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Preparation of electrically conductive nano-powder of zinc oxide and application to transparent film coating

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ABSTRACT

Preparation, characterization and application of electro-conductive nano-powders of zinc oxide (ZnO) are reported. The aim of the present study is to clarify whether reflection or absorption of near infrared ray (NIR) is effective in the transparent conductive films of zinc oxide. It is shown that, in the case of powder coating films, the NIR is absorbed, while, in the case of physical vapour deposition (PVD) films, the NIR is simultaneously absorbed and reflected. These phenomena suggest any difference in relaxation mechanism of plasma oscillation of carrier electrons between different processes.

1. Introduction

It is well-known that metals exhibit brightness because carrier electrons reflect the visible light with lower frequency than plasma oscillation, which is so-called plasma reflection [1]. The lower electrical conductivity leads to the lower frequency of plasma oscillation. In semiconductors it is possible for the plasma oscillation to shift into infrared region, if the conductivity is controlled adequately. On the other hand, zinc oxide is known to be a wide-gap semiconductor with band-gap of 3.3 eV at room temperature [2] and therefore to be an ultraviolet absorber of shorter wavelength than 380 nm. Since zinc oxide becomes also n-type conductor easily, we expect to obtain the band-pass filter which blocks both of UV and IR and passes the visible light. With respects to safety and cost, the zinc oxide has possibility of transparent conducting material in place of indium tin oxide (ITO), if we could control its performance and stability. To do this it is necessary to characterize plasma oscillation in electro-conductive zinc oxides. Some extensive review articles summarized works on transparent conductive oxides (TCO) including carrier properties and processing [3,4]. However, powder coating of TCO has been seldom referred to irrespective of usefulness of powder processing. We have succeeded in preparation of fine powders of electro-conductive ZnO and, moreover, point out experimentally the remarkable discrepancy between powder coating and physical vapour deposition (PVD) of ZnO. We also refer to the difference in relaxation mechanism of carrier electrons between them. A spectroscopic study of powders and PVD films of ZnO is reported below.

2. Experimental and results

Powder samples of zinc oxides used in the present study are listed in Table 1. Al-doped ZnO powders (AZO) with commercial names of '23-K' and 'Pazet CK', and Ga-doped ZnO powder (GZO) with commercial name of 'Pazet GK' were prepared by wet processes in aqueous solution, while non-doped ZnO, pigment grade, was prepared by dry French process. Three doped ones are electro-conductive but non-doped one is non-conductive. Each of them was

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Table 1
Properties of the electro-conductive zinc oxide powders used in this report. For comparison a non-conductive grade is also included.

	Electro-conductive grades			Non-conductive
Composition	Al-doped ZnO Al_2O_3: 1 wt%	Al-doped ZnO Al_2O_3: 1 wt%	Ga-doped ZnO Ga_2O_3: 3 wt%	ZnO Non-doped
Commercial name	23-K	Pazet CK	Pazet GK	Pigment grade
Volume resistivity (Ω cm)[a]	300	1×10^4	30	>10^8
Specific surface area (m^2/g)	5	40	40	4
Primary particle size (nm)[b]	200	25	25	250
Mean particle size (μm)	6	5	5	0.5
Bulkiness (ml/100 g)	250	800	400	500

[a] 10 MPa compressed powder.
[b] By calculation from specific surface area.

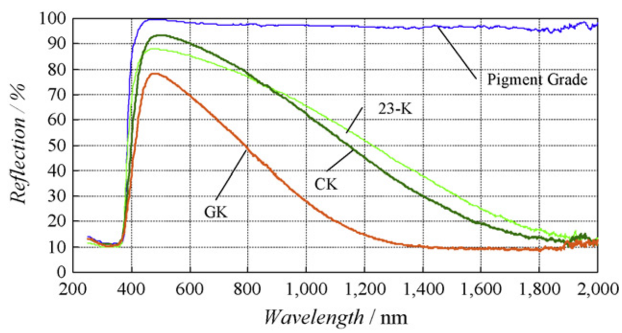

Fig. 1. Reflection spectra of the powders: one is non-conductive 'pigment grade' and the other three are electro-conductive grades; '23-K', 'Pazet CK', and 'Pazet GK'. Each powder sample was filled in a cell and used for measurement.

filled in a cell and its reflection spectrum was measured over the wavelength between 250 and 2000 nm by using a spectrophotometer (JASCO V570). The observed spectra were shown in Fig. 1.

Coating films of electro-conductive GZO were prepared by dispersing of Pazet GK in water and by coating with use of wire bars on PET films of 100 μm thickness. Three coating films with different thickness of 0.9, 1.8 and 2.5 μm were obtained, having electrical resistivities of 2.4, 1.2, 0.7 GΩ cm, respectively. Both of reflection and transmission spectra for the films were measured over wavelength between 200 and 2500 nm, which were shown in Fig. 2. Absorption spectra as shown in Fig. 3 were derived from the transmission and reflection spectra in Fig. 2, such that 'absorption = 100 − (transmission + reflection)'.

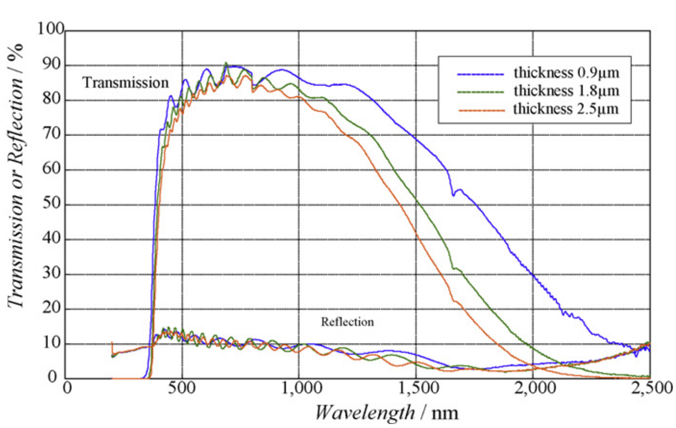

Fig. 2. Transmission and reflection spectra of the coating films of electro-conductive GZO 'Pazet GK' with dry thickness 0.9, 1.8, and 2.5 μm, respectively. The base film is PET with thickness of 100 μm, on which aqueous dispersion of the GZO was coated and dried.

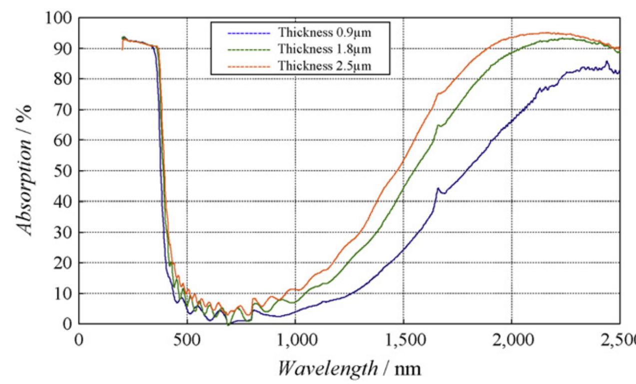

Fig. 3. Absorption spectra of the coating films of electro-conductive GZO 'Pazet GK' with dry thickness 0.9, 1.8, and 2.5 μm, respectively. The spectra were derived from the transmission and reflection spectra in Fig. 2 such as 'absorption = 100 − (transmission + reflection)'.

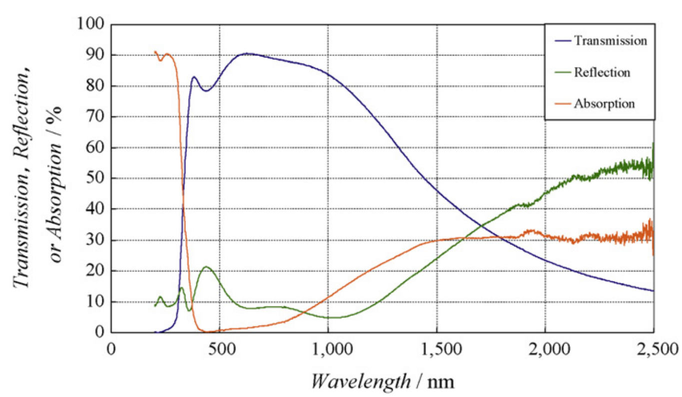

Fig. 4. Transmission, reflection, and absorption spectra of the electro-conductive GZO film with thickness of 300 nm on glass by means of ion plating method. The absorption spectrum was derived from the transmission and reflection spectra in the figure, such as 'absorption = 100 − (transmission + reflection)'.

A physical vapour deposition film was prepared on a glass plate by means of ion plating method [5]. Thickness of the deposited film was 300 nm and its resistivity was 0.3 mΩ cm. We measured both reflection and transmission spectra of the film as shown in Fig. 4. Absorption spectrum was derived in the same way as the wet coating films.

3. Discussion

3.1. Reflection by powders

Fig. 1 shows relatively high reflection in the region of visible light between 400 and 700 nm for all powders used, which means they are apparently almost white powders. Another common feature of spectra is low reflection below the wavelength of 380 nm, corresponding to the direct transition between valence band and conduction band in ZnO semiconductor. In the near infrared (NIR) region non-conductive zinc oxide keeps high reflection but conductive zinc oxides exhibit rapid decrease in reflection between 700 and 2500 nm depending on their electrical conductivities. The lower is the resistivity, the shorter is the wavelength for low reflection in NIR region. The decrease in reflection of the powders is due to NIR absorption as described below.

3.2. Transmission and reflection by wet coating films of GZO nano-powder

Fig. 2 shows transmission and reflection spectra of the wet coating films of electro-conductive GZO. Dry thickness of the films is 0.9, 1.8, and 2.5 μm, respectively. Sheet resistivity of the films is ranged close to 10 to the power of 8 or 9 Ω per square. High transmissions have been observed in the visible light region, which mean that these films are transparent. The lowest transmission has been observed in the UV region. It means UV is blocked by the films almost completely. Lowering of transmission has been observed in the NIR region.

From the transmission and the reflection spectra we have derived the absorption spectra of the wet coating films of GZO as shown in Fig. 3, such that absorption equals to {100%(incident) − (transmission% + reflection%)}. Absorption is highest in the UV region which is attributed to the direct transition of electrons from the valence band to the conduction band in the zinc oxide semiconductors, since the energy band-gap is known to be 3.3 eV corresponding to the wavelength of 380 nm [2]. Absorption is low in the visible light region.

In turn absorption increases in the NIR region as the wavelength increases which is related to electric conductivity and is attributed to the plasma oscillation of carrier electrons. Thus conductivity of the oxide is related to NIR absorption. In other word plasma oscillation of carrier electrons is effective to absorption of NIR, i.e., not reflection.

When we return to the powder reflection in Fig. 1, we have now the solution to the problem of lowering of powder reflections in the electro-conductive zinc oxides. The lowering reflection in the NIR region is related electric conductivity and is attributed to absorption by plasma oscillation of carrier electrons. On the other hand the low reflection of the powders in the UV region is attributed to the transition of electrons from the valence band to the conduction band in the zinc oxide semiconductors.

3.3. Reflection and absorption by dry coating film of GZO

High transparency for visible light was exhibited by the dry coating film as shown in Fig. 4, in which UV absorption was also exhibited. The transmission decreased and at the same time the reflection increased in the wavelength region longer than about 1100 nm. We could obtain the absorption spectrum as shown in Fig. 4 by the same way as the wet coating case as described in the previous section.

There is a marked contrast in reflection spectra in the NIR region between the wet coating film and the dry coating film. The dry coating film has exhibited reflection in the NIR region, but did not the wet coating films. Since reflection and absorption are related to each other via Kramers-Kronig relation [2], the contrast seems to suggest a difference of relaxation mechanism of carrier electrons between the dry and the wet coating films. It is be inferred that the depletion layer of carrier electron is thick in the powder grains compared to that in the dry coating film.

4. Summary

(1) Powders of zinc oxide including electro-conductive ones reflect the visible light well in wavelength between 400 and 700 nm. Electro-conductive powders of ZnO absorb NIR.
(2) Wet coating process of GZO nano-powders gives the transparent films with anti-static resistivity and NIR absorption.
(3) Dry process film of highly conductive GZO is transparent for visible light and reflects infrared. Partial absorption of NIR was also observed.
(4) The contrast in the reflection spectra between the dry and the wet coating films seems to suggest a difference of relaxation mechanism of carrier electrons relating to thickness of depletion layer of grains.

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