Transactions of the Materials Research Society of Japan. Vol. 20
© 1996 MRS-J. All rights reserved.

A New Transparent Conductive Oxide, $InGaZnO_4$

M.Orita[a], H.Sakai[a], M.Takeuchi[a] and Y.Yamaguchi[a]
T.Fujimoto[b] and I.Kojima[b]

[a]HOYA R&D center
3-3-1, Musashino, Akishima, Tokyo, 196, Japan
[b]National Institute of Materials and Chemical Research
1-1, Higashi, Tsukuba, Ibaraki, 305, Japan

$InGaZnO_4$ was found to be a novel candidate material for transparent electrodes. Films of 500 nm thick were prepared on glass substrates by rf-magnetron sputtering. Optical band gap was 3.5 eV. Annealing at 600 ℃ in H_2 atmosphere induced carrier electrons of 1 x $10^{20}/cm^3$. Mobility was 24 cm^2/Vs and conductivity was 500 S/cm. Effective mass was $0.7m_e$. Conduction path of the carrier electrons were specified to be $InO_{3/2}$ layers by measurements of X-ray photoelectron and Bremsstrahlung isochromat spectroscopies and analysis by DV-X α molecular orbital calculation.

1. INTRODUCTION

Optical transparency and high conductivity are fundamental properties for thin film transparent electrode applications. New materials with improved transparency and good conductivity are of interest in electrode applications. Shannon *et al.* measured conductivity of single crystals of $CdSnO_3$, Cd_2SnO_4, In_2TeO_6 and $CdIn_2O_4$, and suggested that edge sharing of Cd^{2+}, In^{3+} and Sn^{4+} octahedra is a necessary criterion for the formation of a transparent conductor.[1)] Kawazoe and co-workers examined several oxides which have linear chains of the edge sharing MO_6 octahedra, and found that $MgIn_2O_4$,[2)] $CdGa_2O_4$, [3)] $ZnGa_2O_4$,[4)] and $Cd_2Sb_2O_7$[5)] were transparent conductors. Cava *et al.* found $GaInO_3$, which had β-gallia-type layer structure composed of GaO_4 corner-sharing tetrahedra and InO_6 edge-sharing octahedra.[7)]

In accordance with the criterion proposed by Shannon and Kawazoe, we have studied and found that $InGaZnO_4$ with $YbFe_2O_4$ structure composed of alternating layers of $InO_{3/2}$ and $ZnGaO_{5/2}$[8)] had high transparency and conductivity.[9)] InO_6 octahedra are connected by edge sharing to form $InO_{3/2}$ layers. In this paper, the properties of thin films prepared by rf-magnetron sputtering were studied.

2.EXPERIMENTAL

Films were prepared by conventional rf-magnetron sputtering using a ceramic target, whose compositon was adjusted to be $InO_{3/2}/GaO_{3/2}/ZnO$ = 1.07/1.00/1.36 to obtain stoichometric films. Deposition was performed with an rf power of 230 W in a mixture of Ar and O_2 gases (Ar/O_2 = 19.5/0.5) at a pressure of 18 mTorr. Substrate temperatures were varied from room temperature to 700 ℃. Thickness of the films was 500 nm, measured using a stylus. The composition of the sputtered films was analyzed by Inductively Coupled Plasma (ICP) and X-Ray Fluorescence (XRF) analyses and

crystal structure was confirmed by X-Ray Diffraction (XRD) technique. Films were reduced for 1 hour in flowing gas mixture of $H_2/N_2 = 0.02$ in order to dope with electrons by oxygen defects. Electric conductivity and Hall mobility were evaluated using the van der Pauw method. Optical transmission was measured in the wavelength range from 250 to 600 nm. Spectra of density of states were taken using X-ray Photoelectron and Bremsstrahlung Isochromat Spectroscopies (XPS and BIS) and analyzed by DV-X α molecular orbital calculations using cluster models.

3.RESULTS AND DISCUSSION

It was confirmed that the crystal structure of the prepared films was $YbFe_2O_4$ type. Fig. 1 shows the XRD pattern of the films deposited at 500 ℃. The film had c-axis orientation. A peak near 29° corresponds to the diffraction from the (009) face of $InGaZnO_4$. Change in the patterns by the reduction treatment is also shown. The peak intensity increased with the reduction temperature up to 600 ℃. At 700 ℃, the pattern of $InGaZnO_4$ was no longer

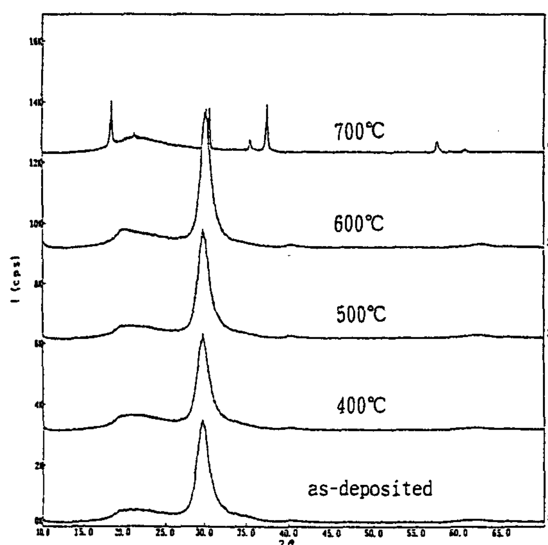

Fig. 1 XRD after reduction treatments.

bserved. Composition analysis showed that amounts of In and Zn were decreased significantly. Unevenness of the film surface was very large. The reduction treatment must be performed at a temperature lower than 700 ℃. Electric conductivity was very low without the reduction, and increased with the temperature (Fig.2). The purpose of the reduction treatment was to dope with electrons by oxygen defects, and consequently carrier density increased by the treatment. In addition, mobility also increased over 400 ℃, which corresponds to the change in the XRD peak intensity.

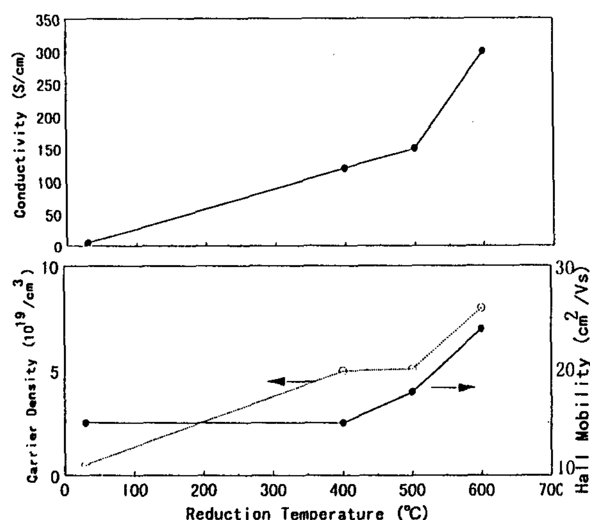

Fig.2 Electric properties after reduction.

Fig. 3 shows the XRD patterns of films deposited at different substrate temperatures. Peak intensities maximized at 500 ℃, indicating this temperature was preferable for crystallization of $InGaZnO_4$ phase. Electric parameters after the reduction at 600 ℃ are shown in Fig. 4. Conductivity increased with the substrate temperature as large as 500 S/cm at 700 ℃. Carrier density was the dominant factor to the increase in the conductivity, while mobility did not changed largely.

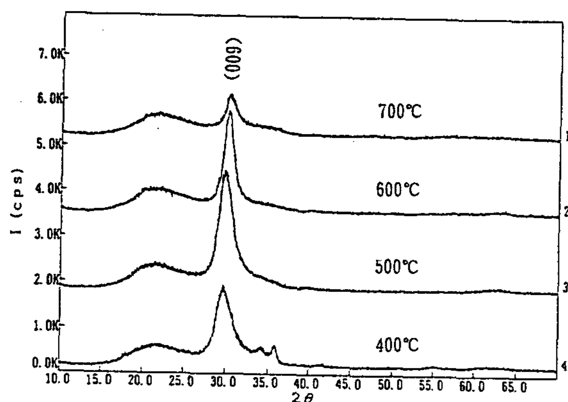

Fig.3 XRD and substrate temperatures.

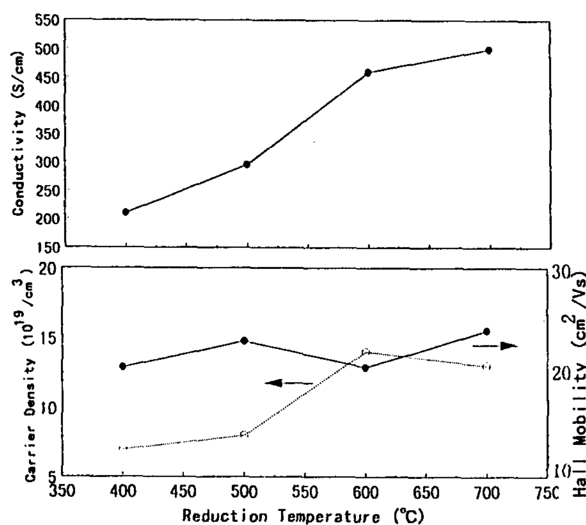

Fig. 4 Change in electric properties.

Transmission spectrum of an $InGaZnO_4$ film is shown in Fig. 5 with spectra of two ITO films. All the films were 500 nm thick. Absorption edge of the ITO film which has carrier density close to that of the $InGaZnO_4$ film was shorter than that of $InGaZnO_4$. Increase in the carrier density of the ITO film shifted the spectrum toward short wavelength side (Burstein-Moss shift), however transmission under 450 nm was still inferior to that of the $InGaZnO_4$. The band gaps determined from relation between absorptivity and photon energy were plotted versus carrier densities in Fig. 6. Intrinsic band gap of $InGaZnO_4$ was 3.5 eV, larger than 3.2 eV of ITO. It is a fundamental property of $InGaZnO_4$ that transparency is superior in the short wavelength region. From the slope of the graphs, effective mass of the carrier electrons were evaluated. The mass for $InGaZnO_4$ was equal to that for ITO, 0.7 me, which indicates that it should be able to increase the mobility of $InGaZnO_4$ to the value of ITO, 30 to 40 cm^2/Vs for the samples in Fig. 6, by removing the factors of carrier scattering, such as lattice boundaries and impurities.

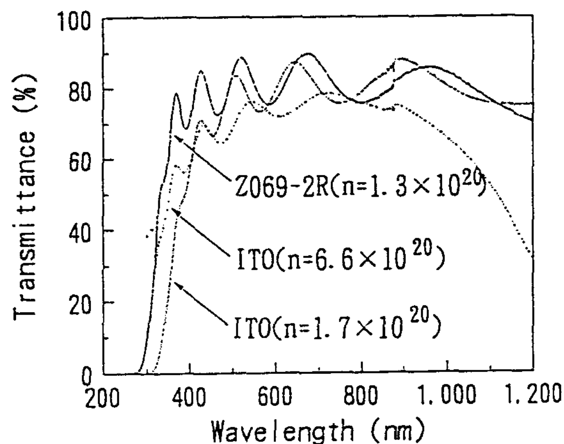

Fig. 5 Transmittance of IGZO and ITO.

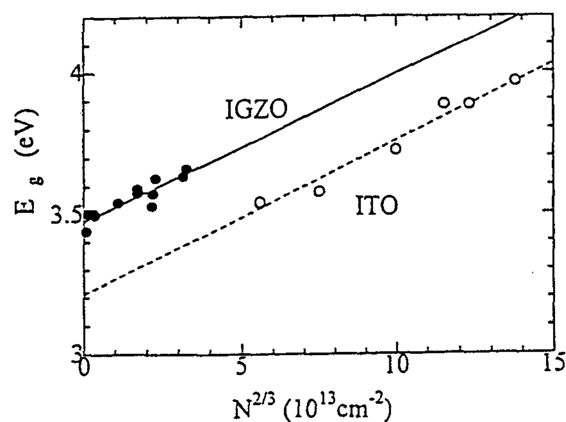

Fig. 6 Band gap and carrier density.

It should be possible to obtain larger mobility by preparing films with much better crystalline properties, however it is still required to increase carrier density in order to realize conductivity superior to that of ITO.

In this experiments, electrons were doped by oxygen defects. Substitution of ions with higher valences is another method to dope with electrons. In this case, it is known that scattering of carriers by substituted ions depress the mobility significantly. If it is possible to separate the substituted ions from the pass of carrier electrons, high carrier density and high mobility can be obtained simultaneously. In order to prepare such system, it is necessary to specify the conduction pass of electrons in $InGaZnO_4$ lattice. For this purpose, spectra of density of states were measured by XPS and BIS (Fig. 7). These spectra corresponds well to DOS curve calculated by DV-X α method, which indicates that the conduction band is mainly composed of In 5s orbitals and delocalized over the $InO_{3/2}$ layers. Since doped electrons occupy bottom of the conduction band, they move along the $InO_{3/2}$ layers, that is, $InGaZnO_4$ is a two dimensional conductor. Mean free path calculated using three dimensional free electron model was about 2 nm, which implied that electrons were scattered while they moved along only 6 In ions. Two dimensional model resulted in 25 nm, which corresponds to the distance between the lattice boundaries evaluated from photographs of cross section of the $InGaZnO_4$ films using a Transmission Electron Microsope. Thus, conduction path in $InGaZnO_4$ lattice is two dimensional and specified to be the $InO_{3/2}$ layers. Dopant ions should be substituted in $ZnGaO_{5/2}$ layers.

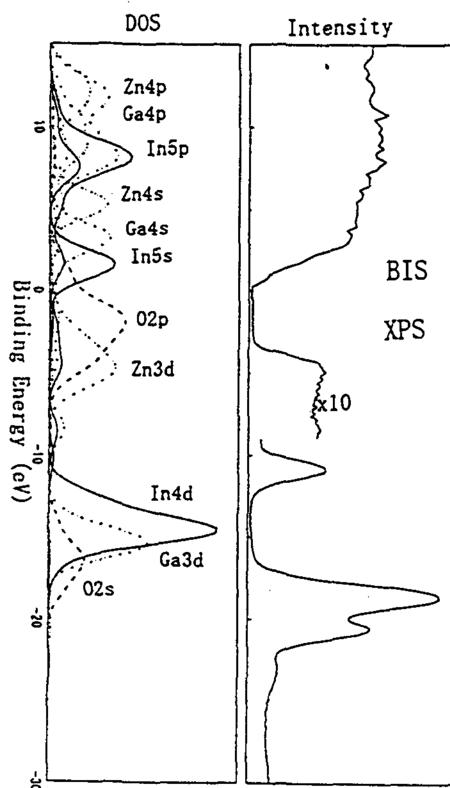

Fig. 7 XPS and BIS of an IGZO (Right) and DOS by DV-X α calculation.

REFERENCES

1)R.D.Shannon, J.L.Gillson and R.J.Bouchard: J.Phys.Chem. Solids 38(1977)877.
2) N.Ueda, T.Omata, N.Hikuma, K.Ueda, H.Mizoguchi, T.Hashimoto and H.Kawazoe: Appl.Phys.Lett.61(1992)1954.
3) T.Omata, N.Ueda, N.Hikuma, K.Ueda, H.Mizoguchi, T.Hashimoto and H.Kawazoe: Apple.Phys.Lett.62(1992)499.
4)T.Omata, N.Ueda, K.Ueda and H.Kawazoe: Appl.Phys.Lett. 64(1994)1077.
5)K.Yanagawa, Y.Ohki, T.Omata, H.Hosono, N.Ueda and H.Kawazoe: Jpn. J.Appl.Phys.33(1994)L238.
6)R.J.Cava, J.M.Phillps, J.Kwo, G.A.Thomas, R.B.van Dover, S.A. Carter, J.J.Krajewski, W.F.Peck, Jr., J.H.Marshall and D.H.Rapkine: Appl.Phys.Lett. 64(1994) 2071.
7)N.Kimizuka and T.Mohri: J.Solid State Chem.60(1985)382.
8)M.Orita, M.Takeuchi, H.Sakai and H.Tanji, Jpn.J.Appl.Phys.34(1995)L1550.