# High Efficiency n-Si(Oxide)(Pt) Photoelectrochemical Cells using Chemically Controlled Tunnel Oxides

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Replacement of the thin native oxide of $SiO_2$ on n-Si photoelectrodes with ionic oxides which may contain other metal ions as dopants enhances the cell voltage and a 12% efficient cell is reported.

Photoelectrochemical (P.E.C.) cells offer a direct route to photoelectrolysis of water, photoreduction of $CO_2$, and integral storage of electricity through the use of solution redox couples. High P.E.C. efficiencies of 10—13% light into electricity conversion have been achieved for bare semiconductor crystals such as GaAs or $WS_2$ immersed in various redox electrolytes.[1] However, bare Si used in aqueous P.E.C. cells slowly oxidizes, and exhibits efficiencies of *ca.* 1% with lifetimes of only minutes, and there is considerable current interest in enhancing the performance of Si cells by the use of thin protective coatings. Lifetimes of many days[2] and efficiencies of up to 8%[3] have been reported for aqueous cells using n-Si photoanodes coated with Pt,[2] PtSi,[3] polypyrrole,[2] and organometallic silicon compounds.[4] However, the voltages are typically *ca.* 0.4 V compared to *ca.* 0.6 V expected from Si. We report how higher voltages can be achieved by chemical control of a thin layer of oxide, typically 10 Å thick to allow electron tunnelling, placed between the Si and an outer coating of Pt.

The photoelectrodes were prepared from n-Si single crystal wafers (Atomergic Chemetals Corp. N.Y.) on which ohmic contacts were made by heavily doping the back faces with phosphorus. The polished front (100) surfaces were etched for 4 min with a 2.9 M HF–9.7 M $NH_4F$ solution and washed for 7 min in a stream of triply distilled water. The crystals were quickly loaded into the vacuum chamber of an electron beam evaporator.† Oxide layers having an optimized thickness of 10 Å‡ were electron-beam deposited, and, after annealing for 5—30 min at 300—600 °C to remove structural defects and possible *X*-ray damage, a 10 Å thick layer of Pt was electron-beam deposited at 100—200 °C. Photoelectrodes were made up using black silicone rubber and were tested in either an aqueous $Br_3^-/Br^-$ or $I_3^-/I^-$ solution using a Pt counter electrode.

Table 1 shows the parameters of the best cells produced for each oxide combination after deposition and annealing conditions had been optimized. The results show that the replacement of $SiO_2$ with combinations of other oxides can result in the open circuit voltage increasing from 0.37 V (cell 6) to 0.57 V (cell 1), with the efficiency increasing from 7 to 12%, a value which is comparable to commercial Si photovoltaic cells. The lifetimes of the photoelectrodes varied considerably with the deposition conditions of the Pt and undoubtedly with the microscopic cleanliness of the surfaces. Integral Pt films could, however, be achieved, since the

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† *X*-Ray photoelectron spectroscopy (XPS or ESCA) revealed no $Si^{4+}$ or $Si^{2+}$ after this time lapse, although the surface was covered with several monolayers of adsorbed oxygen.

‡ As determined from a nearby quartz crystal monitor.

**Table 1.** Photoelectrochemical cell data for the oxidation of bromide ions to bromine at n-Si photoanodes coated with 10 Å of oxide of various compositions, and 10 Å of Pt[a] and illuminated at 1 'sun' external intensity.[b] The final wafers were cut in two, and XPS analyses of the oxide films were obtained, as given below.

| Cell[c] | Oxide | Efficiency, %[d] | $V_{oc}$[e]/V | $I_{sc}$[f]/mA $cm^{-2}$ | FF[g] |
|---|---|---|---|---|---|
| 1 | $Li_2O$–MgO[h] | 12 | 0.57 | 26 | 0.74 |
| 2 | $Li_2O$ (14%) MgO (64%) $SiO_2$ (22%)[h,i,j] | 11 | 0.55 | 30 | 0.59 |
| 3 | $Na_2O$ (0.6%) MgO (77%) $SiO_2$ (22%)[j] | 8 | 0.51 | 27 | 0.52 |
| 4 | MgO (78%) $SiO_2$ (22%)[j,k] | 6 | 0.51 | 25 | 0.45 |
| 5 | MgO (44%) $SiO_2$ (56%)[l] | 7 | 0.48 | 26 | 0.51 |
| 6 | Puratronic $SiO_2$ | 7 | 0.37 | 29 | 0.59 |
| 7 | Puratronic $ZrO_2$ | 7 | 0.41 | 29 | 0.57 |

[a] XPS showed no PtSi. [b] 92 mW $cm^{-2}$ from an Oriel solar simulator with an AM 1 filter. [c] Cells 1, 5, 6, and 7 used 1 Ω cm Si; cells 2, 3, and 4 used 0.1 Ω cm Si. [d] Efficiency of light into electrical conversion using anti-reflective glass but with no correction made for solution absorption. [e] Open circuit voltage. Voltages in the dark were zero. [f] Short circuit current. [g] Fill factor = maximum power/$V_{oc}I_{sc}$. [h] Evaporated from a pellet of MgO containing 7% lithium, obtained by calcination of $Mg(OH)_2$ precipitated in the presence of LiOH. [i] XPS data obtained from a separate coating without Pt, which interferes with Li. [j] $SiO_2$ originates from the n-Si. Only $Si^{4+}$ and $Si^0$ were evident in the XPS spectra, with a typical area ratio of 1 : 4. [k] From a Johnson Matthey (Puratronic) 99.999% MgO pellet. XPS showed *ca.* 100 p.p.m. Na in the coating with no other impurity metals detected. [l] Two stage deposition of MgO then $SiO_2$.

longest-lived cell so far has passed 20 000 C $cm^{-2}$ over 3 weeks continuous operation at 1 'sun' illumination initially in a $Br_3^-/Br^-$ solution (11% efficiency), then for most of the time in an $I_3^-/I^-$ solution (8% efficiency initially).

On the basis of these preliminary results, we suggest that the voltage enhancement originates from fixed negative charges in the mixed oxide films. It is well known in the field of metal–insulator–semiconductor photovoltaic cells that the mere presence of a tunnel oxide can favourably alter the current distribution to increase the voltage.[5] However, further voltage increases are predicted from fixed oxide charges, which induce changes in the semiconductor band bending, and also from certain interface states.[5] For the Si/$SiO_2$ interface, semiconductor chip technology has established that $Na^+$ at the impurity level of 10 p.p.m. will produce noticeable Si band bending owing to the fixed positive charges in the oxide.[6] For our n-Si cells, this would reduce the band bending and lower the voltage (*cf.* cell 6). While the MgO–$SiO_2$ mixed oxides (cells 4 and 5) show higher voltages, the addition of $Li_2O$ (cells 1 and 2) results in the highest voltages. Since the effect of $Li_2O$ with $SiO_2$ alone should be to reduce the voltage, the dominant interaction would appear to be between $Li_2O$ and MgO. In contrast to the interstitial doping of $Na^+$ into the open $SiO_2$ structure to give fixed positive charges, $Li^+$ is known to dope substitutionally into the close-packed MgO structure.[7] We propose that in the thin films, negative fixed charges are formed according to reaction (1), thereby withdrawing electrons from the Si conduction band and increasing the Si band bending and thus the cell voltages.

$$x/2(Li_2O) + (1 - x)MgO + x/4(O_2) + Si_{bulk} \rightarrow Si_{bulk}{}^{x+}/(Li_xMg_{1-x}O)^{x-} \qquad (1)$$

The comparatively low temperatures and short heating times used (3 min at 300 °C for cell 1) would limit the diffusion of Li or Mg into the Si, as confirmed by their absence (<100 p.p.m.) in the XPS spectra of cell 2 after chemical etching down to the Si surface. Since Mg enters Si partly interstitially to give n-type doping,[8] and the smaller Li would be expected to do the same, cell performance would be degraded by such doping, contrary to the results.

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## References

1 See, for example, the review: A. Heller, *Solar Energy*, 1982, **29**, 153.

2 T. Skotheim, L-G. Peterson, O. Inganas, and I. Lundstrom, *J. Electrochem. Soc.*, 1982, **129**, 1737.

3 F.-R. F. Fan, G. A. Hope, and A. J. Bard, *J. Electrochem. Soc.*, 1982, **129**, 1647.

4 A. B. Bocarsly, E. G. Walton, and M. S. Wrighton, *J. Am. Chem. Soc.*, 1980, **102**, 3390.

5 S. J. Fonash, *J. Appl. Phys.*, 1976, **47**, 3597.

6 E. H. Nicollian and J. R. Brews, 'MOS Physics and Technology,' Wiley, New York, 1982, ch. 15.

7 A. Cimino, M. Lo Jacono, P. Porta, and M. Valigi, *Z. Phys. Chem.* (*Frankfurt am Main*), 1968, **59**, 134.

8 H. Sigmund, *J. Electrochem. Soc.*, 1982, **129**, 2809.