얇은막 산화철 광반도성 전극의 제조와 그 특성

PREPARATION AND CHARACTERIZATION ON THIN FILMS OF DOPED IRON OXIDE PHOTOSEMICONDUCTIVE ELECTRODES.

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Abstract - Thin films of MgO-doped and CaO-doped iron oxide were prepared by spray pyrolysis. The films were characterized by X-ray diffraction, scanning electron microscopy and voltammetric techniques. The photoelectrochemical behavior of thin film electrodes depended greatly on the doping level, sintering temperature, substrate temperature and added photosensitizing compounds in solution. Both the MgO and the CaO-doped iron oxide thin films prepared at high temperature showed p-type photoelectrochemical behavior, while the CaO-doped iron oxide thin films prepared at low temperature showed n-type photoelectrochemical behavior. This characteristic change was interpreted in terms of the surface structure change of the thin films and doping effect of metal oxide.

Key words - Iron oxide, Photoelectrochemistry, Thin film.

Iron oxide(α-Fe_2O_3) for the photoelectrolysis of water is inexpensive and stable in aqueous solution[1-2]. It has a relatively small bandgap (Eg=2.2eV) which can utilize more than 40% of solar energy. Gardner[3] and Geiger[4] first reported the p-type photosemiconductivity for a sintered mixture of Fe_2O_3 with MgO or CaO. Somorjai[5] reported the evolution of hydrogen through photoelectrolysis on a p-type photosemiconductor. Matsumoto[6] obtained stable photocathodic current in acidic solution using Pt-Pd alloy coated p-type $CaFe_2O_4$ disk electrode. On the other hand, it has been reported that Fe_2O_3 thin film electrode which has been made by chemical vapor deposition[7]or spray pyrolysis[8]has n-type photosemiconductivity. In this study, CaO and MgO doped Fe_2O_3 thin films are produced using spray pyrolysis method and their characteristics are examined.

Fe_2O_3 thin films are produced rather simply and inexpensively by modulating the sintering condition and spray pyrolysis method. Photoelectrochemical behavior and crystal structure of these CaO and MgO-doped Fe_2O_3 thin films have been examined by X-ray diffraction, scanning electron microscope and voltammetric techniques.

EXPERIMENTAL

Production of thin films: α-Fe_2O_3(Baker GR) and MgO(Mallinckrodt GR) or CaO(Kanto GR) for 0.1-15 wt.% were grounded and mixed well in the crucible and stirred for 1h in methanol. Methanol was evaporated and dried in room temperature. Each mixture was again stirred in nitric acid for 24h and sprayed through a nozzle (diameter : 0.2 mm) at constant pressure (3.5 kg/cm). The Pt foil substrate temperature (200 ℃ and 350 ℃) were maintained and sprayed 10 times for 3 min interval.

Produced films were dried for 1h at each temperature and placed in a Pt coated alumina crucible.The samples were sintered for more than 12h in an electric furnace(Honeywell DCP-7700) at 1100-1400℃ and then quanched in distilled water.

Measurements of structural and photoelectrochemicalcharacteristics: Siemens model D500 X-ray diffractometer (monochromated CuKα radiation) and Hitachi X-650 scanning electron microscope were used to microanalysis of the film surface. Cyclicvoltammogram and capacitance measurements were done by using PAR model 173 Potentiostat/Galvanostat which was equipped with PAR model 175 Universal Programmer. The light of 500W tungsten halogen lamp(General Electric) through quartz tube which was filled in water focused on surface of semiconductor. All the potential values are relported against a normal hydrogen electrode though the Ag/AgCl electrode was mainly used as a reference electrode.

RESULTS AND DISCUSSION

Structural characteristics of thin films : Thin films were produced by doping MgO or CaO with Fe_2O_3 followed by spray pyrolysis with various doping levels (0.1-15 wt.%) and changing the substrate temperature (200℃ and 350℃). The films of the mixture of Fe_2O_3 with MgO or CaO were sintered in a temperature range of 1100-1400℃ and each film was examined by X-ray diffraction analysis and the results are shown in Table 1.

TABLE 1. Characterization of MgO and CaO-doped Fe_2O_3 thin film on a Pt substrate prepared at substrate temperatures 200℃ and 350℃ (sintered at 1300℃).

Substrate Temperatures	Doping Materials	I_{spinel}	$I_{corundum}$	I_{spinel} / (I_{spinel} + $I_{corundum}$)
200 ℃	6 wt.% MgO	235	110	0.49
	8 wt.% MgO	257	88	0.74
	12 wt.% MgO	300	50	0.86
	7 wt.% CaO	179	85	0.68
	8 wt.% CaO	338	125	0.73
	11 wt.% CaO	342	40	0.89
350 ℃	6 wt.% MgO	235	110	0.49
	8 wt.% MgO	257	88	0.74
	12 wt.% MgO	300	50	0.86
	7 wt.% CaO	205	85	0.71
	8 wt.% CaO	370	125	0.75
	11 wt.% CaO	414	40	0.91

Table. 1 shows that the structural changes were obtained by varying the doping concentration and the substrate temperature. These X-ray diffraction patterns have both hexagonal corundum of α-Fe_2O_3 and cubic spinel of Fe_3O_4 ($MgFe_2O_4$ or $CaFe_2O_4$). Dieckman reported 1375℃, but we found the transition temperature from α-Fe_2O_3 to Fe_3O_4 is about 1300℃. Spinel structure formed mostly as $Mg_xFe_{3-x}O_4$ (or $Ca_xFe_{3-x}O_4$) is dependent on the change of substrate temperature and the doping ratio. Hemmatite structure of α-Fe_2O_3 (012, 116, 214) is generally observed with increasing formation of spinal structure when CaO is doped at 200℃ and increased when 8.0 wt.% of CaO is doped. Magnetite structure of Fe_3O_4 (311, 422, 333, 440) is generally appeared rather then hematite structure at 350℃ and it is especially increased when 11 wt.% of CaO is doped.

Photoelectrochemical characteristics of MgO-doped Fe_2O_3 thin films : Photoelectrochemical behavior of MgO-doped Fe_2O_3 thin film electrode was examined in 0.1N NaOH solution and the voltammograms for varying substrate temperature and doping concentration are shown in Fig.1 and Fig. 2. Fig. 1 represents that photocathodic-currnt is increased remarkably as increasing substrate temperature.

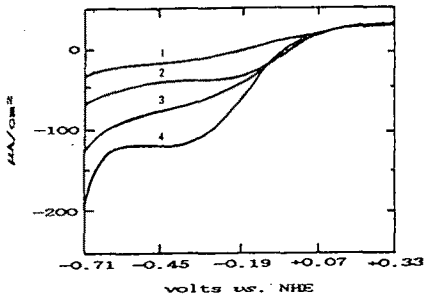

Fig.1. Photocurrent *vs.* potential (NHE) curves in 0.1N NaOH for 8.0 wt.% MgO-doped Fe_2O_3 thin film on a Pt substrate prepared with various substrate temperatures (1) 200℃, (2) 250℃, (3) 300℃ ,(4) 350℃.

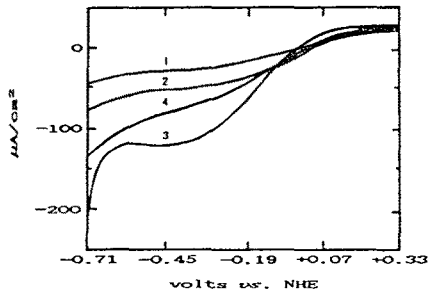

Fig.2. Photocurrent *vs.* potential (NHE) curves in 0.1 N NaOH according doping amounts of MgO in Fe_2O_3 thin films on a Pt substrate prepared at substrate temperature 350℃. (1) 3.0 wt.%,(2) 6.0 wt.%, (3) 8.0 wt.%, (4) 12.0 wt.% MgO.

Fig. 2 represents that photocathodic current is increased with the doping concentration of MgO and maximum p-type current is showed when 8.0 wt.% of MgO is doped.

Photoelectrochemical characteristics of CaO-doped Fe_2O_3 thin film electrodes : In the case of Fe_2O_3 doped with CaO thin film electrode, the relation ship between substrate temperature and photoelectrochemical characteristics has been examined. Photoanodiccurrent (n-type) has been obtained between - 0.3V and + 0.8V when the film was formed at low substrate temperature (200℃). Photocathodic current (p-type) has been obtained between + 0.5V and - 0.6V when the film was produced at high substrate temperature (350 ℃).

Photoanodic current is increased with doped ratio of CaO and the maximum photoanodic current has been obtained when 8.0 wt.% of CaO is doped at 200 ℃ (Fig.3). However the curve is showed maximum photocathodic current (p-type) when 11.0 wt.% of CaO is doped at 350 ℃ (Fig.4).

The intensity of n-type or p-type photocurrent is depended on the formation rate of the spinel structure because the transition from corundum to spinel increases with doped concentration in sintering process at high temperature (1300 ℃). The onset potential of these electrodes is + 0.08V for 8.0 wt.% doped n-type electrode(Fig.5) and is +0.10V for 11.0 wt.% doped p-type electrode(Fig.6)

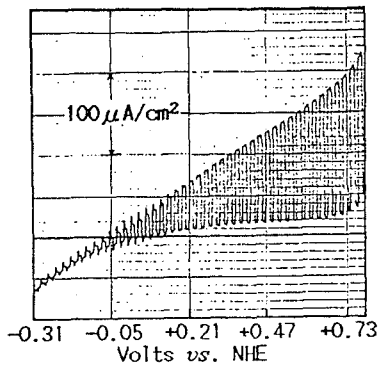

Fig.3. Photocurrent *vs.* potential (NHE) curves in 0.1N NaOH for 8.0 wt.% CaO-doped Fe_2O_3 thin film on a Pt substrate prepared at substrate temperature 200℃.

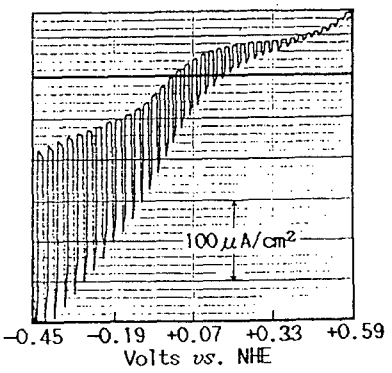

Fig.4. Photocurrent *vs.* potential (NHE) curves in 0.1N NaOH for 11.0 wt.% CaO-doped Fe_2O_3 thin film on a Pt substrate prepared at substrate temperature 350℃.

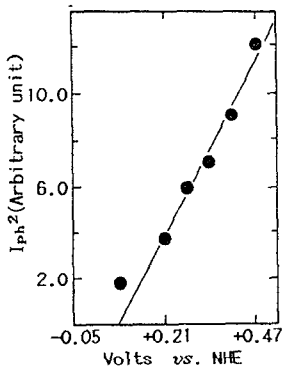

Fig.5. I_{ph}^2 *vs.* potential for 8.0 wt.% aO-doped Fe_2O_3 thin film on a Pt substrate at 200℃.

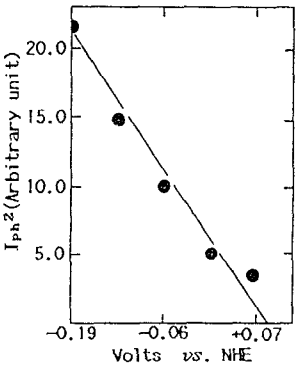

Fig.6. I_{ph}^2 *vs.* potential for 11.0 wt.% CaO-doped Fe_2O_3 thin film on a Pt substrate at 350℃.

These electrodes are relatively stable in 0.1 N NaOH solution but the voltage photocurrent curve had showed a little distortion and unstability due to corrosion of film surface after several hours. In the case of CaO-doped Fe_2O_3, the covalent character of iron-oxygen bond(Fe-O) is strengthened for considering their basicity when calcium shares the oxygen with iron(Ca←−→O−→←− Fe) and the bond formation of calcium -oxygen - -iron competes each other in spinel lattice structure.

Therefore, calcium becomes more unstable than magnesium because the basicity of calcium is stronger than magnesium and this affects spinel structure formation by varying substrate temperature before sintering. In case of the mixture over the specific doping concentration, a phenomena of solid solution formation would rather reduce the photocurrent.

Bandgap energy of doped Fe_2O_3 thin film electrode : Bandgap energy and transition types follow Butler[10] equation. $I_{ph} = (A/h\nu)(h\nu-E_g)^{n/2}$ From the plot of $h\nu$ *vs.* photocurrent $(I_{ph}h\nu)^{1/2}$, all of the doped Fe_2O_3 thin films confirm the proper form of indirect bandgap semiconductor(Fig.7). Each bandgap is 2.1 eV for 8.0 wt.% MgO wt.% CaO doped thin film (p-type) and 2.05 eV for 8.0 wt.% CaO doped thin film (n-type) from Fig.7.

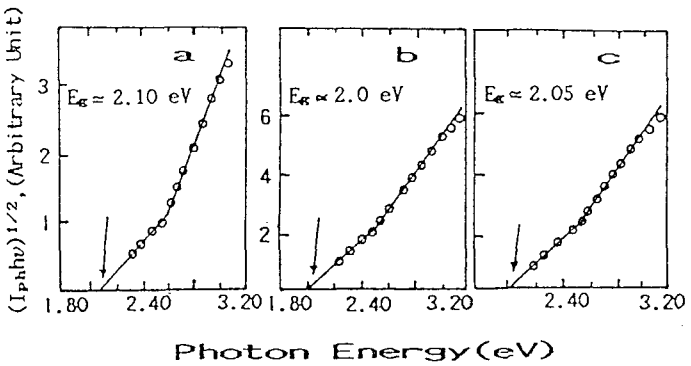

Fig.7. Indirect bandgap plot for the
a) 8.0 wt.% MgO-doped Fe_2O_3,
b) 11.0 wt.% CaO-doped Fe_2O_3,
c) 8.0 wt.% CaO-doped Fe_2O_3.

CONCLUSION CaO or MgO-doped Fe_2O_3 thin film electrodes affected largely on photoelectrochemical behavior by modulating substrate temperature and doping concentration at specific sintering temperature (1300℃). MgO-doped Fe_2O_3 film showed generally p-type photoelectrochemical behavior, whereas CaO-doped Fe_2O_3 depending on substrate temperature showed n-type at 200℃ and p-type at 350℃. P-type photosemi conductivity is increased when sintered at high temperature of substrate and magnetite structure is present. The bandgap energy of CaO or MgO-doped Fe_2O_3 thin film electrode is 2.0-2.1 eV and it is expected to utilize on photoelectrolysis of water.

REFERENCES

1. J. E. Turner, M. Hendewerk, J.Parmetr, D. Neiman and G. A. Somorjai, *J. Electrochem. Soc.*, 131, 1777(1984).
2. K. D. Sieber, C. Sanchez, J. E. Turner and G. A. Somorjai, *J. Chem. Soc., Faraday Trans.* I, 81, 1263 (1985).
3. (a) R. F. G. Gardner, F. Sweet and D. W. Tanner, *J. Chem. Phys. Solids*, 24, 1183 (1963). (b) D. Cormack, R. F. G. Geiger and R. L. Moss, *J. Catal.*, 17, 219 (1970).
4. G. H. Geiger and J. B. Wagner, Jr., *Trans. Metal Soc.* 233, 2092 (1965).
5. K. D. Sieber, C. Sanchez, J. E. Turner and G. A. Somorjai, *Mat. Res. Bull.*, 20, 153(1985).
6. (a) Y. Matsumoto, M. Omae, K. Sugiyama and E. Sato, *J. Phys. Chem.*, 91. 577 (1987). (b) Y. Matsumoto, K. Sugiyama and E. Sato, *J. Electrochem. Soc.*, 135, 98 (1988).
7. M. Sharon and B.M. Prasad, *Solar Energy Mat.*, 8, 457 (1983).
8. K. Itoh and J. O' M. Bockris, *J. Electrochem. Soc.* 131, 1266 (1984).
9. R.Dieckman, *Ber. Bunsenges. Phys. Chem.*, 86, 112 (1982).
10. M. A. Butler, D. S. Ginley and M. Eibschuts, *J. App. Phys.*, 48, 3070(1977).
11. L.R.Yeh and N. Hackerman, *J. Electrochem. Soc.*, 124, 833 (1977).
12. J. S. Curran and W. Gissler, *J. Electrochem. Soc.*, 126, 56 (1979).
13. R. Dieckman, Ber. Bunsenges. *Phys. Chem.*, 86, 112 (1982).
14. G. C. Kuczynski, "Ferrites" Proc. of the Int. Conf. P.87-95, Univer.Park Press, Baltimore, MD (1971).
15. a) M. A. Butler, *J. Appl. Phys.*, 48, 1914(1977). b) M. A. Butler, D. S. Ginley, and M. Eibschuts, *J. App. Phys.*, 48, 3070(1977).
16. L. C. Schumacher, S. M. Afara M. F. Weber, and M. J. Dignam, *J. Electrochem. Soc.*, 132, 2945 (1985).