The Photoelectrochemical Oxidation of n-Si in Anhydrous HF-Acetonitrile

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ABSTRACT

The photoelectrochemical oxidation and dissolution of n-Si has been investigated in the absence of water and oxygen. Etch rates and photocurrents in an anhydrous HF-acetonitrile (MeCN) solution have been found to be directly proportional to light intensity up to at least 600 mW/cm^2, producing a spatially selective etch rate of greater than 4 μm/min. Four electron transfer reactions per silicon molecule were observed with a quantum yield greater than 3.3 due to electron injection from high energy reaction intermediates. The electrochemical oxidation of p-Si in HF-MeCN results in the formation of porous silicon which electroluminesces in an aqueous solution. This shows that molecular hydrogen, and silicon-oxygen species are not necessary in the generation of porous silicon to observe electroluminescence. In an aprotic electrolyte, where tetrabutylammonium tetrafluoroborate was used as both the supporting electrolyte and source of fluoride in MeCN, photo-induced etching of n-Si was observed with a quantum efficiency of 1.9. This indicates that the oxidation and dissolution mechanism of Si in MeCN can occur without protons.

The photoelectrochemical (PEC) dissolution of n-Si in aqueous fluoride containing electrolytes is complicated by the formation of oxide intermediates and the rate of their dissolution.[1,2] Although SiO_2 is soluble in aqueous fluoride solutions, the oxide formation and dissolution process are an important part of the electrochemical behavior of the semiconductor. At modest potentials, a porous silicon layer is formed, along with the evolution of hydrogen gas as the reaction intermediates are chemically oxidized by the electrolyte.[3-6] The mechanism of silicon dissolution in the formation of porous silicon has been the subject of several recent studies because of the luminescence from it (for example, Ref. 5 and 6). At more positive potentials, the reaction rate is governed by the dissolution of a surface oxide intermediate resulting in a polished surface.

The PEC etching and dissolution process is of interest for several reasons. This process offers the possibility of etching three-dimensional features in silicon, such as trench capacitors, lenses, and through wafer via-holes.[7] Second, porous silicon has many potential applications and can be formed electrochemically. Third, the mechanism of chemical etching of silicon, dissolution of SiO_2, and the hydrophobic nature of bare Si is of interest particularly with respect to silicon processing and surface properties. Finally, the investigation of the electrode mechanism and energy levels of the reaction intermediates is important to the development of a fundamental understanding of the oxidation and dissolution processes.

In this paper the photoelectrochemical dissolution of n-Si has been investigated in an anhydrous, fluoride containing electrolyte. The quantum efficiency and electron efficiency of the reaction have been investigated for the first time in the absence of water. The etching process was also studied in the absence of protons using tetrabutylammonium tetrafluoroborate (TBAFB) as both a supporting electrolyte and fluoride complexing agent.

Experimental

The (100) silicon samples were obtained from MEMC (Dallas, Texas). The n-Si was doped with phosphorus to a resistivity of 1-10 Ω-cm. The p-Si was doped and had a resistivity of 11-15 Ω-cm. Ohmic contacts were made to the semiconductors by coating the back with a gallium indium alloy, forming a tunnel diode. The samples were mounted so as to cover a hole drilled through a Teflon block. To protect the MeCN solution from atmospheric moisture and oxygen, the fluoride solution was placed in the drilled cavity while in an inert atmosphere dry box (Vacuum Atmospheres Company, Hawthorne, California) where the oxygen and water content were each maintained below 2 ppm. The electrolyte solution contained in the drilled cavity was covered with, but was not in contact with, a glass window to enable experimentation outside of the dry box. A similar cell construction was also used in which the solution was in contact with a sapphire window. No chemical etching of the sapphire took place. The cell was sandwiched between two Teflon blocks using Teflon o-rings as seals. The cell was fitted with a platinum wire counterelectrode and silver wire pseudo reference. All data obtained in MeCN were corrected to the saturated calomel electrode (SCE). For the aqueous studies, the reactor geometry was maintained; however, slight modifications were made to allow the use of an SCE as the reference electrode.

Anhydrous acetonitrile (<50 ppm H_2O) was obtained from Aldrich Chemical Company Incorporated (Milwaukee, Wisconsin) and was further purified to less than 5 ppm water.[8] The TBAFB was also obtained from Aldrich, and was dried under vacuum. Electrochemical grade tetrabutylammonium perchlorate (TBAP), Fluka Chemical Corporation. (Ronkonkoma, New York), was used as the supporting electrolyte. Semiconductor purity anhydrous HF was obtained from Matheson Gas Products (East Rutherford, New Jersey). Reagent grade aqueous HF, J.T. Baker (Phillipsburg, New Jersey), was used in the aqueous studies. Reagent grade ammonium hydroxide, Fisher Scientific (Fair Lawn, New Jersey) was used to buffer the solution.

The electrochemical measurements were made using an EG&G PARC 273 (Princeton, New Jersey) potentiostat. A 270 W quartz tungsten halogen lamp was used to generate a maximum white light intensity of 600 mW/cm^2. A 0.62 mW HeNe laser with a beam width of 0.47 mm was used in the etching studies.

Results

The PEC behavior of n-Si in 2*M* HF, 0.25*M* TBAP in MeCN, and 2*M* HF, 1*M* NH_4F in H_2O is shown in Fig. 1, curves A and B, respectively. The surface was illuminated with a 300 mW/cm^2 quartz tungsten halogen white light source. Curve C is the dark current response of n-Si in the MeCN solution, which is similar to the dark current in the aqueous solution. The initial potential for the voltage sweeps was negative of the flatband potential (V_{FB}) and the sweep direction was toward positive potentials. The onset of the photo-oxidation current was observed at −0.6 and −0.5 V *vs.* SCE for the MeCN and water solutions, respectively, which is approximately V_{FB} in each solution. This flatband potential is approximately 0.5 V positive of that previously reported by Laser *et al.*[9] but similar to that reported by Byker *et al.*[10] and Chazalviel *et al.*[11] in MeCN with TBAP as the supporting electrolyte. At potentials positive of V_{FB}, a Schottky barrier is formed within the n-Si, and photogenerated holes migrate to the semiconductor-solution interface where they can participate in faradaic processes. At potentials between −0.5 and +0.5 in the aqueous solution (Fig. 1, curve B), hydrogen

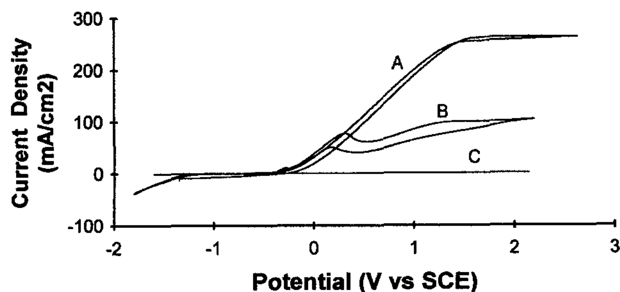

Fig. 1. The i-V behavior of n-Si (scan rate = 0.5 V/s) illuminated with a 300 mW/cm^2 quartz tungsten halogen light source in (A) HF (2*M*), TBAP (0.25*M*), MeCN (B) HF (2*M*), NH_4F (1*M*), H_2O and (C) in darkness in HF (2*M*), TBAP (0.25*M*), MeCN.

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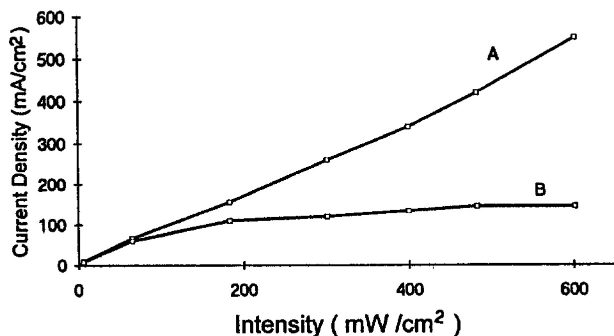

Fig. 2. Curve A: photocurrent vs. white light intensity in HF (2*M*), TBAP (0.25*M*), MeCN at 0.5 V vs. SCE. Curve B: photocurrent at 0.5 V vs. SCE in HF (2*M*), NH_4F (1*M*), H_2O.

bubbles were observed on the silicon surface due to the chemical oxidation of reaction intermediates by water. At higher mass transfer rates, the gas evolution increased. The current peak at +0.3 V is commonly called the critical current, i_{crit}. The potential and magnitude of the peak are dependent upon solution pH, doping density, HF concentration, crystal orientation, and illumination intensity.[1,5] Between the onset current and i_{crit}, a porous silicon layer is formed. At currents sufficiently greater than i_{crit}, the current is limited by the dissolution of the oxide, and polishing takes place. Of particular importance in aqueous solutions at high intensities or potentials are the observations that the current is not directly proportional to the flux of holes, the current density and reaction products are potential dependent, and oxide intermediates determine the rate and nature of the dissolution. The spatial resolution of the PEC etched features in aqueous solutions is limited by the reflection from gas bubbles, and the slow dissolution of the oxides which allows surface diffusion of photogenerated holes.[7]

Although positive feedback was used for Fig. 1, curve A, some uncompensated solution resistance remained which affected the slope of the rising portion of the curve. The illumination intensity was the same as that in Fig. 1, curve B. An intensity limited plateau spanning a wide voltage range with no critical current peak was observed. In contrast to the aqueous system, no hydrogen bubbles were observed at any potential.

The relationship between the photocurrent and illumination intensity was investigated with a white light source and neutral density filters, and is shown in Fig. 2. In MeCN (curve A), the current density was directly proportional to light intensity up to at least 600 mW/cm^2 (the lamp power limit). In the aqueous solution (curve B), the current was directly proportional to light intensity up to approximately 50 mW/cm^2. At higher intensity, the current became nearly independent of light intensity, indicating that the rate limiting process was no longer the supply of holes to the surface, but rather the dissolution of the products.

The photon efficiency and number of equivalents per mole were investigated using a 0.62 mW HeNe laser so that the photon flux could be accurately calculated. The incident intensity was corrected for reflection assuming normal incidence and using the index of refraction at 632.8 nm for each medium through which the beam passed. The measured photocurrent was relatively constant with time. No estimate of recombination within the silicon was made. The spatial profile of the holes etched in n-Si using HF-MeCN was Gaussian shaped and replicated the intensity profile of the laser beam. In the aqueous HF solution, the etched holes did not replicate the profile of the laser beam, and were significantly shallower due to the lower photocurrent. The volume of Si dissolved was determined by assuming radial symmetry and integrating the depth profile of the etched hole. Based on the quantity of material removed, four electrons were associated with the dissolution of each atom of silicon in MeCN, at all intensities investigated. This is in contrast to a value of 2-4 electrons per silicon atom in aqueous solutions.[3,4,12] The evolution of hydrogen gas and 2 electrons per silicon have been observed in aqueous solutions.[6] Based on the beam power and current, 3.3 electrons were measured in the external circuit for each photon incident on the n-Si in MeCN, whereas, the quantum efficiency for the aqueous system using the HeNe laser was 1.2. Thus, in MeCN each photogenerated hole produces at least 3.3 electrons in the external circuit. In aqueous solutions at low intensity (less than 5 μW/cm^2), it has been shown that the quantum efficiency is as high as four electrons per photon (current quadrupling).[2,13,14] However, the quantum efficiency in aqueous solutions approached one at higher intensities and reliable experimental results reportedly[12,14] could not be obtained at high intensities due to surface oxide formation. The reactions in MeCN are not subject to interference by water. An efficiency of four electrons per photon in MeCN would require that only one of the four electron transfer steps is photo-initiated and the remaining three occur through electron injection.

The electrochemical oxidation and dissolution of p-Si in HF-MeCN was investigated and compared to that of n-Si. A sharp rise in the anodic current was observed at potentials positive of about 0.1 V *vs.* SCE (approximately V_{FB} for p-Si) because of the high concentration of holes at the semiconductor-solution interface. Four electrons were observed in the external circuit for each Si atom oxidized. The current density saturated at approximately 1.4 A/cm^2, presumably limited by the solubility of the reaction products. This extraordinarily high current density was more than 25 times that observed in HF-H_2O. Electroluminescence was observed from the p-Si prepared in MeCN when anodized in an aqueous 0.25*M* KCl solution. No luminescence was observed when the p-Si sample was anodized in MeCN with 0.25*M* TBAP. The observation of electroluminescence from p-Si prepared in HF-MeCN, indicates that it is not necessary to form silicon-oxygen (Si-O-) compounds, or molecular hydrogen during the formation of porous silicon, to obtain luminescence.

The surfaces of etched p- and n-type Si were examined using a scanning electron microscope (SEM). The p-Si sample was prepared by electrochemical etching in 2.5*M* HF, 0.25*M* TBAP, MeCN solution for 10 min at 75 mA/cm^2. The n-Si sample was etched for 10 min using a 0.62 mW HeNe laser at 0.5 V *vs.* SCE. The surface of both samples was similar to the topography of porous silicon; however, a detailed analysis has not been undertaken.

To investigate the role of protons in the photo-oxidation of n-Si, a 0.5*M* tetrabutylammonium tetrafluoroborate (TBAFB), MeCN solution was used. Very dry fluoride salts, such as TBAF, are not stable because of MeCN decomposition.[15] Free fluoride slowly reacts with MeCN to form HF_2^- and CH_2CN^- resulting in a yellow discoloration of the MeCN. In MeCN, the dissociation of the fluoroborate ion to F^- and BF_3 is sufficient to complex the photo-oxidized Si surface without the presence of protons. The TBAFB-MeCN electrolyte remained colorless for weeks, demonstrating that the rate of MeCN decomposition and buildup of HF_2^- was slow. This aprotic solvent was used to study the quantum efficiency and number of equivalents/mole for the oxidation of Si. Based on the current and quantity of material removed, 4.2 electrons were observed for the oxidation and dissolution of each Si atom, just as in HF-MeCN. The quantum efficiency was 1.9 electrons per photon which is lower than the value of 3.3 for HF in MeCN. That is, there were two photo-initiated steps and two electron injection steps. The etching of n-Si in TBAFB-MeCN shows that protons are not required for the photo-oxidation and dissolution process.

Discussion

It is of interest to contrast the mechanism for the oxidation and dissolution of silicon in aqueous solutions to these results in MeCN. Figure 3A shows the hydrogen terminated (100) Si surface. Both the (100) and (111) Si faces are chemically and electrochemically stable in aqueous and MeCN fluoride containing electrolytes. That is, there is no spontaneous chemical attack of the silicon by the electrolyte, and there are very low dark currents (corrosion). Recent investigations, such as Ref. 6, suggest that the stable silicon surface in aqueous HF solutions is a hydride as opposed to a fluoride surface.[2] In either case, the silicon oxidation sequence in water is initiated by a hole. One of the Si-H surface bonds (Fig. 3A) is oxidized and the electron density on the Si is reduced which then allows it to be complexed by fluoride (or hydroxide). Due to the polarizing influence of the Si-F bond, the second Si-H bond (Fig. 3B) is susceptible to fluoride (or hydroxide) attack. Electron injection into the semiconductor conduction band then occurs at the second Si-H bond because the fluoride fills the bonding orbital with two electrons and leaves one electron in the antibonding orbital at a sufficiently high energy level. The surface hydrogen atoms leave the silicon in the zero valence state and combine to form molecular hydrogen. This accounts for the current doubling (200% quantum efficiency), production of hydrogen and 2 eq./mole for the oxidation of Si to Si(IV) in water. The electron density in the remaining Si-Si bonds is lowered which leaves them susceptible to attack by HF (or water) resulting in SiF_4 (to be dissolved as SiF_6^{2-}) and the formation of a stable monohydride surface, as shown in Fig. 3C.

The mechanism for the oxidation and dissolution of silicon in a nonaqueous solvent is different from that proposed for aqueous

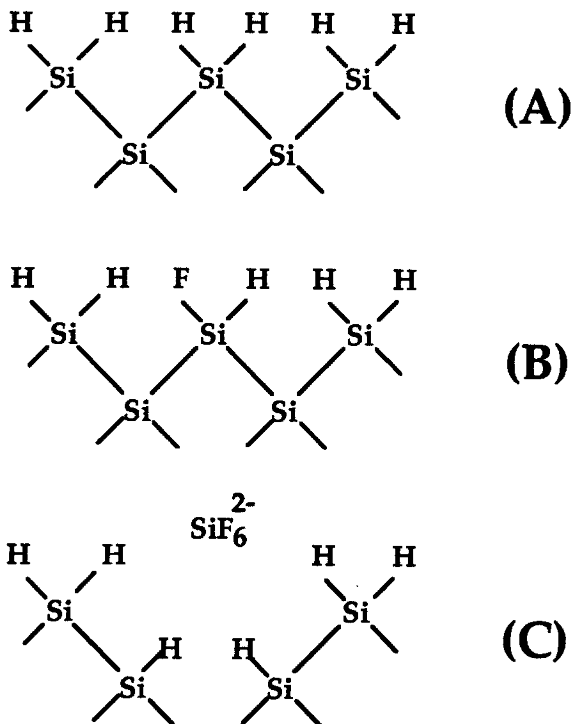

Fig. 3. (100) silicon surface (A) prior to PEC etching, (B) after oxidation and formation of the monofluoride, and (C) after dissolution of one Si atom.

dissolution. In contrast to the mechanism for a hydride surface above, we observe 4 eq./mole, a quantum efficiency of >330%, and no hydrogen gas produced. Assuming that the surface were hydrogen terminated in HF-MeCN, the hydrogen leaving groups would be two protons, and not molecular hydrogen as in water. The initial oxidation of one of the Si-H (dihydride surface) by a hole would be followed by a proton leaving, nucleophilic attack by a fluoride, and electron injection (Fig. 3B). The second Si-H would then be more susceptible to fluoride attack because of the polarity of the first Si-F bond, resulting in the proton leaving and up to two additional electron injection steps as the remaining Si-H is oxidized to Si-F plus H^+. Thus, four electrons are observed in the external circuit for each Si oxidized with up to three of them through electron injection. HF would then add spontaneously across the remaining Si-Si bonds because of their low electron density, just as in the aqueous case. This would leave a stable monohydride silicon and an SiF_4 group to be further complexed by fluoride (Fig. 3C). The absence of water in MeCN eliminates the competition by hydroxide during the nucleophilic fluoride attack and formation of any oxide intermediates. The extraordinarily high current densities achieved in HF-MeCN as compared to HF-H_2O, indicates that the hydroxide competition and dissolution of the oxide intermediates limit the rate of dissolution in water.

The low dark current and chemical stability of silicon in the aprotic case, with TBAFB, suggests that the surface of the silicon is terminated by fluoride (or fluoroborate). The Si-Si bonds for the difluoride surface do not undergo spontaneous attack by F^-, as they would by HF in the discussion above. The reaction of HF with the Si-Si bond is different from that of F^- because the proton stabilizes the surface by forming Si-H (monohydride) as opposed to leaving a Si^-.

Conclusion

A spatially selective, photoelectrochemical etch rate of 4 μm/min using a HeNe laser (peak intensity 365 mW/cm^2) has been achieved in anhydrous HF-MeCN. For MeCN, the rate limiting step is the flux of photogenerated holes, as opposed to aqueous solutions where oxide intermediates and their dissolution govern the etch rate at high currents. Four electrons were measured in the external circuit per silicon etched in HF-MeCN. The quantum efficiency was greater than 3.3 electrons per photon, uncorrected for recombination in the Si. This indicates that there is a current quadrupling due to electron injection into the conduction band from high energy reaction intermediates. Porous silicon was formed by anodically etching p-Si in HF-MeCN. Electroluminescence was observed by anodizing the MeCN prepared p-Si in an aqueous solution. The porous silicon produced in HF-MeCN did not involve the formation of silicon-oxygen species, or molecular hydrogen. The photo-oxidation and dissolution of n-Si was also performed in an aprotic, fluoroborate-MeCN solution at high current densities with current doubling.

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