2574 © *1984 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 57, 2574—2577 (1984)* [Vol. 57, No. 9

Sensitization of Polycrystalline $SrTiO_3$ Photoanodes by Lanthanum Doping

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(Received January 30, 1984)

The behaviors of polycrystalline $La_xSr_{1-x}TiO_3(x\leq 0.05)$ electrodes in a photoelectrochemical cell for water decomposition have been investigated in aqueous NaOH electrolyte. The lanthanum substitution for strontium resulted in impressive visible photosensitization of the corresponding electrodes under anodic polarization. This visible photoresponse is based on the relatively deep subband gap states introduced into the forbidden band by lanthanum doping, in analogy with the polished undoped $SrTiO_3$ electrodes reported previously.

The practical realization of a photoelectrochemical system for the electrolysis of water will depend critically on the development of stable and efficient semiconductor electrodes. $SrTiO_3$ has received a great deal of attention as a semiconducting photoanode for the photodecomposition of water because it is chemically stable and requires no external biasing to generate H_2 and O_2.[1-12] However, it does not show visible light absorption due to its large band energy gap (3.2 ev). This is clearly insufficient for solar energy conversion applications. It is, therefore, very important to extend the $SrTiO_3$ spectral response in the visible region in realizing the efficient photodecomposition of water.

In our previous papers,[13,14] we have reported that mechanical polishing of undoped polycrystalline $SrTiO_3$ electrode surface results in an anomalous visible photoresponse extending to 600 nm with relatively negative onset potential of about −1V (*vs.* SCE, 1 M NaOH (1 M=1 mol dm^{-3})), and that the principal mechanism could be related to the introduction of subband states, $[\mathrm{Ti{:}3d}(t_{2g})]_{\mathrm{sub}}$ near the conduction band and $[\mathrm{O{:}2p}]_{\mathrm{sub}}$ near the valence band, by the mechanical polishing. These results suggests us the importance of controlling the formation of the subband states in the band gap by selected surface modifications or substitutions of Sr and/or Ti sites with appropriate dopants.

It is well-known that the reduced titnates such as *n*-TiO_2 and $SrTiO_3$ have a lot of defect energy levels in the forbidden band. The nature of these defects is largely dependent upon reduction temperature, oxygen activity, impurity additions, Sr/Ti ratio for $SrTiO_3$ and so on.[15-23] In general $SrTiO_3$ can be converted into *n*-type semiconductor by donor doping(*e.g.* niobium) and/or reduction in high vacuum or flowing hydrogen gas.[1,11,16,24] It is reasonable to think that lanthanum can be selected as a dopant of $SrTiO_3$ for three main reasons;

(i) stability in the trivalent state.

(ii) similarity of Sr^{2+} and La^{3+} ionic radii ($r_{Sr^{2+}}$= 0.140 nm, $r_{La^{3+}}$=0.132 nm) which insures a substitutional incorporation of lanthanum within the strontium sublattice.[25]

(iii) the compensation of extra charge resulting from partial $Sr^{2+}\rightarrow La^{3+}$ substitution may occur *via* electronic or lattice defects according to the reduction temperature and the oxygen partial pressure;[26,27]

$$Sr^{+2}_{1-x}La^{+3}_{x}Ti^{+4}O^{-2}_{3+x/2} \xrightarrow[\text{reduction}]{\text{Moderate}} Sr^{+2}_{1-x}La^{+3}_{x}Ti^{+4}_{1-y}Ti^{+3}_{y}O^{-2}_{3+x/2-y/2}, \quad (1)$$

$$\xrightarrow[\text{reduction}]{\text{Strong}} Sr^{+2}_{1-x}La^{+3}_{x}Ti^{+4}_{1-x}Ti^{+3}_{x}O^{-2}_{3}. \quad (2)$$

The presence of Ti^{+3} should confer *n*-character to $SrTiO_3$ and render the corresponding material performing as a photoanode, so La-doping can be expected to be a good method for controlling the formation of the subband states. Recently Odekirk and Blakemore have repored the enhancement of the photoactivity of lanthanum-doped, strongly reduced $SrTiO_3$ in microcrystalline ceramic form; La-doping ($x\leq 0.01$) provides an extention of the spectral response to longer wavelength and improves the quantum efficiency for all wavelengths.[28] Besides, Tsubomura *et al.* described briefly that lanthanum-doping showed week effect on the sensitization of $SrTiO_3$ photoanode at wavelengths longer than 400 nm.[29] The purpose of this paper is to study how lanthanum-doping changes the photoelectrochemical properties of polycrystalline $SrTiO_3$ electrodes and sensitizes it in more detail, in comparision with the mechanical polishing effects.

Experimental

The compounds synthesized in this work correspond to the compositions $Sr_{1-x}La_xTiO_{3+x/2}$ ($x\leq 0.05$). The polycrystalline samples have been prepared by heating the corresponding mixtures of $SrCO_3$, La_2O_3, and TiO_2 in air at 1350 °C for 16 h. The obtained powders were pelletized, sintered in air at 1400 °C for 16 h, and then reduced in flowing hydrogen gas at 1400 °C for 10—20 h to make them *n*-type. The conductivities of the samples after reduction were between 0.01—10 Ω^{-1} cm^{-1}.

Electrode preparation and electrochemical measurement procedures used to characterize the semiconductors have been described elsewhere.[13,14] 1 M NaOH solution was used as an electrolyte and all the potentials were referred to a saturated caromel electrode. To caluculate a quantum efficiency at each wavelength, the observed photocurrents were corrected for the spectral distribution of the light sourse(150W-Xe) and of the monochrometer. Impedance measurements have been performed a 10 kHz to get the flatband potential of the samples.

Results and Discussion

Figure 1 shows visible photocurrent (i_{vis})-potential curve of a La(0.5%)-doped sample (curve 1) under illumination of polychromatic visible light($\lambda \geq 400$ nm). For comparison, a similar curve of an polished undoped sample (curve 2) was also given in it. Dark currents were less than 10^{-6}A between −1.0 and 0.5 volts, and the visible photoreponses were very sharp. One can observed different behaviors of i_{vis}-potential curve for the above two; while the visible photocurrent of the polished undoped sample tends to be saturated as the potential becomes more positive, that of the lanthanum-doped sample increases almost linearly with a raising of the potential, at least below 1V. On the other hand, onset potential of i_{vis} for La-doped sample was found to be −0.8V, being more positive by 0.2V than that for the polished undoped sample. Such properties of the La-doped sample are very similar to those of Cr-doped $SrTiO_3$ photoanodes.[30]

As shown in Fig. 2, the effect of lanthanum-doping on the sensitization of $SrTiO_3$ becomes remarkable for $[La] \geq 0.5\%$. Too high concentration of the dopant ($[La] \geq 2\%$) leads to a decrease in the visible photocurrent as well as the full light photocurrent. Furthermore, mechanical polishing of the La-doped electrodes results in an enhancement of i_{vis} when $[La] \leq 1\%$ as shown in curve 2.

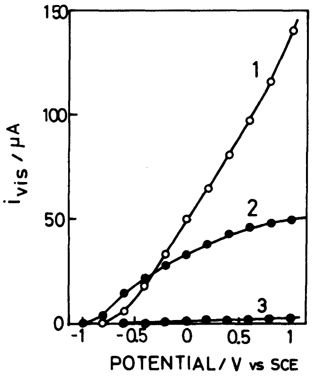

Fig. 1. Visible photocurrent-potential curves of La-(0.5 %)doped electrode(curve 1), the polished undoped electrode(curve 2), and the unpolished undoped electrode(curve 3) in 1 M NaOH ($\lambda \geq 400$ nm).

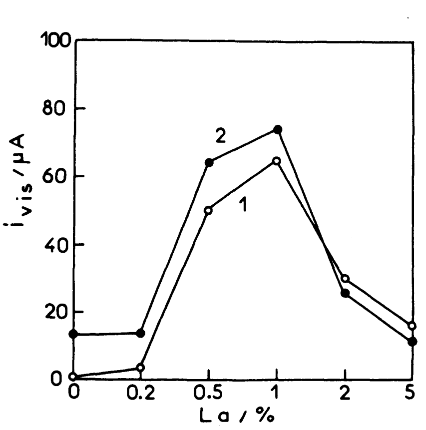

Fig. 2. Effect of the concentration of La-dopant on the sensitization of $SrTiO_3$ photoanode at 0 volt.
curve 1; before polishing, 2; after polishing.

Mott-Schottky plots were constructed from capacitance *vs.* electrode potential measurements a 10 kHz and are shown in Fig. 3. The flatband potentials (V_{fb}), obtained from the intercepts of $1/C^2$ *vs.* potential, were found to be −1.35, −1.30, and −1.20 volts for [La]=0, 0.2 and 0.5%, respectively. This means that La-doping causes V_{fb} to shift to more positive direction. A striking feature of the Mott-Schottky plot is the break near −1V. This feature suggests us the existance of two kinds of donor levels, one very close to the conduction band and the other deep below it, as discussed on n-Fe_2O_3 electrodes.[31] According to Goodenough, counter-cation charge compensation of La^{+3} for Sr^{+2} introduces no anion vacancies to induce Ti^{+4} ion displacements, and the larger charge La^{+3} *vs.* Sr^{+2} ions stabilizes from the conduction band a shallow trap state which sharply reduces electron mobility, hindering electron-hole separation.[32] Typically it may be the case of heavily La^{+3}-doping; the full light photocurrent of La(0.5%)-doped sample at 0 volt was less than one tenth of the undoped sample. Lanthanum has a stronger affinity to oxygen than strontium because of its higher electron negativity. The covalent bond between titanium (mainly Ti^{+3}) and oxygen, neighboring La^{+3} on the opposite side, must be considerably weakened. Therefore, the formation of the above deep donor level could be associated with this lowering in the covalency between Ti^{+3} and O^{-2}. Analogous to the previously proposed mechanism of the sensitization of the polished undoped $SrTiO_3$,[14] it is reasonable to think that the appearance of the visible photoresponse by La-doping should result from the introduction of the deep subband gap states, $[Ti;\ 3d(t_{2g})]_{sub}$, accompanying the simultaneous introduction of the acceptor subband gap states, $[O;\ 2p]_{sub}$, above the valence band.

Figure 4 shows the effect of La-doping on wavelength dependences of the quantum efficiency(η) at 0 volt. It is obvious from comparison for curve 1 with curve 2 that La-doping results in a decrease of U.V. photocurrent, being inconsistent with Odekirk's results.[28] Thus the subband gap energy states introduced by La-doping act as intermediate centers for secondary recombination processes between the photogenerated conduction band

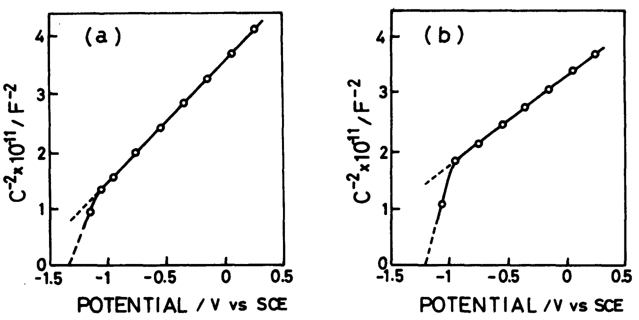

Fig. 3. Mott-Schottky plots at a frequency of 10 kHz for La-doped electrodes in 1 M NaOH.
(a) La(0.2 %), (b) La(0.5 %).

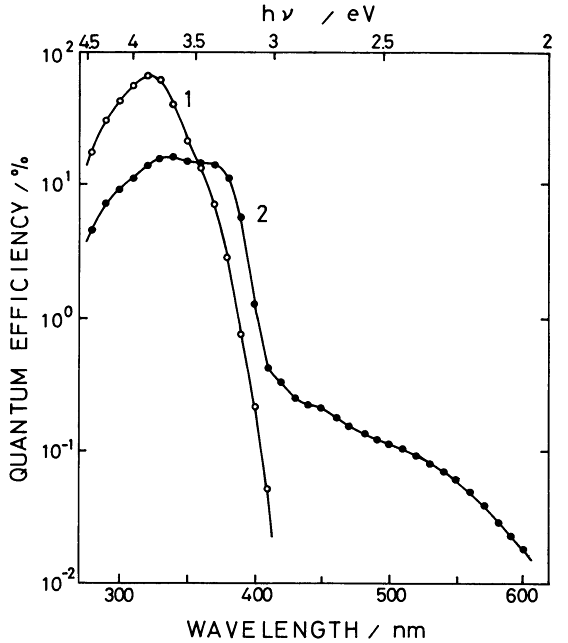

Fig. 4. Wavelength dependences of quantum efficiency of photocurrent for the undoped(curve 1) and La(1 %)doped(cuvre 2) electrodes at 0 volt in 1 M NaOH.

electrons and valence band holes. At the same time, La-doping leads to a remarkable increase of the visible photoresponse down to 600 nm. Besides, one can see the appearance of shoulder near 370 nm in curve 2 for the La-doped sample. From $(\eta h\nu)^{1/2}$ *vs.* $h\nu$ plots by using Fig. 4, we can deduced a reduced value of E_g (3.10 eV) for the La(0.5%)-doped sample together with E_g=3.15 eV for the undoped sample. Furthermore, $(\eta h\nu)^{1/2}$ *vs.* $h\nu$ plots in the longer wavelengths can be extrapolated to E_g'=1.9 eV which probably corresponds to the energy gap between the top of the valence band and [Ti; 3d(t_{2g})]$_{sub}$ or between the [O; 2p]$_{sub}$ and the bottom of the conduction band.

Based on the existence of the two subband gap energy states resulting from La-doping, two main mechanisms could be proposed to explain the production of the visible photocurrent. In mechanism I, the photocurrent is due to a direct electron excitation from the valence band to the empty [Ti; 3d(t_{2g})]$_{sub}$ followed by a tunneling process of the excited electron to the conduction band. In mechanism II the electrons are photoexcited from the [O; 2p]$_{sub}$ to the conduction band by the visible light. The photogenerated holes must then tunnel into the valence band. Both processes I and II could take place simultaneously, especially under high anodic polarization.

Figure 5-(a) illustrates a schematic energy diagram at the flatband potential for the La(0.5%)-doped electrode in 1M NaOH solution when the mechanism I is assumed to be more predominant. From the observed value of V_{fb}=−1.20 volts and an assumption of $E_c-E_f\simeq0.3$ eV, the bottom of the conduction band, E_c, was set at −1.50 volts *vs.* SCE. The [Ti; 3d(t_{2g})]$_{sub}$ states exist not only near the surface but also in the bulk of the electrode, differing from those in the polished undoped sample. As shown in Fig. 5-(b), anodic biasing is necessary for making the [Ti; 3d(t_{2g})]$_{sub}$ states empty and for accelerating the tunneling process. The onset potential of the visible photocurrent must be much more positive than V_{fb}. As described above, the visible photocurrent of the polished undoped sample has a tendency to be saturated as the potential raises up. It appears to reflect the limited state density of the subband gap energy levels which decreases rapidly with the depth from the surface. On the other hand, in the La-doped sample the raising of anodic potential leads to a continuous increase in the empty state density by lowering E_f, and consequently results in the continuous increase of the visible photocurrent, at least below 1 volt.

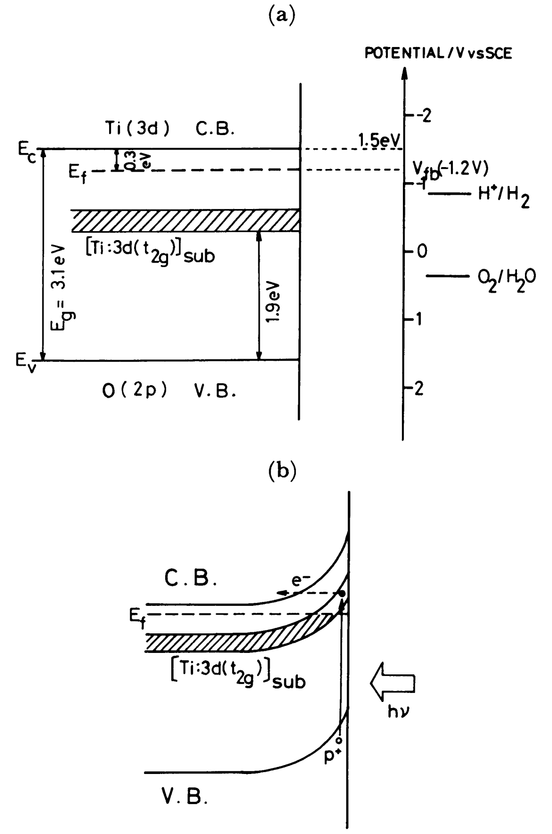

Fig. 5. Energy level diagram for La(0.5 %)-doped $SrTiO_3$ electrode at the flatband potential in 1 M NaOH (a) and a predominant mechanism giving rise to an anodic visible photoresponse (b).

Rerefences

1) T. Watanabe, A. Fujishima, and K. Honda, *Bull. Chem. Soc. Jpn.*, **49**, 355 (1976).

2) M. S. Wrighton, A. B. Ellis, P. T. Walczanski, P. L. Morse, M. B. Abrahamson, and D. S. Ginley, *J. Amer. Chem. Soc.*, **98**, 2774 (1976).

3) M. Okuda, K. Yoshida, and N. Tanaka, *J. Appl. Phys.*, **15**, 1599 (1976).

4) A. K. Ghosh and H. P. Maruska, *J. Electrochem. Soc.*, **124**, 1516 (1977).

5) M. H. Kung, H. S. Jarret, A. W. Sleight, and A. Ferretti, *J. Appl. Phys.*, **48**, 2463 (1977).

6) H. Yoneyama, M. Koizumi, and H. Tamura, *Bull. Chem. Soc. Jpn.*, **52**, 3449 (1979).

7) F. V. Kerchove, J. Vandermolen, W. P. Gomes, and F.

Cardon, Ber. Bunsenges. *Phys. Chem.*, **83**, 230 (1979).

8) F. P. Keffberg, K. Dwight, and A. Wold, *Solid State Commun.*, **30**, 443 (1979).

9) J. Vandermolen, W. P. Gomes, and F. Cardon, *J. Electrochem. Soc.*, **127**, 324 (1980).

10) J. F. Juliao, F. Decker, R. Brenzihofer, and M. Abramovich, *J. Electrochem. Soc.*, **127**, 2067 (1980).

11) J. B. Mavroides, J. A. Kafalas, and D. F. Kolesar, *Appl. Phys. Lett.*, **28**, 241 (1976).

12) M. A. Butler, M. Abramovich, F. Decker, and J, F. Juliao, *J Electrochem. Soc.*, **128**, 200 (1981).

13) B. Chang, G. Campet, J. Claverie, and P. Hagenmuller, *Solid State Commun.*, **43**, 335 (1982).

14) B. Chang, G, Campet, J. Claverie, P. Hagenmuller, and J. B. Goodenough, *J. Solid State Chem.*, **49**, 247 (1983).

15) A. K. Ghosh, F. G. Wakin, and R. R. Addiss, Jr., *Phys. Rev.*, **184**, 949 (1969).

16) E. Simanek, N. L. Huang Liu, and R. L. Wild, *J. Phys. Chem. Solids*, **33**, 951 (1972).

17) K. W. Blazey, R. Koch, and L. G. Bedorz, J. de Physique, Coll. C6, Suppl. No. 7, Tome 41, C6/511, 1980.

18) K. W. Blazey, R. Koch, and K. A. Müller, *Mat. Res. Bull.*, **16**, 1149 (1981).

19) U. Balachandran and N. G. Eror, *J. Solid State Chem.*, **39**, 351 (1981).

20) N.-H. Chan, R. K. Sharma, and D. M. Smyth, *J. Electrochem. Soc.*, **128**, 1762 (1981).

21) W. J. Lo and G. A. Somorjai, *Phys. Rev., B* **15**, 4942 (1978).

22) V. E. Henrich, G. Dresselhaus, and H. J. Zeiger, *Phys. Rev., B* **15**, 4908 (1978).

23) V. E. Henrich, G. Dresselhaus, and H. J. Zeiger, *J. Vac. Sci. Technol.*, **15**, 534 (1978).

24) H. P. R. Frederikse, W. R. Thurrer, and W. R. Hosler, *Phys. Rev.*, **134**, A442 (1964).

25) U. Balachandran and N. G. Eror, *Commun. Amer. Ceram. Soc., C* **64**, 75 (1981).

26) N. G. Eror and U. Balachadran, *J. Solid State Chem.*, **40**, 85 (1981).

27) B. Odekirk, U. Balachandran, N. G. Eror, and J. S. Blakemore, *Mat. Res. Bull.*, **17**, 199 (1982).

28) B. Odekirk and J. S. Blakemore, *J. Electrochem. Soc.*, **130**, 321 (1983).

29) M. Matsumoto, M. Hiramoto, and H. Tsubomura, *J. Electrochem. Soc.*, **130**, 326 (1983).

30) B. Chang, unpublished.

31) J. H. Kennedy and K. W. Frese, Jr., *J. Electrochem. Soc.*, **125**, 723 (1975).

32) G. Campet, M. P. Dare-Edwards, A. Hamnett, and J. B. Goodenough, *Nouv. J. Chimie*, **4**, 501 (1980).