The relationship between the mean dopant-ion radii and conductivity of co-doped ZnO systems, $Zn_{1-x-y}M_xM'_yO$ (M, M' = Al, In, Ga, Y)

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The conductivities of the $Zn_{1-x-y}M_xM'_yO$ (M, M' = Al, In, Ga, Y) and $Zn_{1-x}M_xO$ (M = Al, In, Ga) systems were measured from room temperature to 1173 K in order to elucidate a dominant parameter of the conducting mechanism. The conductivity at 873 K first increased with the dopant content. However, it showed a maximum value at a given dopant content, and then gradually decreased. For the samples with the same dopant content, their conductivity at 873 K was strongly dependent on the mean dopant-ion radii, and reached a maximum value at around 0.51 Å of the mean dopant-ion radii. The results suggested that the conductivity of the system would be influenced not only by the dopant content, but also by the mean dopant-ion radii. It was found that the co-doped ZnO system of $Zn_{0.995}Al_{0.003}In_{0.003}O$ had a conductivity higher than that of the other usual mono-doped system. © *2003 Kluwer Academic Publishers*

1. Introduction

Optically transparent and high conducting materials are useful for transparent electrodes, which are used in liquid-crystal displays, solar cells, and antistatic coatings. In_2O_3, ZnO and SnO_2 are the representative materials for the electrodes, which are wide-gap semiconductors and show a high conductivity by doping with a small amount of impurity [1–4].

ZnO, which has the wurzite structure, is formed by a close-packed structure and is an *n*-type semiconductor with the wide band-gap of 3.3 eV [5]. The conduction band and valence band are formed by the sp^3 hybrid orbital that originates from Zn4*s* and $O2p^9$. In the gap between the two bands, the impurity level of Vö, $Zn_i^{\cdot}$ or $Zn_i^{\cdot\cdot}$ would act as a donor level and play an important role in the conductivity [3, 6]. The dopant of Al, Ga or In also acts as a donor level in the ZnO system and the conductivity of the doped system is higher than that of the non-doped ZnO in addition to good transparency in the visible region [7, 8]. Moreover, in the study of the thin films of the ZnO systems, it was reported that the electrical conductivity was very sensitive to the deposition technique, preparation conditions and film thickness [9, 10]. Therefore, the precise control of these factors is needed to clarify the conducting mechanism of the ZnO system.

In this paper, the conductivities of the bulk samples for the $Zn_{1-x-y}M_xM'_yO$ (M, M' = Al, In, Ga, Y) systems ($0 \leqq x + y \leqq 0.01$) and $Zn_{1-x}M_xO$ (M = Al, In, Ga) systems ($0 \leqq x \leqq 0.007$) were measured in the tem-perature range from room temperature to 1173 K and was discussed from the viewpoint of the dopant-ion content and the mean dopant-ion radii. Additionally, the absorption spectra of these systems were also measured to check the transparency in the ultraviolet-visible range.

2. Experimental procedures

Powder samples of the ZnO system were prepared by a solid-state reaction. The starting materials of ZnO (99.99%, High Purity Chemical Co, Ltd.), γ-Al_2O_3 (99.99%, Wako Chemical Co, Ltd.), Y_2O_3 (99.99%, High Purity Chemical Co, Ltd.), In_2O_3 (99.99%, High Purity Chemical Co, Ltd.), and Ga_2O_3 (99.99%, High Purity Chemical Co, Ltd.) were mixed for 24 h using a ball mill. The mixture was dried at 373 K for several hours, and then calcined at 873 K for 10 h. The powder, which was sieved to under 54 μm, was pressed at 50 kgf/cm² into a rectangular shape (30 mm × 5 mm × 5 mm) and then isostatically pressed again at 2000 kgf/cm². These samples were sintered at 1673 K for 10 h in air. The crystal structure of the sintered sample was determined by X-ray diffactome-try (Rigaku Co, Ltd.) using Cu K_α radiation at room temperature.

The conductivity of the sintered samples was mea-sured by the DC four-probe method from room temper-ature to 1173 K. Platinum electrodes were attached to the samples by firing at 1173 K for 1 h in air. The high electrical conductivity above 573 K was measured after

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maintaining the given temperature for several hours in order to attain an equilibrium state.

To obtain the precise absorption spectra, a well-polished single crystal or flat thin film is needed. However, the KBr method for the sake of a powder sample is also useful to obtain qualitative results for a high optical absorption system, because the multiple reflections are not affected in the high absorption spectra. The powder samples were mixed with KBr powder in an agate mortar and pressed into pellets at 400 kgf/cm^2 in a vacuum. The optical absorption spectra of the pellets were measured at room temperature in the photon energy range between 1.3 eV and 4.2 eV using an ultraviolet-visible spectrometer (Shimadzu Co, Ltd. UV-1600).

3. Results and discussion

The X-ray powder diffraction patterns of the $Zn_{1-x-y}M_xM'_yO$ (M, M' = Al, In, Ga, Y) systems ($0 \leqq x + y \leqq 0.01$) and $Zn_{1-x}M_xO$ (M = Al, In, Ga) systems ($0 \leqq x \leqq 0.007$) were identified with that of ZnO except for slight shifts in the diffraction angles. When the total dopant was added above the solubility limit, the spinel phase of ZnM_2O_4 (M = Al, In) or an unknown phase were detected as impurities in all the systems. Therefore, the conductivity was measured for the samples, which included the dopant under the solubility limit. When the total dopant content increased in the single phase, the color of the sintered samples was changed from white to dark green. The relative density of all the sintered specimens, which was estimated from their dimensions and weight, was over 95%.

Arrhenius plots of the conductivity for the $Zn_{1-x}M_xO$ (M = Al, In, Ga: $0 \leqq x \leqq 0.003$) systems are shown in Fig. 1(a). According to the conduction behavior of the system, the materials changed from semiconducting conduction to a metallic one with the increasing dopant content. The mother substance of ZnO has the conduction band and the valence one originated from the sp^3 hybrid orbital of Zn4s and O2p, and has the donor level of Vö, $Zn_i^{\cdot}$ or $Zn_i^{\cdot\cdot}$[9]. In the $Zn_{1-x}M_xO$ (M = Al, In, Ga) systems, the donor level created by doping an aliovalent cation would also be added to the electronic structure and would overlap with the conduction band [3, 6]. The overlap would occur in the metallic conduction of the ZnO system. The same behavior was appeared in the $Zn_{1-x-y}M_xM'_yO$ (M, M' = Al, In, Ga, Y: $x + y = 0.003$) and $Zn_{0.997-y}Al_{0.003}In_yO$ ($0 \leqq y \leqq 0.007$) systems, which are shown in Fig. 1(b).

It was reported that a conductivity hysteresis versus temperature appeared in a low-temperature range at times and that the sintering condition influenced the conductivity of the ZnO system [9]. Therefore, the high-temperature conductivity is useful for obtaining the reproducible results, because the equilibrium of the defect state is easily attained and the defect content is precisely controlled [11, 16–18]. The compositional dependency of the conductivity for $Zn_{1-x}M_xO$ (M = In, Ga, Al) at 873 K is shown in Fig. 2(a). The conductivity of the $Zn_{1-x}M_xO$ (M = In, Ga) system increased with the dopant content at first. However, it showed a maximum value at $x = 0.003$, and then slightly decreased. The conductivity of the $Zn_{1-x}Al_xO$ system behaved simi-
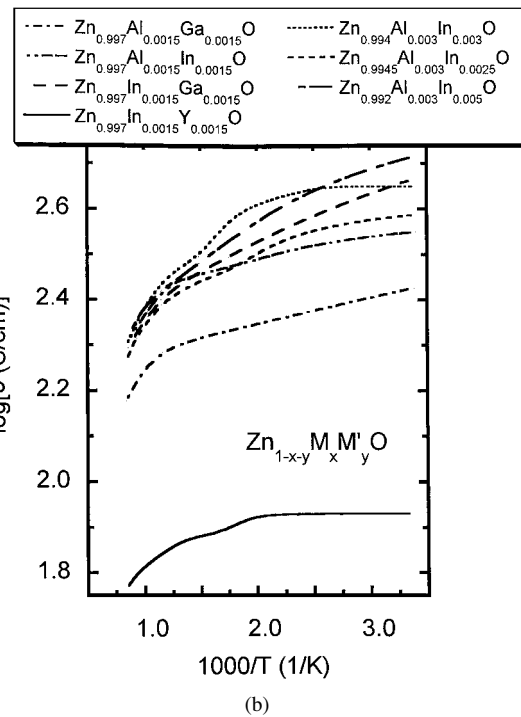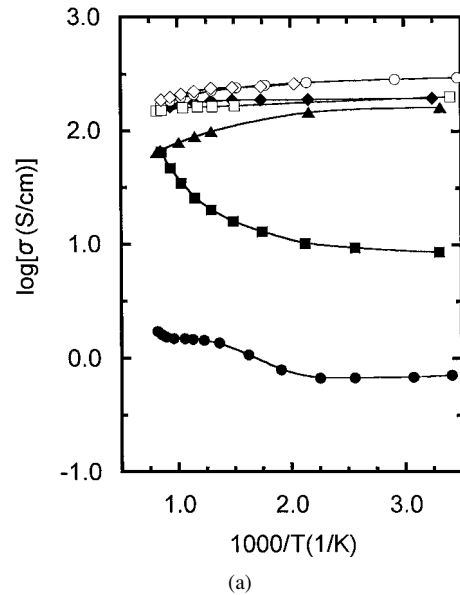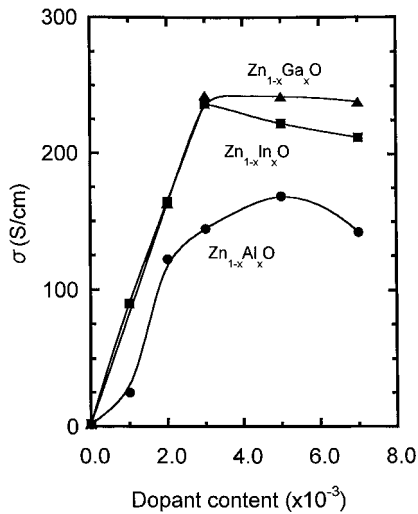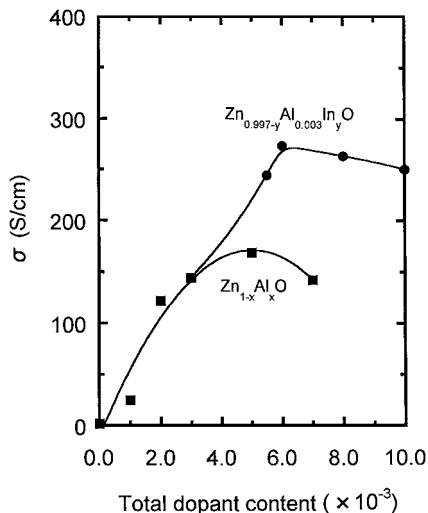
lar to that of the $Zn_{1-x}M_xO$ (M = In, Ga) system and showed a maximum value at $x = 0.005$. From the Hall coefficient measurement of the $Zn_{1-x}M_xO$ (M = In, Ga) system [12, 13], the electrical conductivity is influenced not only by the conduction carrier, but also by the impurity scattering effect.

On the other hand, the conductivity of the $Zn_{0.997-y}Al_{0.003}In_yO$ system at 873 K is shown as a function of the total dopant content in Fig. 2(b). In the same figure, the conductivity of the $Zn_{1-x}Al_xO$ system at 873 K is also displayed for comparison. The conductivity of the $Zn_{0.997-y}Al_{0.003}In_yO$ system was higher than that of the $Zn_{1-x}Al_xO$ system, when the total dopant content was the same. This result suggested

Figure 1 (a) Arrhenius plot of the $Zn_{1-x}M_xO$ (M = Al, In, Ga) system. Solid circle is ZnO: Solid square is $Zn_{0.999}Al_{0.001}O$: Solid diamond is $Zn_{0.997}Al_{0.003}O$: Solid triangle is $Zn_{0.999}In_{0.001}O$: Open circle is $Zn_{0.997}In_{0.003}O$: Open square is $Zn_{0.999}Ga_{0.001}O$: Open diamond is $Zn_{0.997}Ga_{0.003}O$. (b) Arrhenius plot of the $Zn_{1-x-y}M_xM'_yO$ (M, M' = Al, In, Ga, Y) system.

(a)

(b)

Figure 2 (a) The conductivity of $Zn_{1-x}M_xO$ (M = Al, In, Ga) system at 873 K as a function of dopant content. (b) The conductivity of $Zn_{0.997-y}Al_{0.003}M'_yO$ and $Zn_{1-x}Al_xO$ systems at 873 K as a function of the total dopant content.

Figure 3 The conductivity of the $Zn_{1-x}M_xO$ (M = Al, In, Ga: $x = 0.003, 0.005$) system and $Zn_{1-x-y}M_xM'_yO$ (M, M′ = Al, In, Ga, Y: $x = 0.003, 0.005$) system at 873 K as a function of the mean dopant-ion radii. The solid line represents the conductivity of the samples with the total dopant content of 0.005. The dotted line represents the conductivity of the samples with the total dopant content of 0.003.

samples with the total dopant content of 0.005. The dotted line represents the conductivity of the samples with the total dopant content of 0.003. It was found that each line was strongly dependent on the mean dopant-ion radii and that the maximum value of each line appeared around 0.51 Å of the mean dopant-ion radii. This result suggested that the degree of impurity scattering would be weak and the co-doping would be preferable for increasing the conductivity, when the mean ionic radii of the co-doped cations was about 0.51 Å.

In order to elucidate its behavior, the temperature dependency of the resistivity was examined in detail. For the composition having a metallic conduction, the resistivity (ρ) obeys Mattisen's law, which is explained by Equation (2).

$$\rho = \rho_{th} + \rho_i \quad (2)$$

The ρ_{th} is described in Equation (3)

$$\rho_{th} = mv/(ne^2) \cdot \frac{T}{\alpha} \quad (3)$$

in which m is the mass of the electron, v is the drift velocity of the electron, n is the carrier density, e is the electron charge, T is the temperature, and α is the proportionality constant. The ρ_{th} value is connected to the scattering of phonons and is proportional to temperature. The residual resistivity (ρ_i) is independent of temperature and is defined by formula (4),

$$\rho_i = mv/(ne^2) \cdot \frac{x_i}{a} \quad (4)$$

in which x_i is the impurity-atom density and a is the distance between the nearest neighbor of ions. In Fig. 4(a), the resistivity of the $Zn_{0.997}M_{0.003}O$ (M = Al, In, Ga) system and $Zn_{0.997}M_{0.0015}M'_{0.0015}O$ (M, M′ = Al, In, Ga) system is shown as a function of temperature. The slope of the resistivity of the systems containing the same total dopant content was almost the same as

that the mobility of the $Zn_{0.997-y}Al_{0.003}In_yO$ system would be higher than that of the $Zn_{1-x}Al_xO$ system. In the ZnO system, impurity scattering is reported to be one of the important factors for mobility [14]. The magnitude of the impurity scattering for this system would be strongly dependent on the dopant species because of their different ionic sizes. Therefore, the conductivity of the $Zn_{1-x}M_xO$ (M = In, Ga, Al) and $Zn_{1-x-y}M_xM'_yO$ (M, M′ = Al, In, Ga, Y) systems at 873 K as a function of the dopant-ion radii is displayed in Fig. 3. In the co-doped systems, the mean dopant-ion radii, which is defined by the following Equation (1), was introduced.

$$\text{mean dopant-ion radii} = r_M \times [x/(x + y)]$$
$$+ r_{M'} \times [y/(x + y)] \quad (1)$$

where r_M and $r_{M'}$ are the dopant-ion radii (Zn : 0.60 Å, Al : 0.39 Å, In : 0.62 Å, Ga : 0.47 Å, Y : 0.90 Å), which were reported by Shannon [15], and x and y are the composition ratios of the two respective kinds of dopant ions. The solid line represents the conductivity of the
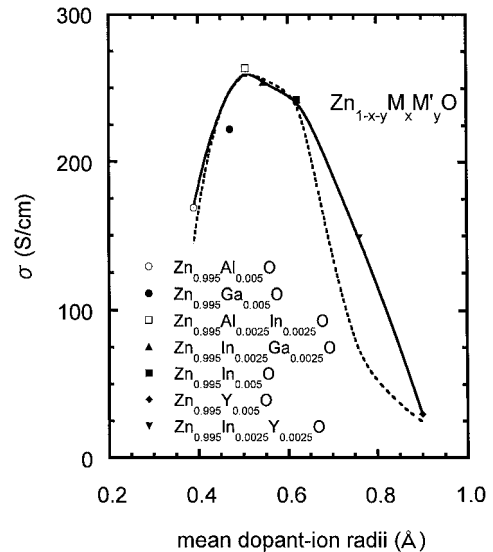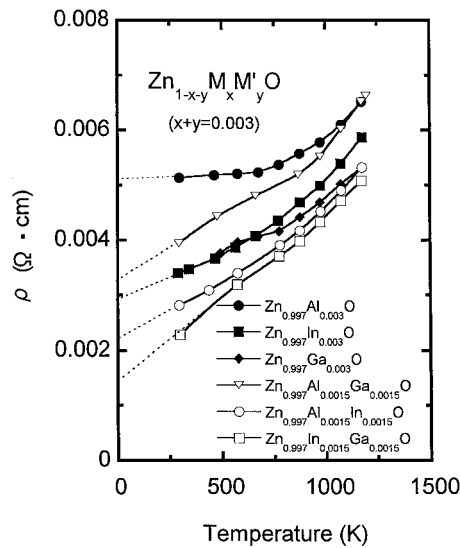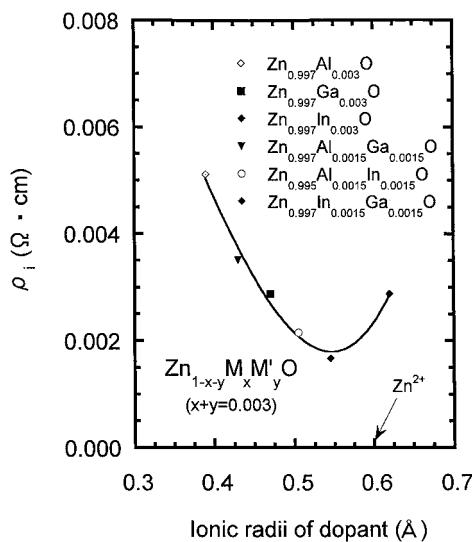
(a)

(b)

Figure 4 (a) The resistivity of the $Zn_{0.997}M_{0.003}O$ (M = Al, In, Ga) system and $Zn_{0.997}M_{0.0015}M'_{0.0015}O$ (M, M' = Al, In, Ga) system as a function of temperature. (b) The residual resistivity of the $Zn_{0.997}M_{0.003}O$ (M = Al, In, Ga) system and $Zn_{0.997}M_{0.0015}M'_{0.0015}O$ (M, M' = Al, In, Ga) system as a function of the mean dopant-ion radii.

the other in the temperature range above 873 K. Therefore, the difference in each resistivity (ρ) would depend on the residual resistivity (ρ_i). In this study, the resistivity was estimated from the intersection with the y-axis, when the resistivity was extrapolated to 0 K. The estimated residual resistivity is summarized in Fig. 4(b). The residual resistivity was found to depend on the mean dopant-ion radii and the minimum radii value appeared around 0.51 Å. In formula (4), the terms of $mv/(ne^2)$ and $1/a$ would be almost same compared with those of each system, because the dopant content and lattice parameter were the same. It is proposed that, if the dopant ion radii is greater than 0.51 Å, the aliovalent cation would more effectively work as a origin of the impurity scattering. This effect would increase the residual resistivity (ρ_i) as a result of the increase in x_i of formula (4).

In order to apply the ZnO system for transparent materials, the transparency in the visible region would be needed. In Fig. 5, the absorption
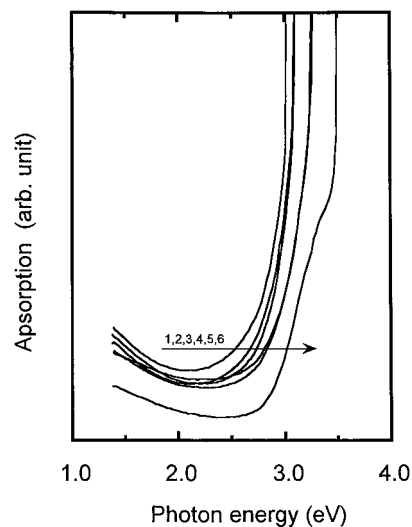

Figure 5 The absorption spectra of the $Zn_{1-x-y}M_xM'_yO$ (M, M' = Al, In) system and $Zn_{1-x}M_xO$ (M = Al, In, Ga) system. (1) $Zn_{0.997}Al_{0.003}O$: (2) $Zn_{0.997}In_{0.003}O$: (3) $Zn_{0.997}Ga_{0.003}O$: (4) ZnO: (5) $Zn_{0.997}Al_{0.0015}In_{0.0015}O$: (6) $Zn_{0.994}Al_{0.003}In_{0.003}O$.

spectra of the $Zn_{0.997}Al_{0.0015}In_yO$ system and $Zn_{0.997}M_{0.003}O$ (M = Al, In, Ga) system were displayed. The absorption edge of $Zn_{0.997}Al_{0.0015}In_{0.0015}O$ and $Zn_{0.994}Al_{0.003}In_{0.003}O$ shifted to high energy rather than that of ZnO. In the ZnO system, the donor level overlaps the conduction band when doping aliovalent cations and the metal-semiconductor transition occurs as shown in Fig. 1(a) and 1(b). In this case, the Bernstein-Moss shift [7, 8] would occur in the system and the electron excitation from the valence band to the conduction band would need a higher energy compared to the band gap of ZnO. Moreover, all these samples were found to show a high transparency in the visible region, so that the system would be suitable for transparent materials in the visible region.

4. Conclusions

In order to elucidate the dominating parameter of conductivity in the ZnO system, the conductivity of the $Zn_{1-x-y}M_xM'_yO$ (M, M' = Al, In, Ga, Y) $(0 \leqq x + y \leqq 0.01)$ and $Zn_{1-x}M_xO$ (M = Al, In, Ga) systems $(0 \leqq x \leqq 0.007)$ were measured from room temperature to 1173 K. The conductivity in the equilibrium state was strongly dependent not only on the dopant-ion content but also on the dopant-ion radii. The maximum conductivity appeared around 0.51 Å for the mean dopant-ion radii for all dopant contents. It is concluded that, if these mean dopant-ion radii were controlled in the ZnO system, the co-doping is preferable for improving the conductivity and widen the transparent optical region.

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