{2-}$ layers are stacked alternately along the c-axis, which may be responsible for the wide gap and the high stability of exciton. The top of the valence band is composed of Cu 3d–S 3p–Se 4p hybridized orbitals and the covalency usually increases in the order of O, S, and Se among these chalcogen ions. Thus, we expect that LaCuOS$_{1-x}$Se$_x$ has larger hole mobility than Cu-containing wide-gap p-type oxides. Moreover, it is expected that large mobility is possible in LaCuOS$_{1-x}$Se$_x$ even under heavily doped states because the (La$_2$O$_3$)$_{2+}$ and (Cu$_5$S$_{1-x}$Se$_x$)$_{2-}$ layers may work as spatially-separated doping and conduction layers, respectively. However, these expectations have not yet been verified with adequately reliable results because of the lack of high-quality thin films.

In the present letter, we applied a reactive solid-phase epitaxy (R-SPE) technique, previously reported for LaCuOS, to LaCuOS$_{1-x}$Se$_x$ solid solutions and prepared epitaxial films on MgO (001) in whole compositional range.

Hole transport properties as well as optical properties are examined and discussed herein in relation with their crystal and electronic structure. A degenerate p-type electrical conduction was achieved in Mg-doped LaCuOSe. LaCuOS$_{1-x}$Se$_x$ ($x=0–1$) films (~150 nm in thickness) were prepared on MgO (001) substrates with the R-SPE technique. First, we deposited a thin metallic copper layer (~5 nm) on a MgO substrate under high-vacuum conditions (~10$^{-5}$ Pa) at 400°C by a pulsed-laser deposition (PLD) technique. Amorphous (a-) LaCuOS and a-LaCuOSe layers were then sequentially deposited, using sintered disks of LaCuOS and LaCuOSe as targets, respectively, on the Cu/MgO at 25°C in the same PLD chamber. Thickness ratios between the two amorphous layers were varied to control the film composition (x in LaCuOS$_{1-x}$Se$_x$). The multilayer films were annealed at 1000°C in an evacuated SiO$_2$ glass tube containing a small amount of LaCuOS or LaCuOSe powder. To determine the x values of the films, we measured optical absorption spectra of the annealed films at room temperature and estimated the x values by comparing the absorption edge energies of the films with those of polycrystalline bulks, which vary almost linearly between 2.8 and 3.1 eV for the selenide and sulfide.

The structures of the annealed films were examined by high resolution x-ray diffraction (using HRXRD, ATX-G, RIGAKU-Co.). Out-of-plane HRXRD patterns ($\omega$–2θ scans) showed only {001} diffraction peaks from the LaCuOS$_{1-x}$Se$_x$ and the substrate in a manner similar to that of the previously observed data on LaCuOS. We did not find detectable split in the LaCuOS$_{1-x}$Se$_x$ diffraction peak for all the compositions. This was also confirmed by (110) diffraction in in-plane HRXRD patterns ($\phi$–2θx scans). These observations verify that the annealing causes compositional mixing between the two amorphous layers, forming single-phase LaCuOS$_{1-x}$Se$_x$ films grown epitaxially on MgO (001) substrates for all x values from 0 to 1. In Fig. 1, the lattice constants of the a-axis and c-axis for the LaCuOS$_{1-x}$Se$_x$ films are plotted against Se content, showing that they increase linearly with Se content in the films. These values agree well with those measured on powders, indicating...
ing that film compositions closely reflect the determined values and that the crystal lattice is distorted slightly.

The epitaxial LaCuOS\(_{1-x}\)Se\(_x\) films exhibit a sharp PL peak near the absorption edge, which shifts to a lower energy side with the Se content in parallel to the shift of the absorption edge. The PL intensities remain almost unchanged below \(\sim 50\) K, while decreasing at higher temperatures, as shown in Fig. 2. On the assumption that the decrease of the PL intensity results from the thermal decomposition of the exciton, then the binding energy of the exciton is estimated using the equation:

\[
I(T) = I(0) / [1 + C \exp(-E/kT)]
\]

where \(I(T)\) and \(I(0)\) are integrated PL intensities at temperatures \(T\) and \(0\) K, respectively, and where \(C\), \(E\), and \(k\) represent the scaling constant, exciton binding energy, and Boltzmann constant, respectively. The binding energies evaluated from a curve fitting were \(\sim 50\) meV for all samples, which is consistent with the value \(>42\) meV reported previously for LaCuOS\(^5\).

Figure 3 shows electrical conductivity \(\sigma\), Hall mobility \(\mu\), and carrier concentration \(n\) for the LaCuOS\(_{1-x}\)Se\(_x\) epitaxial films measured by the van der Pauw method at room temperature as a function of the Se content. The Seebeck coefficient \(S\) is also plotted. Both the Hall and Seebeck coefficients are positive for all the films, indicating that LaCuOS\(_{1-x}\)Se\(_x\) films are \(p\)-type semiconductors for all compositions. The electrical conductivity of the LaCuOS epitaxial film was sensitive to the atmosphere in the annealing process and varied widely from \(\sim 10^{-2}\) to \(0.66\) S cm\(^{-1}\) at room temperature\(^1\).\(^1\) The conductivity of films containing Se, on the other hand, was not influenced significantly by the preparation condition.

As Se content was increased, the electrical conductivity and Hall mobility steadily increased, and the LaCuOSe epitaxial film exhibited the largest values of \(\sigma = 24\) S cm\(^{-1}\) and \(\mu = 8.0\) cm\(^2\) V\(^{-1}\) s\(^{-1}\) at room temperature (the maximum Hall mobility of \(16\) cm\(^2\) V\(^{-1}\) s\(^{-1}\) is observed at \(150\) K, as shown in Fig. 4). As the carrier concentration was kept almost constant against Se content, an increase in the mobility with the Se contents leads to the larger electrical conductivity of the LaCuOSe than that of LaCuOS. The Hall mobility obtained in the LaCuOSe epitaxial film is noticeably larger than those of wide-gap \(p\)-type chalcogenide and oxide semiconductors, including BaCu\(_2\)S\(_3\) (\(\mu = 3.5\) cm\(^2\) V\(^{-1}\) s\(^{-1}\))\(^1\)\(^1\) and Cu(Al, Ga)O\(_2\).
modulate the valence band dispersion in the modification of anion species is an effective way to operative in the LaCuOSe film as demonstrated in Fig. 4. In other evaporation using an La0.8M0.2CuOSe target. As a result, only into LaCuOSe epitaxial films were examined for carrier generation using an La0.8M0.2CuOSe target. As a result, only

doped (solid symbols) LaCuOSe epitaxial films grown on MgO (001).

\(\mu = 0.1 - 0.2 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}\), and SrCu2O2 (\(\mu = 0.46 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}\)) and is even comparable to that of a p-type III–V compound semiconductor GaN:Mg (\(\mu = 8 - 9 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}\)).

In addition, Hall mobility increases systematically in the order of oxides, (oxy)sulfides, and (oxy)selenides, which corresponds to the enhancement of chemical bond-covalency and hybridization of the relevant anion orbitals. This result is consistent with our model that hole conduction paths are hybridized states with a large contribution of anions.3,4 Thus, the modification of anion species is an effective way to modulate the valence band dispersion in p-type wide-gap semiconductors.

To further increase electrical conductivity, doping of three kinds of divalent ions (\(M^{2+} = \text{Sr}^{2+}, \text{Ca}^{2+}\), or \(\text{Mg}^{2+}\)) into LaCuOSe epitaxial films were examined for carrier generation using an La0.8M0.2CuOSe target. As a result, only Mg2+ ions worked as an effective acceptor in the R-SPE process. Figure 4 shows \(\sigma, \mu, \text{ and } n\) as a function of temperature for the Mg-doped film, as well as those of undoped LaCuOSe film. The carrier concentration increases to 2.2 \(\times 10^{20} \text{ cm}^{-3}\) by one order of magnitude with Mg doping, indicating that Mg2+ ions substitute at La3+ sites preferentially. On the other hand, Hall mobility decreases only to 4.0 \(\text{cm}^2\text{V}^{-1}\text{s}^{-1}\) by a factor of 2 in spite of the large increase in the carrier concentration. As a result, the electrical conductivity goes up to 140 S cm\(^{-1}\) and is temperature insensitive in the LaCuOSe film as demonstrated in Fig. 4. In other words, by Mg doping in the LaCuOSe we were able to obtain a p-type degenerate semiconductor, which to date had not been realized among such p-type wide-gap semiconductors as ZnSe:N (\(n < 10^{18} \text{ cm}^{-3}\)) and GaN:Mg (< 10\(^{19} \text{ cm}^{-3}\)).

The moderate decrease in Hall mobility and the degenerate conduction can be understood by considering that Mg2+ ions are doped in the (La2O2)2+ layers by substituting at La3+ sites, while the hole carriers released from Mg2+ ions migrate to the (Cu2Se2)2+ layers.

In conclusion, we grew epitaxial films of p-type wide-gap LaCuO$_{1-x}$Se$_x$ (\(x = 0 – 1\)) solid solution on MgO (001) substrates. We used Se content to systematically vary such typical material parameters as energy band gap, lattice constant, and Hall mobility, thus enabling us to control emission energy and electrical conductivity in order to comply with various device design specifications. Binding energy of exciton for LaCuO$_{1-x}$Se$_x$ is elucidated to be \(\sim 50 \text{ meV}\) by temperature dependence of PL intensities of the epitaxial films. Further, Mg-doped LaCuOSe epitaxial films show a p-type degenerate semiconducting behavior with a conductivity of 140 S cm\(^{-1}\). The degenerate states occur presumably due to the separation of the doping layer from the conducting layer as well as the enhanced chemical bond-covalency in LaCuOSe. These features make the LaCuO$_{1-x}$Se$_x$ film very promising for a diverse range of applications such as an active layer or a p(+) layer of UV-LED and a transparent p-electrode in an organic LED.

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