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Orita, M ...[et al]. Mechanism of electrical conductivity of transparent InGaZnO4. PHYSICAL REVIEW B 2000, 61(3): 1811-1816

ISSUE DATE:
2000-01-15

URL:
http://hdl.handle.net/2433/39837

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Mechanism of electrical conductivity of transparent InGaZnO$_4$

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(Received 1 April 1999; revised manuscript received 2 September 1999)

The electronic structure of InGaZnO$_4$, which has a layered structure with alternating layered layers of InO$_2$ and GaZnO$_2$, was calculated in order to investigate the mechanism of electrical conductivity. In the crystal structure obtained through relaxation calculations using classical two-center potentials, the Ga ion in the GaZnO$_2$ layer has pentagonal coordination forming a bipyramid with five oxygen ions, while the Zn ion in the same layer has tetrahedral coordination, losing a bond with the oxygen at the top of one pyramid. The molecular orbitals of model clusters for the relaxed structure, which were calculated by the discrete variational $\chi$ method using a model cluster, show strong two-dimensional structures. The electronic states at the edge of the conduction band are the result of overlapping between In 5$s$ orbitals, and delocalize in the InO$_2$ layer. The energy in the Ga 4$s$ and Zn 4$s$ states in the GaZnO$_2$ layer was too large to be doped with electrons. The In 5$s$ states are considered to be conduction paths for carrier electrons. A very high conductivity can be expected in the case where dopant ions are introduced into the GaZnO$_2$ layers.

I. INTRODUCTION

Some oxides of $p$-block metals such as ZnO, In$_2$O$_3$, and SnO$_2$ feature both transparency for visible light and electrical conductivity. The electronic structure of these crystals is characterized by a wide band gap of over 3.0 eV, and highly concentrated donor levels of oxygen defects just below the conduction band. The wide gap causes transparency in the visible region, and electrons at the shallow donor levels provide electrical conductivity. In the case of In$_2$O$_3$, it has been reported that a bulk single crystal has conductivity of 0.10 S/cm and mobility of 160 cm$^2$/V s at room temperature. The conductivity of In$_2$O$_3$ can be increased significantly through doping with electrons by introducing a solution of Sn ions.

In the case of the tin-doped In$_2$O$_3$ (ITO), conductive electrons are scattered by the tin ions distributed uniformly in the lattice. If it were possible to separate the tin ions from the space in which conductive electrons move, a high carrier density without a significant decrease in mobility could be realized. We refer to this effect as ”spatial separation” because the two functions of carrier generation and carrier movement are expected to be separated spatially in a lattice. Based on the concept of spatial separation, Kawazoe and co-workers studied the transparency and conductivity of some complex oxides, including MgIn$_2$O$_4$, ZnGa$_2$O$_4$, and Y$_2$Sb$_2$O$_7$. They found that these oxides are transparent conductors, and suggested that the chain structure of the edge sharing MO$_6$ octahedra, where M is a $p$-block metal ion surrounded by six oxygen ions, might serve as a path for electrons, thereby facilitating electrical conductivity. They have suggested that the other sites containing metal ions or vacant spaces outside the chains in the complex oxides could serve as sites for dopant ions due to the fact that they are separated from the space in which the conductive electrons move. However, no study has been reported so far on effective dopant ions or changes in carrier density and mobility due to concentrations of the dopant ions.

InGaZnO$_4$ is one of the complex oxides that has the structure of the edge-sharing MO$_6$ octahedra. It is an YbFe$_2$O$_4$-type layered structure with alternating laminated layers of YbO$_2$ and Fe$_2$O$_2$. In the case of InGaZnO$_4$, InO$_2$ substitutes for the YbO$_2$ layers, and GaZnO$_2$ layers replace the Fe$_2$O$_2$ layers (Fig. 1). These layers accumulate in the following order: InO$_2$, GaZnO$_2$, GaZnO$_2$, InO$_2$, GaZnO$_2$, GaZnO$_2$, InO$_2$, GaZnO$_2$, and GaZnO$_2$. That is, three InO$_2$ layers and three pairs of GaZnO$_2$ layers accumulate alternatively to form one unit cell. Since the InO$_2$ layer is composed of edge-sharing oxygen octahedra centered by In ions, it could serve as a path for carrier electrons. It is also possible that the GaZnO$_2$ layer could serve as a carrier path, due to the fact that the local structure around the Zn ions is similar to that of ZnO, which is well known to be a transparent conductor. The conductivity and transparency of InGaZnO$_4$ have been confirmed using sintered bodies and thin-film specimens on quartz glass substrates deposited by a conventional rf magnetron sputtering method.
mens had a carrier density of $1.2 \times 10^{20}$ cm$^{-3}$, a mobility of 24 cm$^2$/Vs, and a conductivity of 500 S/cm. The table shows that the carrier density of a commercial ITO film was measured to be $1.4 \times 10^{21}$ cm$^{-3}$.

Such heavy doping in the InGaZnO$_4$ lattice may result in a conductivity greater than that of ITO, since elimination of the oxygen defect, which should disturb the conduction, and doping with the ion substitution at appropriate sites may result in an enhancement not only in carrier density but also in mobility.

In order to realize such a high conductivity in an InGaZnO$_4$ system based on the concept of spatial separation, it is important to specify the paths of conductive electrons in the lattice. If the InO$_2$ layers work as the conduction paths, dopant ions should be introduced at the sites of Ga or Zn ions. On the other hand, if the ZnGaO$_2$ layers serve as the conduction paths, In ions should be substituted with some dopant ions. In this paper, in order to specify the conduction paths of electrons in the InGaZnO$_4$ lattice, the electronic structure of the crystal was calculated based on discrete-variational (DV) $X\alpha$ theory using cluster models.

### II. MODELS AND CALCULATIONS

Because the precise crystal structure of InGaZnO$_4$ has not yet been clarified, the positions of atoms were derived from the lattice parameters of InGaZnO$_4$ (Ref. 10) and the fractionally coordinated atomic positions in YbFe$_2$O$_4$, as shown in Fig. 1. As the crystal structure is complicated, a simplified view is shown in Fig. 2(a). Five oxygen ions surround a Ga or Zn ion to form a trigonal bipyramidal $MO_5$. A polyhedron model is used to show the bipyramids in the GaZnO$_2$ layers in Fig. 2(b). The bipyramidal polyhedrons connect with each other at the corners to form a GaZnO$_2$ layer (shaded darker), on which there is another GaZnO$_2$ layer (shaded brighter). Ga and Zn are located at an identical site at the center of the bipyramids.

Regarding the chemical bond, however, the bond lengths of Ga-O and Zn-O should be different, and this could result in some differences in electronic structure. In order to obtain a reasonable crystal structure, relaxation calculations using classical two-center potentials were performed using the General Utility Lattice Program (GULP). Forces are assumed to be of the two-body type, and a function only of the distance between atoms. The interatomic interactions are divided into long-range Coulombic and short-range forces, with the short-range term described using the following analytical function:

\[
\begin{align*}
\text{TABLE I. Electrical and optical properties of an InGaZnO}_4 \\
\text{sputtered film with those of an In}_2\text{O}_3 \text{ film deposited by an electron}
\text{ beam evaporation method (Ref. 3) and an ITO film commercially produced.}
\end{align*}
\]

<table>
<thead>
<tr>
<th></th>
<th>InGaZnO$_4$</th>
<th>In$_2$O$_3$</th>
<th>ITO</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Band gap (eV)</strong></td>
<td>3.5</td>
<td>3.2</td>
<td>3.2</td>
</tr>
<tr>
<td><strong>Conductivity S/cm</strong></td>
<td>$5.0 \times 10^2$</td>
<td>$1.7 \times 10^3$</td>
<td>$7.0 \times 10^3$</td>
</tr>
<tr>
<td><strong>Mobility (cm$^2$/Vs)</strong></td>
<td>24</td>
<td>130</td>
<td>30</td>
</tr>
<tr>
<td><strong>Carrier density (S/cm$^3$)</strong></td>
<td>$1.2 \times 10^{20}$</td>
<td>$0.8 \times 10^{20}$</td>
<td>$1.4 \times 10^{21}$</td>
</tr>
</tbody>
</table>
MECHANISM OF ELECTRICAL CONDUCTIVITY OF...  

TABLE II. Parameters used for optimization of atom positions in the InGaZnO4 lattice using the two-center potential of scheme 1 in the text.

<table>
<thead>
<tr>
<th>Interaction type</th>
<th>A (eV)</th>
<th>ρ (Å)</th>
<th>C (eV Å⁻⁶)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In⁢⁺—O²⁻</td>
<td>1293.600</td>
<td>0.331</td>
<td>4.325</td>
</tr>
<tr>
<td>Zn²⁺—O²⁻</td>
<td>600.300</td>
<td>0.337</td>
<td>0.000</td>
</tr>
<tr>
<td>Ga³⁺—O²⁻</td>
<td>2339.766</td>
<td>0.274</td>
<td>0.000</td>
</tr>
<tr>
<td>O²—O²</td>
<td>25.410</td>
<td>0.694</td>
<td>32.320</td>
</tr>
</tbody>
</table>

where \( A_{ij} \), \( \rho_{ij} \), and \( C_{ij} \) are parameters particular to each ion-ion interaction. Parameters determined by Bush et al.\(^{14}\) and Fisher et al.,\(^{15}\) as listed in Table II, were used.

For the nonrelaxed and relaxed crystal structure, nonrelativistic first-principles molecular orbital (MO) calculations were made by the DV-Xα method\(^{16,17}\) using the SCAT program.\(^{17}\) MO were constructed by linear combination of atomic orbitals (AO) as

\[
\phi_i(r_k) = \sum_j C_{ij} \chi_j(r_k),
\]

where \( \chi_j(r) \) is the AO and \( r_k \) is one of the sampling points in the DV calculation. The number of sampling points was set at 1400 per atom. The numerical basis functions were obtained by solving the radial part of the Schrödinger equations. Minimal basis sets of \( 1s\cdot2p \) for O; \( 1s\cdot3d \), \( 4s \), and \( 4p \) for Zn and Ga; and \( 1s\cdot4d \), \( 5s \), and \( 5p \) for In were used.

Overlap population is a useful characteristic to examine when studying the interactions between orbitals, though it is inherently arbitrary. The overlap population between the \( i \)th AO and the \( j \)th AO at the \( l \)th MO is given by

\[
Q_{ij}^l = C_{il} C_{jl} \sum_k \omega(r_k) \chi_i(r_k) \chi_j(r_k),
\]

where \( \omega(r) \) is the integration weight or reciprocal of the sample point density at \( r_k \). The sum of \( Q_{ij} \) with respect to \( l \) for occupied orbitals provides the net overlap population between the \( i \)th AO and \( j \)th AO; in other words,

\[
Q_{ij} = \sum_l Q_{ij}^l.
\]

The overlap population between atoms \( A \) and \( B \) is given by

\[
Q_{AB}^l = \sum_{i \in A} \sum_{j \in B} Q_{ij}^l.
\]

Diagrams of overlap population are made by broadening \( Q_{AB}^l \) at individual MO’s using Gaussian functions of 1.0-eV full width at half maximum.

TABLE III. Bond lengths between metals and oxygens in the InGaZnO4 lattice.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Bond type</th>
<th>Bond length</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>nonrelaxed</td>
</tr>
<tr>
<td>In</td>
<td>a</td>
<td>2.180</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>2.020</td>
</tr>
<tr>
<td></td>
<td>c</td>
<td>1.923</td>
</tr>
<tr>
<td>Ga</td>
<td>a</td>
<td>2.020</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>1.923</td>
</tr>
<tr>
<td></td>
<td>c</td>
<td>2.237</td>
</tr>
<tr>
<td>Zn</td>
<td>a</td>
<td>2.020</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>1.923</td>
</tr>
<tr>
<td></td>
<td>c</td>
<td>2.237</td>
</tr>
</tbody>
</table>

The relaxed structure of the crystal was calculated under...
certain restrictions using GULP. The lattice constants were fixed at the values from experimental data reported for a InGaZnO$_4$ crystal. The $X$ and $Y$ values used as Cartesian coordinates for all the atoms and lattice constants were fixed, while the $Z$ values were optimized due to the fact that the bonds Zn-O ($c$) and Ga-O ($c$) are parallel to the Z axis. Restriction by inversion symmetry was also applied. The arrangement of Ga and Zn ions on the GaZnO$_2$ layer has been considered to be random by Li et al.,$^{19}$ since no extra diffraction spots were formed in x-ray diffraction patterns. Calculations with some arrangement of Ga and Zn ions were performed, and no significant difference was seen in the results of the structural relaxation and electronic state. The bond lengths following the optimization are also listed in Table IV. The orbital with the highest energy is O $2p$, which in the case of Ga-O ($c$), in which a set of molecular orbitals is often referred to as a band, in the descriptions below the set of molecular orbitals corresponding to a certain partial DOS curve is noted as a partial band. Differences in the DOS curves for the nonrelaxed and relaxed structure were little and not important, and that for the relaxed structure are plotted in Fig. 4. The zero point on the vertical energy axis was adjusted to the top of the valence band, that is, the energy of In 5$s$ was not altered while that of Ga 4$s$ was increased by 1.6 eV. The main reason for the shift in Ga 4$s$ is undoubtedly related to the change in the bond length between Ga and O. Relaxation reduced the distances [7% in the case of Ga-O ($c$)], which in turn increased the static potential at the Ga site. On the other hand, the bond lengths between In and O did not change significantly (less than 2%).

Electronic state calculations were performed using a cluster of In$_{13}$Ga$_{30}$Zn$_{18}$O$_{118}$ as a model for the crystal (Fig. 3). An InO$_2$ layer is laminated with two GaZnO$_2$ layers on both sides. The cluster was embedded in the Madelung potential generated by point charges. In order to analyze the origins of the conduction band and valence band, a series of eigenvalues for molecular orbitals were obtained using DV-$X\alpha$ calculations, and the eigenvalues were broadened by Gaussian functions for 0.5-eV full width at half maximum (FWHM) to obtain the total and partial density of states (DOS) state curves. Since a set of molecular orbitals is often referred to as a band, in the descriptions below the set of molecular orbitals corresponding to a certain partial DOS curve is noted as a partial band. Differences in the DOS curves for the nonrelaxed and relaxed structure were little and not important, and that for the relaxed structure are plotted in Fig. 4. The zero point on the vertical energy axis was adjusted to the highest occupied molecular orbital (HOMO) of the cluster. The top of the valence band is located at zero energy because the valence band is fully occupied by electrons while the conduction band is empty. The valence band is formed pri-
The characteristics of the electronic interaction can be studied by overlap population analysis. The distribution of overlap populations between the metal ions is plotted in Fig. 5. The positive and negative values of the population indicate bonding and antibonding characteristics of the interactions between two atomic orbitals. At the bottom of the conduction band, the In-In bonding population is dominant, indicating that the electronic interaction that stabilizes the energy of the In 5s partial band is due to In-In bonding. The peak of the Ga-Ga bonding population is slightly higher than the In-In bonding peak. A peak for Ga-Zn is also seen at the same energy region. The Ga-Zn population has another peak 3.4-eV higher than the band edge. These characteristics indicate significant interactions between the In 5s and Ga 4s orbitals in InGaZnO 4 , which correspond to interactions across the layers, are very small along the entire energy axis. The electronic structure of InGaZnO 4 has strong two-dimensional characteristics, reflecting its crystal structure, and this implies that the In 5s, Ga 4s, or Zn 4s bands localize in the InO 2 layer or GaZnO 2 layer.

The electrons in the donor levels just below the conduction-band edge can be excited up to conduction band at room temperature and made to display electrical conductivity. Since the edge of the conduction band is formed by the In 5s band, it is thought that the In 5s band provides a path for electrical conductivity in the crystal, that is, the InO 2 layers should serve as conduction paths. The spatial distribution of the In 5s band can be seen in contour maps of the wave functions of the original molecular orbitals. Figure 6 shows the wave function for the LUMO, which corresponds to the edge of the conduction band. The wave function was displayed along two planes on which a chain of In ions is located. A chain of Ga ions or Zn ions is also seen on the In-Ga and In-Zn planes, respectively. It can be seen that the wave functions of In 5s orbitals overlap each other with the same phase, localizing along the In chain.

In the case of a heavily doped system, the possibility that the Ga 4s band also works as a carrier path should be discussed. For film specimens with a carrier density of \(1 \times 10^{21}/\text{cm}^3\), the Fermi level of the InGaZnO 4 film specimens would be located 1-eV higher than the edge of the conduction band (this value being estimated based on data on the Burstein-Moss shift of the absorption edge as a function of carrier density). Since the base of the Ga 4s partial band is located 2-eV higher than the band edge, as shown in Fig. 7 of a magnified version of the DOS curves for the conduction band given in Fig. 4, which in turn has twice as much energy as the shift, and because the number of states of the In 5s band under the edge of the Ga 4s band is estimated to be \(2 \times 10^{23}/\text{cm}^3\) (electron density: \(4 \times 10^{23}/\text{cm}^3\)) based on the area of the curve and the density of In atoms, the Ga 4s band may not play an important role even in such a heavily doped system. Furthermore, the Zn 4s band is not likely to serve as a conduction path, as its energy is far higher. Surprisingly, although ZnO has great conductivity comparable to In 2 O 3 , the Zn 4s orbitals in InGaZnO 4 do not play an important role in the electrical conductivity. The ZnGaO 2 layers thus do not serve as conduction paths.

Since the In 5s band is the only band to serve as a conduction path, dopant ions in the GaZnO 2 layers may play little or no part in scattering electrons that move within the InO 2 layer. In other words, in a system heavily doped by substituted ions, the reduction in mobility is restrained. Experimental research is underway on the relationship between...
the electrical properties of polycrystalline specimens and the concentration of dopant ions.

IV. CONCLUSION

The electronic structure of InGaZnO$_4$ with a YbFe$_2$O$_4$-type crystal structure was calculated by the DV-Xα method in order to study the mechanism of electrical conductivity. A reasonable crystal structure was obtained using the GULP program to perform relaxation calculations with classical two-center potentials. While Ga retained pentagonal coordination bonding to three oxygen ions at the corners of a basal triangle and two oxygen ions at the tops of the two pyramids, Zn had tetragonal coordination, with a missing bond between Zn and oxygen at the top of one of the pyramids.

The electronic structure of the relaxed InGaZnO$_4$ crystal was two dimensional. The electronic state at the edge of the conduction band was formed by overlapping between In 5s orbitals, which delocalize in the InO$_2$ layer. The energies of the Ga 4s and Zn 4s bands were too high for those bands to be doped with electrons. The In 5s band may be mainly occupied by the electrons and work as conduction paths even in a heavily doped system. The spatial separation effect, that is, the restraining of a reduction in mobility under a high concentration of dopant ions, can be expected, since the dopant ions introduced in the GaZnO$_2$ layers may have little effect in scattering carriers in the InO$_2$ layers.

ACKNOWLEDGMENTS

The authors would like to thank Dr. J. D. Gale for allowing us to use the GULP program, Professor N. Kimizuka at Sonora University for useful comments and suggestions, and F. Ohba at Kyoto University and H. Ohta of HOYA Corporation for their help in this study.