Modulation of Flat-band Potential and Increase in Photovoltage for n-Si Electrodes by Formation of Halogen Atom Terminated Surface Bonds

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The flat-band potential (U_{FB}) of n-Si electrodes in concentrated hydrogen halide (HX) solutions, as determined from Mott-Schottky plots and the onset potential of photocurrent, shifts largely toward the negative with the decreasing electronegativity of halogen atoms. XPS studies have shown the presence of halogen atoms on the Si electrodes which were beforehand immersed in the HX solutions. The shift in U_{FB} can be explained as due to changes in surface potential by formation of Si-halogen surface termination bonds.

The flat-band potential (U_{FB}) of semiconductor electrodes is a key quantity in photoelectrochemistry because it determines the surface band energies with respect to the redox level in solution, or in other words, it determines the heights of energy barriers at semiconductor/solution interfaces and hence photovoltages of photoelectrochemical solar cells. The U_{FB} is closely related with surface potential and surface atomic structure of semiconductors, which are important in semiconductor solid devices. Theoretically, the U_{FB} of a semiconductor electrode is determined by surface dipoles arising from surface polar bonds and a potential drop in the outer Helmholtz layer arising from ion adsorption equilibria, as well as the electron affinity of the semiconductor and a small energy difference between the bottom of the conduction band and the Fermi level in the interior of the semiconductor.

It is well known that the U_{FB} of most semiconductor electrodes such as Si, GaAs, TiO_2, etc. is solely determined by solution pH (or adsorption equilibrium of H^+ or OH^-),[1] almost independent of adsorption of other ions and molecules, with an exception of CdS and analogs in low and medium pH solutions.[2] Therefore many workers have believed that it is very difficult to control U_{FB}. Recently Chazalviel reported that the U_{FB} of n-Si in acetonitrile shifted by ca. 0.4 V toward the negative by pre-treatment in methanol vapor and attributed the shift to the formation of surface Si-OCH_3 bond,[3] though such a bond is easily hydrolyzed in aqueous solution. In the present paper we report our new finding that the U_{FB} of n-Si in concentrated hydrogen halide (HX) solutions shifts toward the negative in the order of HF, HCl, HBr and HI, resulting in a large increase of photovoltage in HI/I_2 solutions. The shift can be attributed to the formation of surface Si-X (X = halogen atom) bonds.

Single crystal n-Si wafers [Shin-Etsu Handotai Co., CZ, (100), 0.8-1.16 Ωcm and (111), 1.30-1.75 Ωcm] were cut into pieces 8 × 8 mm^2 in area, washed in boiled acetone for 2 min, and etched with CP-4A (a mixture of H_2O, 50% HF, 60% HNO_3 and 99.7% CH_3COOH, 22:3:5:3 in volume) for 2 min and 50~1% HF for 2~10 min. Electrolyte solutions were prepared using special grade chemicals and ultrapure water purified from deionized water with a Milli Q SP. TOC. Water Purification System (with TOC less than 10 ppb as shown in catalog).

Figure 1 shows photocurrent-potential (j-U) curves for n-Si (100) in 7.6 M HI/0.05M I_2 and 8.6 M HBr/0.05 M Br_2 redox solutions. The n-Si surface is modified with colloidal Pt particles, by dropping a Pt colloid solution prepared by Bredig's method.[4] Firstly we found that the open-circuit photovoltagaes (V_{oc}) for n-Si in 7.6 M HI/0.05 M I_2 were sometimes much higher than the values obtained previously in the same solution,[5] reaching a value nearly the same as the V_{oc} for n-Si in 8.6 M HBr/0.05 M Br_2 (Figure 1). Later detailed experiments have shown that oxide-free n-Si just HF-etched gives such a high V_{oc} whereas n-Si having a thin Si-oxide layer gives low V_{oc} as previously obtained.[5] The thin Si-oxide layer was formed spontaneously when n-Si electrodes were kept in air or dipped in 8.6 M HBr/0.05 M Br_2 or 60% HNO_3.

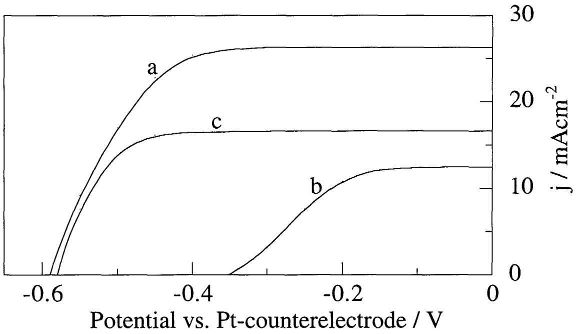

Figure 1. Solar cell characteristics for n-Si (100) : (a) thin oxide covered n-Si in 8.6 M HBr / 0.05 M Br_2, (b) the same n-Si as (a) in 7.6 M HI / 0.05 M I_2, and (c) oxide-free n-Si in 7.6 M HI / 0.05 M I_2.

In order to investigate why such a high V_{oc} is obtained for the just HF-etched n-Si in the HI/I_2, we measured the differential capacitance of the n-Si in various HX solutions (not containing X_2 as an oxidizing agent) and obtained Mott-Schottky plots. An example is shown in Figure 2. Very good straight lines, parallel to each other, are obtained. The result clearly shows that the U_{FB} shifts toward the negative in the order of HF, HCl, HBr and HI. The U_{FB} in the HI/I_2 redox solution was similar to or even slightly more negative than that in the HI solution, the details of which will be reported in a separate paper. Thus we can conclude that the high V_{oc} for the just HF-etched n-Si in the HI/I_2 is due to the shift of U_{FB} toward the negative in the HI/I_2 solution. Similar results were

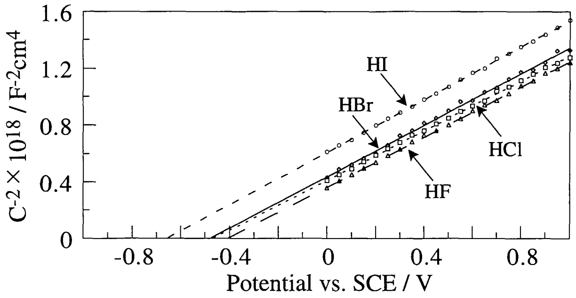

Figure 2. Mott-Schottky plots for n-Si (100) in various HX solutions.

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obtained for n-Si (111) electrodes.

In order to confirm the above conclusion, we also measured the onset potential of photocurrent (U_{on}) for just HF-etched n-Si in various HX solutions. The onset potential was determined as a potential at which the sign of photocurrent changes from anodic to cathodic. Figure 3 plots the obtained U_{on} values, together with U_{FB} determined from the Mott-Schottky plots, as a function of the electronegativity of halogen atoms.[6] A nearly linear relation between U_{on} (or U_{FB}) and the electronegativity of halogen atoms strongly indicates that the shifts of U_{FB} and U_{on} in the HX solutions are caused by the formation of surface Si-X bonds. This is because the surface potential (ϕ^s) arising from the surface Si-X bond is in proportion to the electrical dipole (μ^s) of the bond, which is, in turn, in proportion to the difference in the electronegativity of Si and X atoms ($\chi_{Si} - \chi_X$), provided that the surface concentration of the Si-X bond ($N_{Si\text{-}X}$) is the same in all the HX solutions.

$$\phi^s = N_{Si\text{-}X}\, \mu^s/\epsilon_0 \qquad (1)$$

$$\mu^s = \chi_X - \chi_{Si} \qquad (2)$$

where ϵ_0 is the permittivity of vacuum and μ^s is given in a Debye unit (1 debye = 3.334×10^{-30} C m) when Pauling's values are used for χ.[6,7]

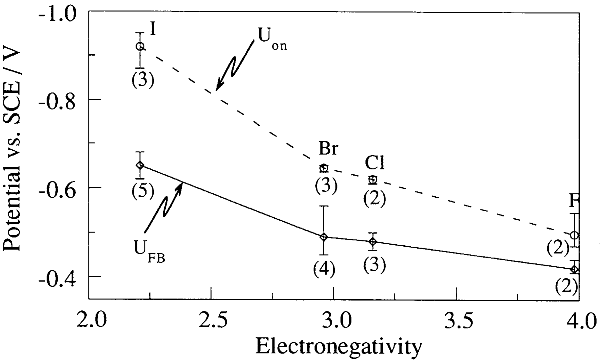

Figure 3. Plots of the onset potential of photocurrent (U_{on}) and the flat-band potential (U_{FB}) determined from Mott-Schottky plots for n-Si (100) against the electronegativity of halogen atoms. Circles represent averages of observed values whose distribution is shown by horizontal lines. Numerals in parentheses are the number of tested electrodes.

Inversely, the observed linear relation between U_{FB} (or U_{on}) and ($\chi_{Si} - \chi_X$) suggests that $N_{Si\text{-}X}$ is nearly the same in all the HX solutions. This can be explained as follows: It is reported that the surface O/Si atomic ratio, $\gamma_{O/Si}$, for Si (100) etched with 50% HF and washed with water is ca. 0.15,[8] as calculated from O and Si XPS peaks by correcting the contributions from inside Si atoms according to a method of Himpsel et al.[9] This implies that the HF-etched Si surface is covered with ca. 15% Si-OH, the remaining surface being covered with hydrides and a small amount of Si-F.[8] The Si-H bond is chemically stable,[10] but the Si-OH bond with a large ionic character will be able to cause the following substitution reaction when it is in contact with concentrated HX solutions.

$$\text{Si-OH} + X^- + H^+ \rightarrow \text{Si-X} + H_2O \qquad (3)$$

Thus we can expect that $N_{Si\text{-}X}$ is determined by the concentration of pre-existing Si-OH and becomes nearly constant in all the HX solutions.

Figure 4 shows an I 3d XPS spectrum for n-Si (100) which was beforehand immersed in 7.6 M HI and washed with water. The spectrum shows two peaks at 630.6 and 619.2 eV, assignable to I $3d_{3/2}$ and I $3d_{5/2}$, respectively. This result indicates that I atoms are really present on the HI-treated Si surface and that the Si-I bond is stable in aqueous solution, not undergoing hydrolysis on washing in water. The surface I/Si atomic ratio, $\gamma_{I/Si}$, was calculated from the XPS peaks by the same method as the literature[8,9] and we obtained a value of 0.027 after washing in water. By using this value and assuming equation (3) for the formation of the Si-I bond, a change in surface potential ($\Delta\phi^s$) can be estimated from equation (1) to be about 0.10 V, which is of the same order in magnitude as the observed shift of U_{FB}.

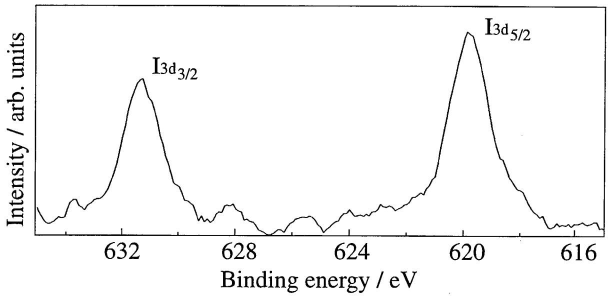

Figure 4. XPS spectrum in the I_{3d} region for n-Si (100) which was beforehand immersed in 7.6 M HI and washed in pure water.

The negative shift of U_{FB} in the HI/I_2 solution increases V_{oc} very much as already mentiond (Figure 1), which is an interesting result from the view-point of development of efficient and stable solar cells because the HI/I_2 is much less corrosive than the HBr/Br_2. Very recently it is reported that the modification of Si with iodine has a beneficial effect on the surface passivation,[11] making the minority carrier life time longer.[12] Thus, halogen atom termination at the Si surface may open a new promising aspect in Si technologies.

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