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Recent progress in transparent oxide semiconductors: Materials and device application

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Abstract

This paper reviews our recent research progress on new transparent conductive oxide (TCO) materials and electronic and optoelectronic devices based on these materials. First, described are the materials including p-type materials, deep-UV transparent TCO(β-Ga_2O_3), epitaxially grown ITO with atomically flat surface, transparent electrochromic oxide (NbO_2F), amorphous TCOs, and nanoporous semiconductor $12CaO \cdot 7Al_2O_3$. Second, presented are TCO-based electronic/optoelectronic devices realized to date, UV/blue LED and UV-sensors based on transparent pn junction and high performance transparent TFT using n-type TCO as an n-channel. Finally, unique optoelectronic properties (p-type degenerate conduction, transfer doping of carriers, RT-stable exciton, and large optical nonlinearity) originating from 2D-electronic nature in p-type layered oxychalcogenides are summarized along with the fabrication method of epitaxial thin films of these materials.

Keywords: Transparent conductive oxide; Oxide; Semiconductor

1. Introduction

It is generally believed that high optical transparency is incompatible with high electronic conduction, since optical transparency requires band gaps larger than 3.3 eV and such a large gap makes carrier doping very difficult. In this sense, transparent conductive oxides (TCOs) are exceptional materials. The first TCO, In_2O_3:Sn (ITO),was reported by Rupperecht [1] in 1954, followed by other TCOs: SnO_2 and ZnO.

Although TCOs have been commercialized intensively transparent metal such as transparent window electrodes and interconnections, there is almost no application as transparent semiconductors because of the absence of p-type TCO; no active electronic devices such as bipolar transistors and diodes can be fabricated without pn junctions. A breakthrough was the finding of the first p-type TCO, $CuAlO_2$ in 1997 by our group [2] (Fig. 1), which triggered the development of a series of p-type TCOs and transparent pn junction devices such as UV-light emitting diodes (LEDs). The achievement has significantly changed our conception of TCOs and has opened a new frontier called "transparent oxide semiconductors (TOSs)". Therefore, we now consider that TOSs have the potential to develop new functionalities useful for novel optoelectronic devices that are hard to realize by current Si-based semiconductor technology.

The discovery of the p-type TOS resulted from rational considerations regarding to the design of new TOSs based on knowledge about electronic structures that has been accumulated experimentally and theoretically. Our material design concept has been proven to be valid by the development of new TOSs including p-type TOSs. These new TOSs led to transparent electronic devices such as UV-LEDs and transparent thin film transistors (TFTs). In addition, we have proposed that the use of natural nanostructures embedded in crystal structures of TOSs is very effective in the cultivation of new functions in oxides. Such structures exist in layered and nanoporous compounds. From a processing point of view, techniques for growing high-quality single crystals or epitaxial thin films of the compounds are necessary to fabricate the devices. They are also essentially important for clarifying intrinsic properties associated with the structures. We invented a unique epitaxial film growth technique, "reactive solid-phase epitaxy (R-SPE)", which is particularly suited for growing the layered compounds.

In this review article, we first discuss the guiding principles for the development of new TOSs and then briefly review recent achievements we have made, which have opened the new

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frontier of TOSs. Finally, we introduce distinct optoelectronic properties associated with low-dimensional electronic structures, taking R-SPE-grown oxychalcogenide films as an example.

2. Guiding principles for developing new TOSs

The conduction band minimum (CBM) of most metal oxides is made of spatially spread spherical metal s orbital. Therefore, electrons in the metal oxides have small effective masses, and high electronic conduction is possible if high-density electron doping is achieved. This is the reason why several n-type TOSs have been found to date. In contrast, the valence band maximum (VBM) is made of oxygen 2p orbitals, which are rather localized, leading to small hole effective masses. Furthermore, the dispersion of the valence bands tends to be small, and thus the VBM level is so deep that hole doping is difficult. Therefore, p-type TOS was not discovered before 1997. We proposed an idea that the use of metal d orbitals with energy levels close to those of O 2p orbitals may form highly hybridized orbitals with O 2p, expecting that it might raise the VBM level and make hole doping easier. The $3d^{10}$ configuration of Cu^+ was chosen as a candidate because the Cu 3d energy level is just above the O 2p level. Further, the closed shell configuration of Cu^+ allows for large band gaps and optical transparency. This idea actually led to the discovery of $CuAlO_2$ [2]. This was followed by the subsequent discovery of new Cu^+-based p-type TOSs such as $CuGaO_2$ and $SrCu_2O_2$.

However, neither high-concentration hole doping nor large hole mobility was achieved in these Cu^+-based p-type TOSs. Therefore, the material design concept was extended to use the chalcogen (S, Se and Te) p orbitals instead of those of oxygen. That is, what we intended was to increase the valence band dispersion by forming hybridized orbitals between Cu 3d orbitals and chalcogen p orbitals that are more delocalized than that for O 2p. Layered oxychalcogenides were chosen because they are optically transparent in the visible light region, although simple chalcogenides are transparent only in the IR region.

Electron mobility in amorphous TOSs is expected to maintain a large value (e.g. >20 cm^2 V^{-1} s^{-1}), comparable to those of corresponding crystalline materials, because electron transport paths (i.e., CBMs) are made of spherically spreading metal s orbitals [3,4]. Such expectations are distinctly different from those in covalent amorphous semiconductors such as amorphous hydrogenated silicon (a-Si:H), where mobility in amorphous states is largely reduced from that of the crystalline state due to CBM and VBM being formed by the sp^3 hybrid orbitals.

3. Novel TOS materials and device application

3.1. TOS materials

3.1.1. p-type TOSs: Cu^+-bearing oxides

In 1997, we reported $CuAlO_2$ thin films as the first p-type TOS along with a chemical design concept for exploring p-type TOSs [1,2]. After that, a series of p-type TOSs based on Cu^+-bearing oxides such as $CuGaO_2$ [5] and $SrCu_2O_2$ [6] were found.

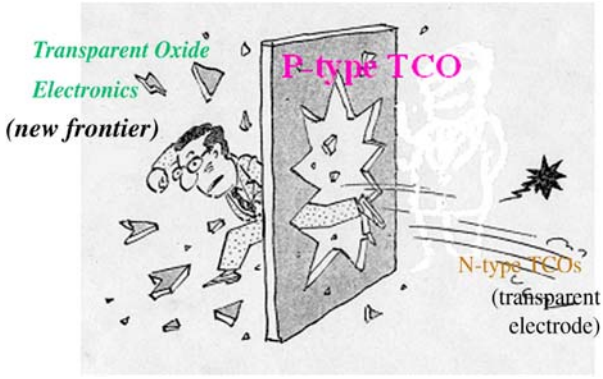

Fig. 1. Impact of discovery of p-type transparent conductive oxides. New frontier of a transparent oxide semiconductor was opened from a transparent conductive oxide toward transparent electronics.

In order to clarify the origin of p-type conduction, the electronic structure of $SrCu_2O_2$ was examined by photoelectron spectroscopy and band structure calculations using LDA [7]. The electronic structure around the band gap was found to be similar to that of Cu_2O despite a large difference in the band gap energies. That is, the admixed orbitals of 3d, 4s and 4p of the Cu^+ ion are hybridized with 2p orbitals of the O^{2-} ligands, which constitute the VBM.

3.1.2. Alternative p-type TOSs: $ZnRh_2O_4$

It is known that transition metal ions with $4d^6$ configurations located in an octahedral crystal field have a low-spin configuration in the ground state, which may be regarded as a "quasi-closed shell" configuration. On the basis of the idea that such ions are expected to behave similarly to Cu^+ ions with $3d^{10}$ closed shell configurations and to enhance the dispersion of the valence band, we have found that normal spinel $ZnRh_2O_4$ is a p-type wide-gap semiconductor with a band gap of $\sim$2.1 eV [8]. The electrical conductivity of the sputtered film was 0.7 S cm^{-1} at 300 K without intentional doping. Magnetic susceptibility, photoelectron spectroscopy, and optical measurements revealed that the band gap originated from the ligand-field split of Rh^{3+} d orbitals in octahedral symmetry, while the valence bands were made of fully occupied t_{2g}^6 (low-spin state) and the conduction band of empty e_g^0.

3.1.3. Deep-UV (DUV) TOS: β-Ga_2O_3

Conventional TCOs such as ITO and ZnO are opaque for DUV light ($<$300 nm) due to their small band gap ($\sim$3 eV), although the DUV region will be important for future biotechnologies such as DNA detection. DNA detection may be possible by electrical sensing or DUV optical absorption measurements. It is necessary to improve molecular selectivity to realize the DNA detection function. Our idea is to control the selectivity by applying voltages to the adsorption surface. Therefore, DUV-transparent TCOs are needed for these applications. β-Ga_2O_3 is considered to be a good candidate because this material has a large band gap of 5 eV and good electronic conduction by bulk single-crystal β-Ga_2O_3 was reported [9]. We successfully fabricated conductive β-Ga_2O_3