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Photochemistry Group, Institute of Fundamental Studies, Hantana, Kandy (a) and Department of Physics, University of Ruhuna, Matara[1] (b)

Doping of Semiconductor Particles with Salts

By

K. TENNAKONE (a, b), S.W.M.S. WICKRAMANAYAKE (a),
P. SAMARASEKARA (b), and C.A.N. FERNANDO (b)

Studies of the properties of semiconductor particles have attracted much attention, especially in the context of solar energy conversion /1 to 3/. The characteristics of a semiconductor particle could differ significantly from those of the bulk material. It is known that the "size effect" alters band positions, band gap, and exciton energies /4 to 7/. In this note we point out that interesting phenomena not observed in bulk crystals could arise when semiconductor particles are doped with foreign molecules. The ionic constituents of the molecules can remain adsorbed at the surface or diffuse into the interior of the particle. The species adsorbed at the surface and those inside form two sets of donor or acceptor levels. Both types of levels can inject electrons and/or holes into the conduction and/or valence bands (Fig. 1). The important fact to note is that, unless the molecule as a whole (which is unlikely) or both its ionic constituents diffuse freely into the lattice, the doping of large crystals with molecules results in states populated near the immediate vicinity of the surface (i.e., in molecules that ionize into small and large components, the smaller cannot diffuse very far into the interior of the lattice, because of the electrostatic attraction of larger ions on the surface). It is clear that such states cannot contribute to bulk properties of a macroscopic crystal. In this note we present our observations on electrical transport properties of compacted amorphous titanium dioxide powder doped with different salts. The results clearly demonstrate that thermal activation energies and carrier mobilities of semiconductor particles can be easily altered by doping with different salts.

TiO_2 (anatase, Aldrich 99.9 %, particle size ≈ 5 nm) was doped with LiCl, LiI, NaI, KCl, CsI, Na_2SO_4, NH_4Cl, LiOH by the following method: 10 g of TiO_2

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[1] Matara, Sri Lanka.

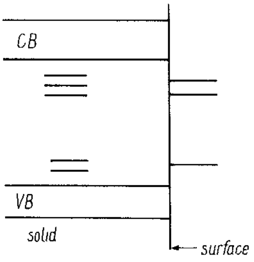

Fig. 1. Donor and acceptor levels located on the surface and the interior of a semiconductor particle

was mixed with a known weight of the salt (1 to 5 mg) and the mixture grounded after moistening with water was heated to 800 °C for several hours (in the case of ammonium salts the mixture was heated to 150 °C to avoid sublimation). The doped powder (allowed to cool in a water vapour free N_2 atmosphere) was compacted between gold coated stainless steel electrodes in a pyrex tube (diameter ≈ 0.6 cm) to a pressure of ≈ 10^2 MPa until a pellet (≈ 0.5 cm) was formed. Ends of the tube were sealed with epoxy resin, samples immersed in a thermostatic oil bath, and dc conductivities were measured (Computing Digital Multimeter, Takeda Riken). Current-voltage characteristics were found to be linear and no polarization effects were detected (this indicates that ionic conduction is negligible or absent). The sign of majority charge carriers in the samples was determined by Hall tests. If the compactation was carried out at a pressure exceeding 10^2 MPa reproducible results were obtained. Activation energies and sign of the majority charge carriers were found to be insensitive to changes in pressure.

Fig. 2a shows the plot of ln σ versus T^{-1} for TiO_2 doped with NaCl (at two different levels of doping) and undoped TiO_2 (dehydrated by heating to 800 °C).

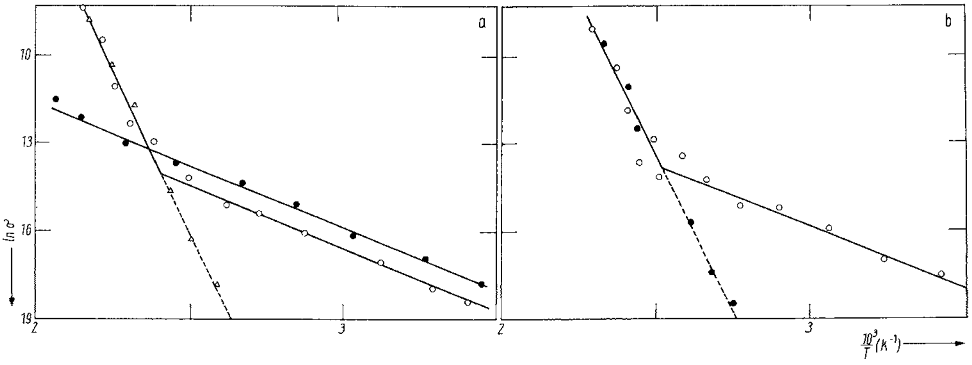

Fig. 2. Plot of ln σ (σ in Ω^{-1} m^{-1}) versus T^{-1} for TiO_2 a) doped with NaCl (● 10^{-4} wt%, ○ 10^{-5} wt%, △ undoped), and b) ○ hydrated (0.5 x 10^{-4} wt% H_2O), ● dehydrated

Table 1

Thermal activation energies (E) and sign of the majority charge carrier of TiO_2 doped with different compounds

impurity	E (eV)	type
undoped	1.80	n
LiCl	0.90	p
LiI	0.60	p
NaCl	0.35	p
NaF	0.40	n
KCl	0.36	p
CsI	0.78	n
Na_2SO_4	0.41	p
LiOH	0.92	n
NH_4Cl	0.49	n
H_2O	0.45	n

The activation energy for doped powder is ≈ 0.35 eV compared to 1.8 eV for the undoped powder. Furthermore when the level of doping is small, the intrinsic behaviour is seen at higher temperatures. This can be understood, when the level of doping is small,acceptor or donor levels get fully occupied or emptied. Samples doped with other salts show a similar behaviour. The activation energies and the sign of the majority charge carrier of TiO_2 doped with different salts are given in Table 1. It is important to note that water can also dope TiO_2 particles. Fig. 2b compares plots of ln σ versus T^{-1} for hydrated and dehydrated samples of TiO_2. Hydrated samples show intrinsic behaviour at higher temperatures.

The following observation shows that smaller ions diffuse into the lattice leaving larger ones on the surface. When TiO_2 doped with LiI is digested in water I^- is found to leach into solution (I^- on the surface is replaced by OH^-) and analysis by atomic absorption spectroscopy shows that there is no significant

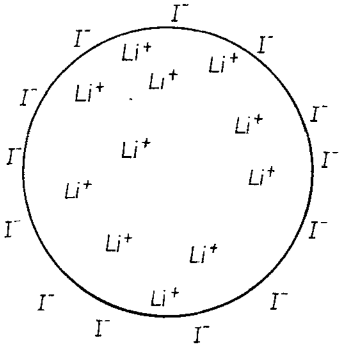

Fig. 3. TiO_2 particle doped with LiI

change in the lithium content of the powder (Fig. 3).

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References

/1/ A. J. BARD, Science 207, 139 (1980).
/2/ R. T. ROSS and A. J. NOZIK, J. appl. Phys. 53, 3813 (1982).
/3/ M. GRÄTZEL and A. J. FRANK, J. phys. Chem. 86, 2964 (1982).
/4/ J. L. ROSSETTI, J. L. ELLISON, J. M. GIBSON, and J. BRUS, J. chem. Phys. 80, 4464 (1984).
/5/ H. WELLER, U. KOCH, M. GUTIERREZ, and A. HENGLEIN, Ber. Bunsenges. phys. Chem. 88, 649 (1984).
/6/ H. WELLER, A. FOJTIK, and A. HENGLEIN, Chem. Phys. Letters 117, 485 (1985).
/7/ J. KIWI and C. MORRISON, J. phys. Chem. 88, 6146 (1984).

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