New *n*-Type Transparent Conducting Oxides

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Introduction

Most research to develop highly transparent and conductive thin films has focused on *n*-type semiconductors consisting of metal oxides. Historically, transparent conducting oxide (TCO) thin films composed of binary compounds such as SnO_2 and In_2O_3 were developed by means of chemical- and physical-deposition methods.[1–3] Impurity-doped SnO_2 (Sb- or F-doped SnO_2, e.g., SnO_2:Sb or SnO_2:F) and In_2O_3:Sn (indium tin oxide, ITO) films are in practical use. In addition to binary compounds, ternary compounds such as Cd_2SnO_4, $CdSnO_3$, and $CdIn_2O_4$ were developed prior to 1980,[1,2] but their TCO films have not yet been used widely.

For the purpose of obtaining lower resistivities than that of TCO films such as ITO and impurity-doped SnO_2, other TCO materials have been developed as alternatives. In the 1980s, impurity-doped ZnO, an inexpensive and abundant binary compound material, was developed.[3] Recently, ZnO:Al and ZnO:Ga thin films have attracted much attention as the transparent electrode for thin-film solar cells; a resistivity of the order of 1×10^{-4} Ω cm was obtained in these films prepared by various deposition methods.

To obtain TCO films suitable for specialized applications, new TCO materials have been actively studied in recent years. In the 1990s, new TCO materials consisting of multicomponent oxides have been developed—for example, combinations of binary compounds such as ZnO, CdO, In_2O_3, and SnO_2. In these materials systems, new TCO materials consisting of ternary compounds such as Zn_2SnO_4,[4] $MgIn_2O_4$,[5] $CdSb_2O_6$:Y,[6] $ZnSnO_3$,[7] $GaInO_3$,[8] $Zn_2In_2O_5$,[9] and $In_4Sn_3O_{12}$,[10] as well as multicomponent oxides composed of combinations of these ternary compounds, were developed.[11] The use of multicomponent oxide materials makes possible the design of TCO films suitable for specialized applications because their electrical, optical, chemical, and physical properties can be controlled by altering their chemical compositions.

This article introduces newly developed *n*-type TCO materials consisting of binary and ternary compounds and multicomponent oxides. Although TCO films are usually evaluated by their resistivity and transmittance in the visible range, the following discussion focuses on resistivity, since the transmittance of TCO films can be controlled by altering film thickness.

Binary Compound TCO Materials

One advantage of using binary compounds as TCO materials is that their chemical composition in film depositions is relatively easier to control than that of ternary compounds and multicomponent oxides. Until now, impurity-doped SnO_2, In_2O_3, ZnO, and CdO films have been developed as TCO materials consisting of binary compounds. It is well known that the transparent conducting thin films of these metal oxides can also be prepared without intentional impurity doping.[1–3] These films are *n*-type degenerated semiconductors, with free-electron concentrations of the order of 10^{20} cm^{-3} provided by native donors such as oxygen vacancies and/or interstitial metal atoms. However, undoped binary compound materials are not in practical use because impurity-doped materials can use both native and impurity donors. Although CdO:In films have been prepared with a resistivity of the order of 10^{-5} Ω cm for flat-panel displays and solar cells, they are of no practical use because of Cd toxicity.

In practical TCO films, the lowest resistivity, approximately 1×10^{-4} Ω cm, can be obtained in ITO films prepared by various deposition methods. Figure 1 shows the resistivities of binary TCO films that have been reported in the past 30 years. As can be seen in this figure, the obtained minimum resistivities of impurity-doped SnO_2 and In_2O_3 (ITO) films have essentially remained unchanged for the past 20 years: $3–5 \times 10^{-4}$ Ω cm for impurity-doped SnO_2 films and $1–2 \times 10^{-4}$ Ω cm for ITO films. In contrast, the obtained resistivity of impurity-doped ZnO films is still decreasing. Note that several preparations of ZnO:Al and ZnO:Ga thin films with a resistivity of the order of 1×10^{-4} Ω cm have been reported in the past three years. Impurity-doped ZnO, an *n*-type TCO material developed in the 1980s, uses ZnO or Zn—inexpensive, abundant, and harmless materials. In contrast, if the use of ITO films for flat-panel displays and solar cells continues to increase, In will be depleted in the near future. As can be seen in Figure 1, it is believed that impurity-doped ZnO is an alternative material for ITO.[12]

In the next section, the present status and prospects for further development of impurity-doped ZnO films are surveyed.

Impurity-Doped ZnO

Transparent conducting films using ZnO:Al (AZO) prepared by rf-magnetron sputtering and undoped ZnO (ZO) by spray pyrolysis were reported by Wasa et al.[13] in 1971 and Aranovich et al.[14] in 1979, respectively. Although undoped ZnO films with a resistivity of 4.5×10^{-4} Ω cm were prepared by rf-magnetron sputtering in 1982,[12] they were found to be unstable in temperatures above about 150°C.[15] Transparent conducting impurity-doped ZnO films with a low resistivity of the order of 10^{-4} Ω cm were reported by Chopra et al. in 1983. In that study, ZnO:In (IZO) films with a resistivity of 8.1×10^{-4} Ω cm were prepared by spray pyrolysis.[1] For the purpose of improving stability at high temperatures, Minami et al. reported in 1984 that ZnO:Al films prepared by rf-magnetron sputtering with a resistivity of 1.9×10^{-4} Ω cm were stable in use at temperatures as high as 400°C.[16] In the 1980s, transparent conducting ZnO films with resistivities of the order of 10^{-4} Ω cm were prepared by impurity doping with a Group III element[17] such as Al, Ga, In, and B, or a Group IV element[18] such as Si, Ge, Ti, Zr, or Hf substituted to a Zn atom site, and with a Group VII element[19,20] such as F substituted to an O atom site. In addition, other ZnO films with resistivities of the order of 10^{-4} Ω cm, prepared by doping with a rare-earth element such as Sc or Y substituted to a Zn atom site, were reported in 1999.[21]

Table I summarizes the minimum resistivities and the maximum carrier concentrations obtained for ZnO films prepared with optimal doping content for various dopants and deposition methods reported

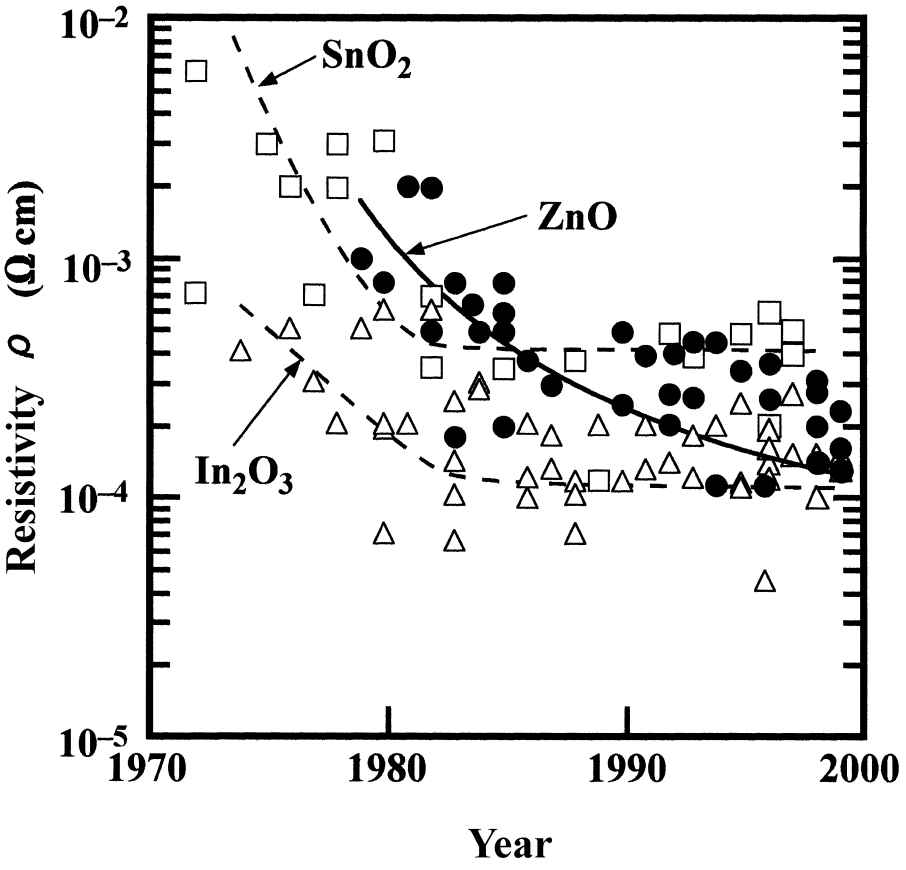

Figure 1. Reported (1970–2000) resistivities of binary transparent conducting oxide (TCO) materials: undoped and impurity-doped SnO_2 (□), In_2O_3 (△), and ZnO (●).

Table I: Resistivities, Carrier Concentrations, and Dopant Content for ZnO Films Doped with Various Impurities.

Dopant	Doping Content (at.%)	Resistivity (10^{-4} Ω cm)	Carrier Concentration (10^{20} cm^{-3})
Al	1.6–3.2	1.3	15.0
Ga	1.7–6.1	1.2	14.5
B	4.6	2.0	5.4
Y	2.2	7.9	5.8
In	1.2	8.1	3.9
Sc	2.5	3.1	6.7
Si	8.0	4.8	8.8
Ge	1.6	7.4	8.8
Ti	2.0	5.6	6.2
Zr	5.4	5.2	5.5
Hf	4.1	5.5	3.5
F	0.5	4.0	5.0

to date. The ZnO:F and ZnO:B films were prepared by metalorganic chemical vapor deposition (MOCVD); all other impurity-doped ZnO films were prepared by magnetron sputtering deposition (MSD), pulsed laser deposition (PLD), or arc-discharge ion plating (ADIP).[22] The optimal impurity doping content was dependent on the film deposition method as well as the dopant used. Recently, ZnO:Al and ZnO:Ga films with resistivities of the order of 1×10^{-4} Ω cm were prepared by PLD[23,24] and ADIP. The effect of the Al impurity doping has been extensively investigated in ZnO using various film deposition methods. As a result, ZnO:Al films have been used in practical flat-panel displays and thin-film solar cells. Recently, Ga has attracted much attention as a dopant, and low-resistivity ZnO:Ga films have been prepared by PLD and ADIP.

In the preparation of highly conductive and transparent ZnO films, controlling the oxidation of Zn is much more difficult than that of other binary compounds such as SnO_2 and In_2O_3 because Zn is more chemically active in an oxidizing atmosphere than either Sn or In. This may be attributed to the binding energy of Zn and O. The activity and amount of oxygen must be precisely controlled during the deposition. As a result, ZnO films with low resistivity are attained only by depositions in oxidizing atmospheres that are weaker than those used with depositions of In_2O_3 and SnO_2 films. For example, in the preparation of ZnO:Al films on large-area substrates by dc MSD using an oxide target, the difficulty in resolving this problem results in a spatial distribution of resistivity on the substrate surface corresponding to the target erosion-area pattern.[17,25–27] This is mainly attributed to the distribution of activity and the amount of oxygen reaching the substrate surface, depending on the sputter deposition conditions and target preparation conditions. For the purpose of improving the distribution, various sputtering techniques have been developed; however, the problem has not yet been resolved completely.[28]

The electrical conduction mechanism of transparent conducting impurity-doped and undoped ZnO films is affected by the oxidizing atmosphere during deposition. The results of the theoretical and experimental examination of the relationship between Hall mobility (μ) and carrier concentration (n) for low-resistivity undoped and impurity-doped ZnO films with carrier concentrations of 10^{19}–10^{21} cm^{-3} are shown in Figure 2. The mobility (μ_I) dominated by ionized impurity scattering was calculated by two methods: using the Brooks-Herring-Dingle (B-H-D) theory by taking into account degeneracy, and using both degeneracy and nonparabolicity of the conduction band.[29,30] In addition, the mobility (μ_G) dominated by grain-boundary scattering was calculated.[30] The experimental data in the figure summarize reports of impurity-doped ZnO films prepared using various dopants and deposition methods. In addition, undoped ZnO films were prepared by MSD under various sputter conditions using the same ZnO target. As shown in Figure 2, the Hall mobility of degenerated semiconductors with carrier concentrations of 10^{20}–10^{21} cm^{-3} was mainly dominated by ionized impurity

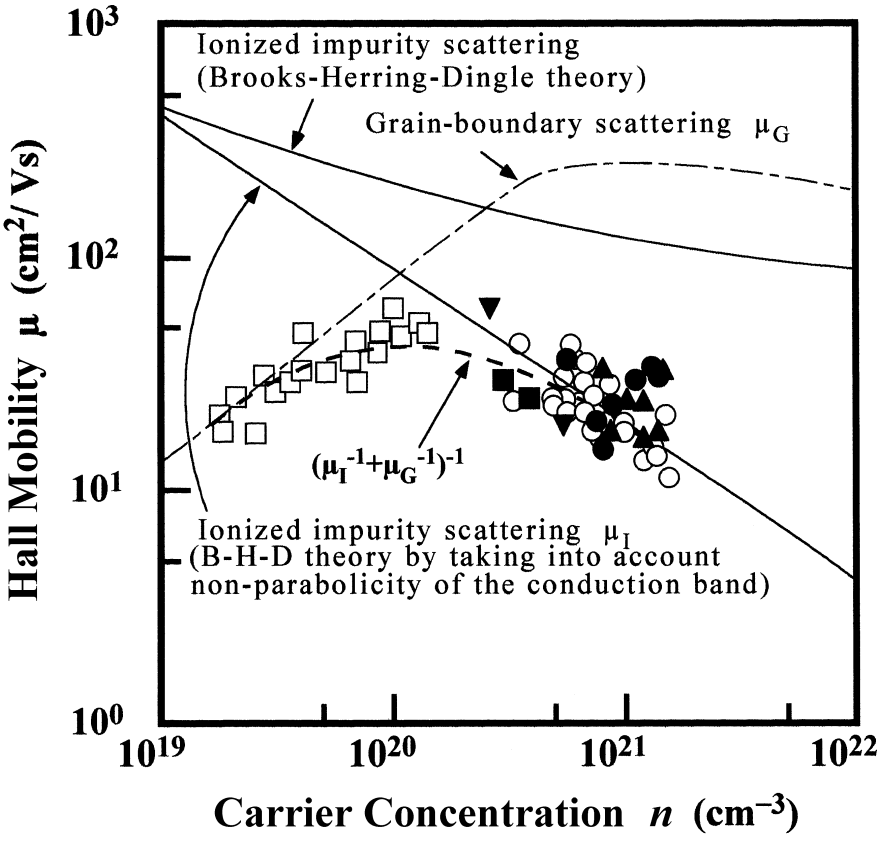

Figure 2. Measured Hall mobility versus carrier concentration of undoped ZnO films (□) and impurity-doped ZnO films: ZnO:Al (○,●), ZnO:Ga (▲), ZnO:B (■), and ZnO:other (▼). The upper solid line represents ionized impurity scattering using the Brooks-Herring-Dingle (B-H-D) theory; the lower solid line shows the ionized impurity scattering μ_I-n relationship, and the dashed line shows the grain-boundary scattering μ_G-n relationship.

scattering. However, impurity-doped and undoped ZnO films were also affected by grain-boundary scattering. The grain-boundary scattering is characterized by the increase in Hall mobility with increased carrier concentration, up to approximately 10^{21} cm^{-3}, resulting from increases in the potential barrier height as well as the trapping of free electrons due to oxygen adsorbed on grain boundaries and the film surface. The oxygen adsorption is affected by the oxidizing atmosphere during the deposition. Note, particularly, that a Hall mobility of 120 cm^2/V s could be obtained in an undoped ZnO film with a carrier concentration of about 2×10^{20} cm^{-3} as long as the oxidizing atmosphere was controlled during MSD.[12] It can be concluded that controlling the oxidizing atmosphere during the deposition is very important for the preparation of low-resistivity transparent conducting thin films of ZnO; a more spatially uniform and weaker oxidizing atmosphere is required than for the deposition of other TCO materials.

Resistivities of $1–3 \times 10^{-4}$ Ω cm, refractive indexes of approximately 2.0, and average transmittances above 85% in the visible range have been obtained in ZnO:Al and ZnO:Ga films prepared by various deposition methods. In addition, the optical absorption of ZnO films is generally lower than that of other TCO films. Transparent conducting impurity-doped ZnO films have both advantages and disadvantages in practical applications. As an example, several problems now exist in the use of impurity-doped ZnO films for the transparent electrodes of flat-panel displays as alternatives to ITO. For example, it is difficult to apply the presently used photolithography process to wet treatments because ZnO films are easily etched by both acid and alkaline solutions. However, this can be resolved by using an all-dry method because an oxygen ashing process can be applied to ZnO films.[31] In addition, the development of deposition techniques capable of producing spatially uniform and low-resistivity films on large-area substrates is required to overcome the problems associated with dc MSD.

In contrast, impurity-doped ZnO films can be advantageously used with thin-film solar cells because milky ZnO films with a textured surface structure are more easily produced on relatively low-temperature substrates than milky SnO_2 films.[20,32–36] The use of milky ZnO transparent electrodes for solar cells can improve efficiency as a result of a light-confinement effect. Several researchers have reported the preparation of milky ZnO:Al, ZnO:Ga, and ZnO:B films using various deposition methods such as MSD and atmospheric-pressure or low-pressure MOCVD and CVD.

Binary–Binary Compound Systems

Historically, TCO materials were developed using binary compounds such as SnO_2 and In_2O_3, and subsequently, ternary compounds such as Cd_2SnO_4, $CdSnO_3$, and $CdIn_2O_4$. Recently, multicomponent oxides have been attracting much attention as new TCO materials. For the purpose of developing TCO films suitable for specialized applications, Minami et al. reported a new TCO material in 1994, ZnO-SnO_2 multicomponent oxides, which not only have the advantages of ZnO but also those of SnO_2.[7,11,37] In addition, TCO films that used materials consisting of multicomponent oxides composed of combinations of binary compound TCO materials such as ZnO, In_2O_3, and SnO_2 were developed. For example, Figure 3 shows resistivity (ρ) and carrier concentration (n)

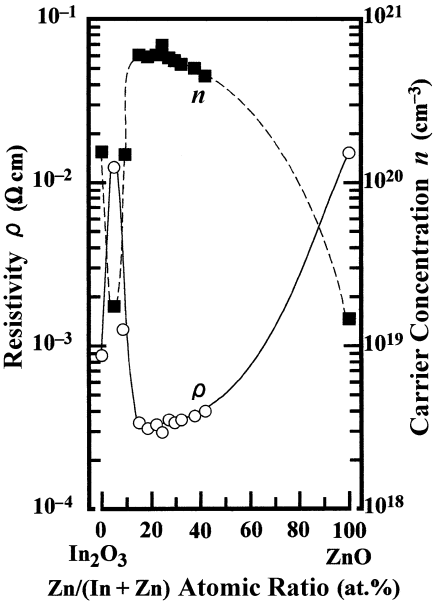

Figure 3. Resistivity (○) and carrier concentration (■) as functions of Zn content for ZnO-In_2O_3 films prepared at room temperature by dc magnetron sputtering deposition (MSD).

as functions of chemical composition for multicomponent oxide ZnO-In_2O_3 thin films prepared by dc MSD.[9,11,38] In addition, Figure 4 shows the etching rate (R_E) and bandgap energy (E_g) as functions of the chemical composition of these films. The ZnO-In_2O_3 thin films were prepared using ZnO-In_2O_3 powder targets with a Zn content [Zn/(In + Zn) atomic ratio] of 0–100 at.% under these optimal sputter-deposition conditions: an atmosphere of pure Ar gas, a sputter pressure of 0.6 Pa, and a substrate temperature equal to room temperature (RT). The Zn content in deposited films approximately equaled that in the target, as measured by energy-dispersive x-ray spectroscopy (EDXS) analyses. The bandgap energy was estimated by subtracting the Burstein-Moss shift energy from the measured absorption edge, resulting in an accuracy of ±0.01 eV to 0.20 eV, which depended on the carrier concentration of the films. The etching rate was measured using 0.2 M HCl at 25°C.

It should be noted that transparent conducting films could be prepared in multicomponent oxides composed of all composition ratios of ZnO and In_2O_3. The minimum resistivity, corresponding to the maximum carrier concentration, was obtained by altering the Zn content. The maximum carrier concentration was generated from native donors such as oxygen vacancies. The ZnO-In_2O_3 films prepared at RT with a Zn content of 24.5 at.% exhibited a low resistivity of 2.9×10^{-4} Ω cm, comparable to ITO films. In addition, the bandgap energy of films prepared with Zn contents around 24.5 at.% exhibited a minimum value of 2.9 eV. All films <400 nm thick exhibited an average transmittance above 80% in the visible range. As can be seen in Figure 4, the etching rate of ZnO-In_2O_3 films increased as the Zn content was increased from about 20 at.%, whereas films prepared with Zn contents of 0 at.% to about 20 at.% were not etched. As evidenced from x-ray diffraction (XRD) analyses, ZnO-In_2O_3 films prepared at RT with Zn contents of about 24.5–42.2 at.% were amorphous.

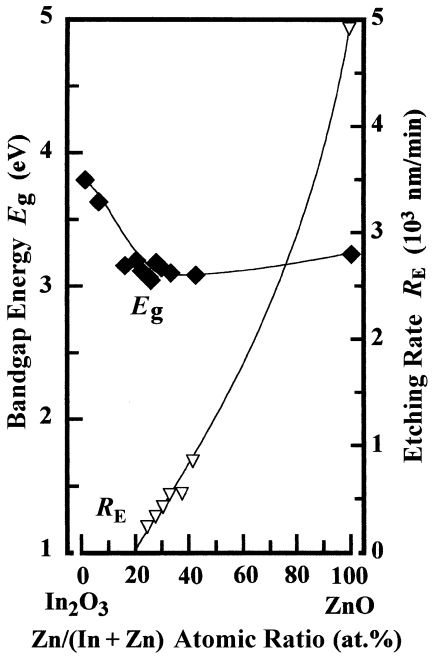

Figure 4. Etching rate (▽) and bandgap energy (◆) as functions of Zn content for ZnO-In_2O_3 films prepared at room temperature by dc MSD.

Similar results in regard to the composition dependence of the electrical, optical, and chemical properties in ZnO-In_2O_3 films, as described earlier, were also obtained in multicomponent oxides composed of ZnO and SnO_2 or In_2O_3 and SnO_2. For example, transparent conducting thin films were prepared in multicomponent oxides composed of all composition ratios of ZnO and SnO_2. The chemical stability and etching rate changed as the composition was altered in ZnO-SnO_2 films prepared by MSD. It can be concluded that in multicomponent oxides composed of combinations of binary compound TCO materials, transparent conducting films could be prepared in all composition ratios by various deposition methods.[11]

Ternary Compounds

As previously mentioned, ZnO-In_2O_3 films prepared with around 24.5 at.% Zn exhibited minimums in bandgap energy as well as in resistivity. It is well known that many compounds such as $Zn_mIn_2O_{3+m}$ (m = 2–7) exist in the ZnO-In_2O_3 system. In order to investigate their crystallographic properties, ZnO-In_2O_3 films were prepared on high-temperature substrates with various Zn contents. Minami et al. have reported that ZnO-In_2O_3 films prepared at 350°C with about 24–43 at.% Zn could be identified as polycrystalline $Zn_2In_2O_5$, a new TCO material, as evidenced from XRD analyses.[9] The $Zn_2In_2O_5$ thin films have a bandgap energy of 2.9 eV and a refractive index of 2.1–2.4 in the visible range, higher than the refractive index of about 2.0 seen in conventional TCO thin films such as ZnO, ITO, and SnO_2. For the purpose of obtaining lower resistivity, the doping of an impurity such as Sn was attempted in the $Zn_2In_2O_5$ films; however, a significant decrease in resistivity could not be attained.

Recently, thin films of multicomponent oxides composed of combinations of binary compounds such as ZnO, MgO, In_2O_3, Ga_2O_3, and SnO_2 have been prepared by MSD using powder targets calcined with various chemical compositions: ZnO-, MgO-, and Ga_2O_3- or SnO_2-In_2O_3, and Ga_2O_3- or SnO_2-ZnO systems. For example, Minami et al. have reported that SnO_2-In_2O_3 films with Sn contents [Sn/(In + Sn) atomic ratio] of 40–60 at.% could be identified as $In_4Sn_3O_{12}$, another new TCO film material.[10] A resistivity of 2×10^{-4} Ω cm, comparable to ITO films, was obtained in $In_4Sn_3O_{12}$ films prepared with 50 at.% Sn on substrates at 350°C. In addition, the $In_4Sn_3O_{12}$ films were very stable in acid solutions and in an oxidizing atmosphere at high temperatures. Thus, $In_4Sn_3O_{12}$ films, which are lower in cost than ITO films with their higher content of In (an expensive and scarce material), are very promising as TCO films. Table II sum-

Table II: Resistivity and Deposition Method of Reported Transparent Conducting Thin Films Composed of Ternary Compound TCO Materials.

Material	Resistivity ρ (Ω cm)	Deposition Method (Substrate Temperature)	Reference
Zn_2SnO_4	1.7×10^{-2}	rf MSD*	4
$ZnSnO_3$	4×10^{-3}	rf MSD (RT)	7
$MgIn_2O_4$	4.3×10^{-3}	rf sputtering*	5
	7.9×10^{-4}	rf MSD (RT)	11
$GaInO_3$	2.7×10^{-3}	rf MSD*	8
$(Ga,In)_2O_3$	5.8×10^{-4}	dc MSD (RT)	39
$Zn_2In_2O_5$	3.9×10^{-4}	rf MSD (RT)	9
	2.9×10^{-4}	dc MSD (RT)	38
$In_4Sn_3O_{12}$	2.0×10^{-4}	dc MSD (350°C)	10

Note: TCO is transparent conducting oxide; MSD is magnetron sputtering deposition; RT is room temperature.
* Postannealed

marizes the new ternary compound TCO materials found in recent years. Phillips et al. have reported that transparent conducting undoped and impurity-doped $GaInO_3$ thin films prepared by PLD and reactive sputtering exhibited resistivities of the order of 10^{-3} Ω cm, very low optical absorption coefficients in the visible range, and a refractive index of 1.65.[8] It should be noted that there are three types of $GaInO_3$: hexagonal, monoclinic, and $(Ga,In)_2O_3$.[39] Un'no et al. have reported that transparent conducting $MgIn_2O_4$ films were prepared by rf sputtering.[5] Note that TCO films could be obtained using a ternary compound, such as $(Ga,In)_2O_3$ in the In_2O_3-Ga_2O_3 system or $MgIn_2O_4$ in the In_2O_3-MgO system, composed of a transparent conductor and an insulator. Furthermore, TCO films could be prepared in all compositions of the In_2O_3-$(Ga,In)_2O_3$ and In_2O_3-$MgIn_2O_4$ systems when the components were TCO materials. On the contrary, the resistivity of $(Ga,In)_2O_3$-Ga_2O_3 and $MgIn_2O_4$-MgO films increased considerably as the insulating (Ga_2O_3 or MgO, respectively) content was increased.[11]

Ternary–Ternary Compound Systems

In developing TCO films suitable for specialized applications, Minami et al. reported the $Zn_2In_2O_5$-$MgIn_2O_4$ multicomponent oxide as a new TCO material in 1995.[40] The TCO films were prepared by magnetron sputtering using materials consisting of multicomponent oxides composed of combinations of ternary compounds such as $MgIn_2O_4$, $ZnSnO_3$, $GaInO_3$, $Zn_2In_2O_5$, and $In_4Sn_3O_{12}$. As an example, Figure 5 shows resistivity (ρ) and etching rate (R_E) as functions of $In_4Sn_3O_{12}$ content for $Zn_2In_2O_5$-$In_4Sn_3O_{12}$ thin films prepared by MSD using RT substrates, a pure Ar gas atmosphere, and a sputter gas pressure of 1.2 Pa; in addition, Figure 6 shows carrier concentration (n), bandgap energy (E_g), and work function (ϕ) as functions of $In_4Sn_3O_{12}$ content.[11] All multicomponent oxide films prepared on RT substrates were amorphous, regardless of the composition. As can be seen in Figures 5 and 6, the electrical, optical, physical, and chemical properties changed monotonically as the composition was altered.

It can be concluded that TCO films could always be obtained in multicomponent oxides composed of all composition ratios of ternary compound TCO materials such as $Zn_2In_2O_5$-$MgIn_2O_4$, $GaInO_3$-$Zn_2In_2O_5$, $Zn_2In_2O_5$-$In_4Sn_3O_{12}$, $ZnSnO_3$-$In_4Sn_3O_{12}$, $ZnSnO_3$-$Zn_2In_2O_5$, and $GaInO_3$-$In_4Sn_3O_{12}$.[11] On the contrary, when thin films of multicomponent oxides composed of a ternary compound TCO material and a ternary compound insulator were prepared, the resistivity and carrier concentration of the resulting films decreased as the ternary compound insulator content was increased; for example, ρ and n for $Zn_2In_2O_5$-$ZnGa_2O_4$ films decreased as the $ZnGa_2O_4$ content was increased.[11]

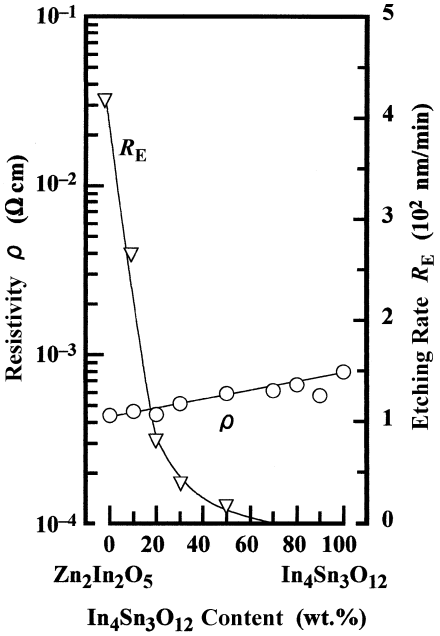

Figure 5. Resistivity (○) and etching rate (▽) as functions of $In_4Sn_3O_{12}$ content for $Zn_2In_2O_5$-$In_4Sn_3O_{12}$ films prepared at room temperature by rf MSD.

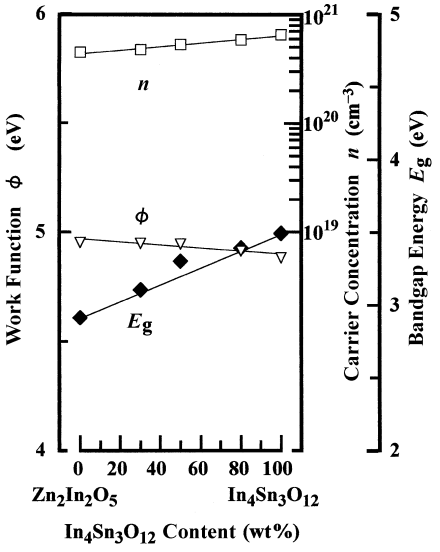

Figure 6. Carrier concentration (□), bandgap energy (◆), and work function (▽) as functions of $In_4Sn_3O_{12}$ content for $Zn_2In_2O_5$-$In_4Sn_3O_{12}$ films prepared by rf MSD.

TCO Material Design

Although *n*-type TCO materials have been investigated for more than 40 years, the only TCO materials in practical use are SnO_2, In_2O_3, ZnO, ternary compounds, and multicomponent oxides, all containing at least one metal element, as shown in Figure 7. In this figure, binary and ternary compound materials or multicomponent material systems resulting in TCO films are indicated with circles (binary compounds), triangles (ternary compounds), or lines (multicomponent oxides). Most practical TCO materials, besides single-crystalline TCO materials, are binary compounds such as impurity-doped In_2O_3 and ZnO. In particular, ITO is the best material at present. However, as has already been noted, the principal material of ITO, In, is a very expensive and scarce material. In addition, recent developments in optoelectronic devices have frequently required improvements in the physical properties as well as chemical properties of TCO films used in their applications. In order to develop TCO films for specialized applications, TCO material design using multicomponent oxides has been proposed.[11,40] By using TCO films made of multicomponent oxides, not only their electrical, optical, and chemical properties but also physical properties such as bandgap energy and work function can be controlled by altering the chemical composition; as examples, the relationships between chemical composition and bandgap energy or work function are shown in Figures 7 and 8, respectively. As can be seen in Figure 8, however, the work functions of TCO materials usually decreased as their carrier concentration was increased.[41] From the results described here, it can be concluded that the following points should be taken into account when designing TCO materials for practical use:[11] (1) the composition-dependence of resistivity in multicomponent oxide films has been found to be similar to the mechanism in metal alloys; (2) the composition-dependence of optical properties in multicomponent oxide films is similar to that in mixed films of dielectric materials; and (3) the chemical properties of multicomponent oxide films are basically determined by the kinds and amounts of metal elements they contain. For example, the etching rate in an acid solution increased as the Zn content was increased, but it decreased as the Sn content was increased. Notably, the obtainable properties of TCO films using multicomponent oxides can be

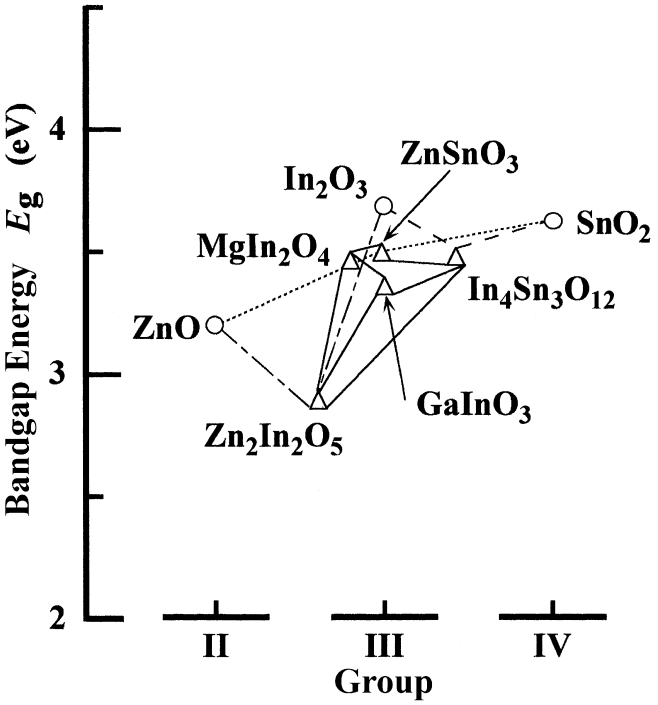

Figure 7. Bandgap energy of TCO materials: binary (○) and ternary compounds (△) and multicomponent oxides (lines).

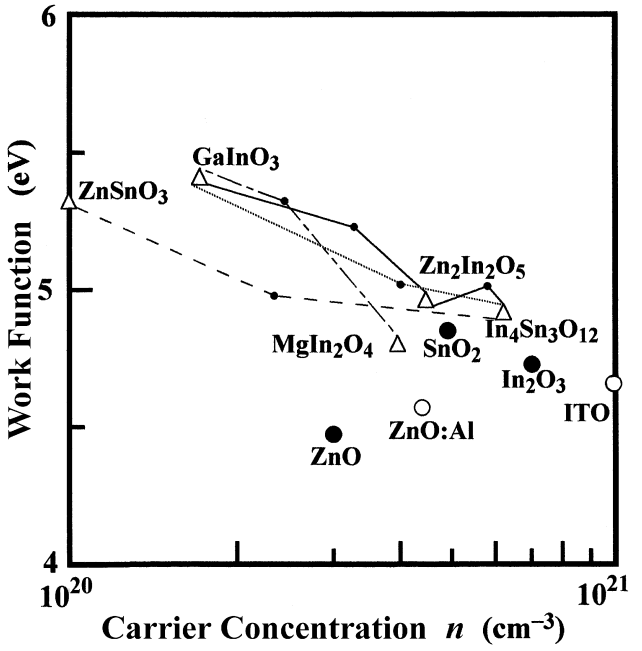

Figure 8. Relationship between work function and carrier concentration of TCO films: binary (○, ●) and ternary (△) compounds and multicomponent oxides (•) prepared with a composition of 50 wt%.

estimated from those of binary or ternary compound TCO materials.

Conclusions

New *n*-type TCO material development is necessary in order to realize transparent conducting films with lower resistivities than ITO and with properties suitable for specialized applications. Although resistivities lower than in ITO films have not yet been reported for new TCO materials, multicomponent oxides newly developed as TCO materials are suitable for specialized applications. In transparent conducting multicomponent oxide films, their electrical, optical, and chemical properties, as well as physical properties such as bandgap energy and work function, can be controlled by altering the chemical composition. In addition, it is very important that transparent conducting oxide materials for practical use be inexpensive and harmless. Developing alternatives to indium tin oxide is desirable because of the high cost and scarcity of indium; impurity-doped ZnO, such as ZnO:Al and ZnO:Ga, is very promising as one such alternative. However, further development of deposition techniques is required to enable the production of these impurity-doped ZnO films on large-area substrates with high deposition rates. In addition, the sintered targets used for magnetron sputtering need further development in order to produce transparent conducting multicomponent oxide films for specialized applications.

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