

Photoelectrochemistry of *n*-silicon semiconductor in fluoride media

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Abstract. The effect of adding $[\text{Ru}(\text{bpy})_3]^{2+}$ complexes during photoelectrochemical etching of *n*-silicon on the photocurrent generation is studied. Remarkable enhancement of photocurrent is induced due to the presence of the dye redox system. Redox stabilization of silicon via electron transfer process based on remarkable interfacial interaction between reducing species and the photoelectrode is efficiently achieved. Transient photoelectrochemical measurements during anodic dissolution of *n*-silicon in the presence of the complex redox system resulted in inhibition of photocurrent oscillations which was observed at high potentials in the absence of dye redox system. Practically, all photogenerated holes reaching the silicon electrode surface will be efficiently reacted with the coordination redox system resident at the electrode surface. A mechanism of current oscillations, based on periodic buildup and decay (hole/electron recombination) of space charge within the superficial oxide layer is proposed.

Keywords. Semiconductor; *n*-silicon; photoelectrochemistry; ruthenium complexes.

1. Introduction

A great amount of work concerning the behavior of *n*-type and *p*-type silicon in aqueous and nonaqueous electrolytes have been reported in the literature. The etching of silicon in fluoride solutions has been the subject of intensive study^{1–18}. The importance of such a study stems from the technological potential and industrial application of silicon photonics and electronic circuit fabrications.

The appearance of current oscillations of silicon in fluoride-containing solutions at high potentials was addressed recently by several authors. Different models have been proposed. These oscillations can be due to a nonlinear correlation between formation and dissolution of the oxide layer⁵. It may also be due to competition between surface islands of oxide dissolution and free silicon dissolution⁸. Oscillations may be attributed to local fluctuations in the thickness of the surface oxide^{9,10}. The presence of a dielectric layer could be responsible for the observed oscillations¹². Lewerenz and Schlichtorl¹⁵ proposed the possibility of a spatially anisotropic thickness during the oscillations. Aggour and his co-workers¹⁶ investigated the oscillatory behaviour of the anodic dissolution of Si in ammonium fluoride media. They suggested the so-called fluctuating pore model to interpret their results.

The photocorrosion of *n*-type silicon can, in principle, involve both hole capture and electron injection steps^{19,20,21,22}. It has been suggested by Eddowes²³ that the

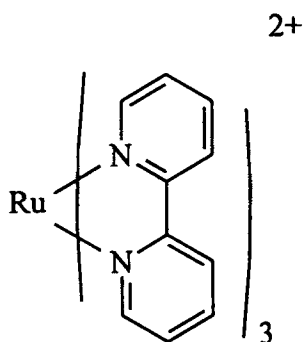
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photodissolution of *n*-Si corresponds to divalent species under low light intensities. On the other hand, Lewerenz and his co-workers¹⁹ and Peter and his co-workers²⁰ proposed a simple reaction mechanism in which divalent silicon appears only as a transient surface bound intermediate which can either inject an electron or capture photogenerated hole to form tetravalent silicon.

Preliminary measurements in our laboratory show that photocurrent oscillations for the *n*-Si/fluoride system exist even at low potentials of electropolishing regime. This prompted us to study the conditions and factors affecting the appearance/disappearance of photocurrent oscillations particularly the effect of adding dye sensitizers to the system. This will provide more specific information on the interfacial processes to develop a model for interpreting photocurrent modulation in this system.

2. Experimental

The ready-for-use *n*-Si(111) samples used were supplied by J-N Chazalviel group at Ecole Polytechnique, Paris. The *n*-Si samples were of resistivities of 0.3 Ωcm. Ohmic back contacts were made with Sb/Au thin film. Silver paste was used to adhere the silicon disks to the Au rotating disk electrode. The electrochemical measurements were taken using a platinum counter electrode and saturated Ag/AgCl electrode as a reference electrode. Electrical control was provided by a potentiostat-galvanostat (EF&G 273A). Electrolytes were prepared from ammonium fluoride and purified water. The *pH* was adjusted by the addition of concentrated sulphuric acid. All solutions were purged with argon to remove the dissolved oxygen. For sample illumination a 75 W Xe lamp was used. Prior to the experiments, the cell was cleaned intensively in HNO₃ + H₂O₂ + H₂O (1:1:1). The primary treatment of silicon surface consisted of a photoelectrochemical oxidation in 0.1 M NH₄F at *pH* 4.0 at 3.0 V and illumination with white light (50 mW cm⁻²) under the conditions of photocurrent oscillation for 15 min. The oxide layer was then removed in the absence of light without a change in the applied potential. The general structure of the [Ru(bpy)₃]²⁺ complexes is as shown in the following scheme.



Scheme 1.

3. Results and discussion

A typical linear sweep voltammogram of the *n*-Si disc under illumination obtained for *n*-type silicon in 0.1 M (+ 0.9 M NH₄Cl solution) fluoride media at *pH* 4.0 is shown in figure 1. The steep increase in the current corresponds to the formation of porous

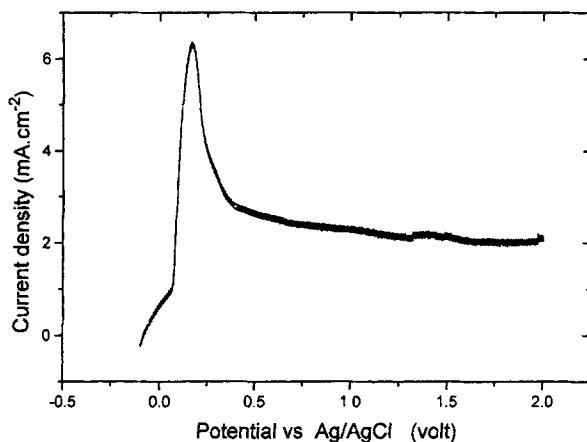


Figure 1. Current vs potential curve obtained for *n*-type silicon in 0.1 M (+ 0.9 M NH_4Cl solution) fluoride media at pH 4.0 with scan rate 50 mV/s, rotation rate 600 rpm.

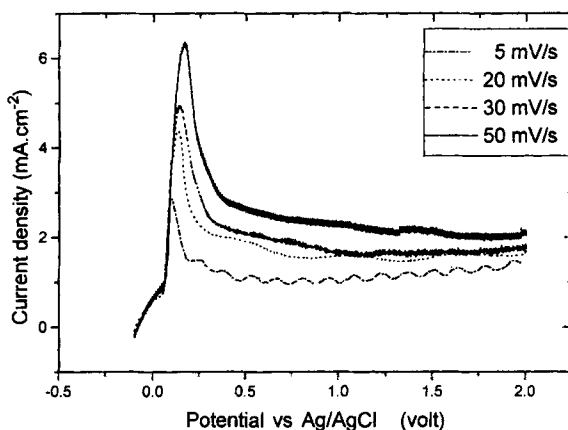


Figure 2. Current vs potential curves obtained for *n*-type silicon in 0.1 M (+ 0.9 M NH_4Cl solution) fluoride media at pH 4.0 with different scan rates; (a) 5 mV/s, (b) 20 mV/s, (c) 30 mV/s and (d) 50 mV/s, rotation rate 600 rpm.

silicon. Although the curve does not resemble most of the results in the literature¹¹, yet the presence of a one current peak resembles some of the results obtained in earlier studies^{24,25} due to the limited potential range used. The early work by Memming and Schwandt²⁴ which was later confirmed by Eddowes²³ showed that silicon dissolution in the region of porous silicon formation appears to be divalent corresponding to the liberation of one molecule of hydrogen per dissolved silicon atom i.e. hydrogen production efficiency is 100%. Turner⁴ in his work did not report the current corresponding to the formation of porous silicon but he noticed that only one peak was directly proportional to the concentration of fluoride ion used. Figure 2 shows the effect of scan rate (5–50 mV/s) on the current-voltage characteristics. As indicated by the figure, the value of the photocurrent increases by increasing the scan rate. The

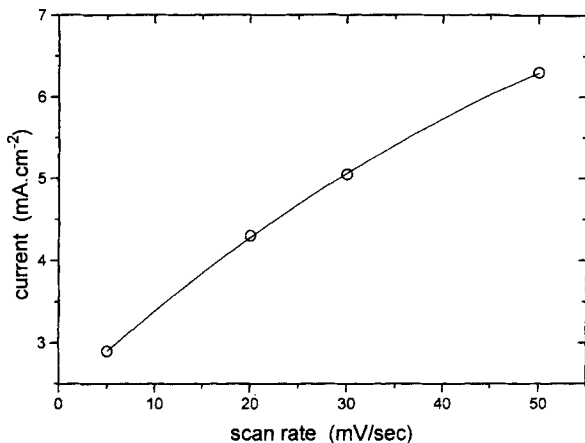


Figure 3. The measured current density at different scan rates of the *n*-type silicon in 0.1 M (+ 0.9 M NH_4Cl solution) fluoride media at pH 4.0, rotation rate 600 rpm.

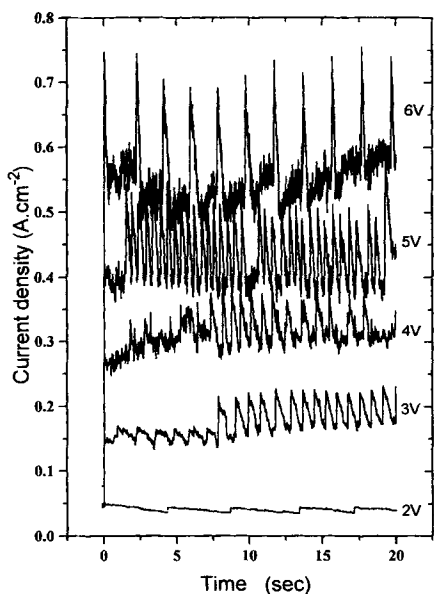


Figure 4. Chronoamperometric measurements at different potential steps for *n*-type silicon in 0.1 M (+ 0.9 M NH_4Cl solution) fluoride media at pH 4.0, rotation rate 600 rpm, initial voltage 2 V; step voltages are indicated in the figure.

magnitude of the observed current peak height is shown to vary exponentially with the scan rate as illustrated in figure 3.

A large number of electrochemical systems can show oscillatory behavior¹⁶. The appearance of current oscillations in silicon in fluoride media has been reported by several authors^{4,5,10,16}. Photocurrent oscillation, as a function of time, is observed at different step potentials for *n*-Si in 0.1 M (+ 0.9 M NH_4Cl solution) fluoride media at pH 4.0 as is shown in figure 4. In more acidic solutions the oscillations become larger.

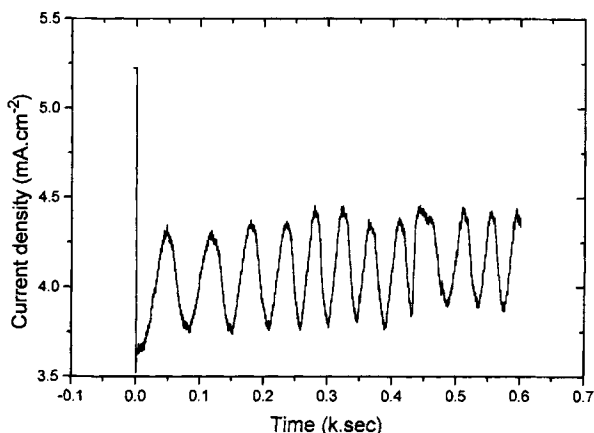


Figure 5. Sustained oscillations as a function of time obtained by applying step voltage 0.001 V for *n*-type silicon in 0.1 M (+ 0.9 M NH_4Cl solution) fluoride media at pH 4.0, rotation rate 600 rpm, initial voltage 0.599 V.

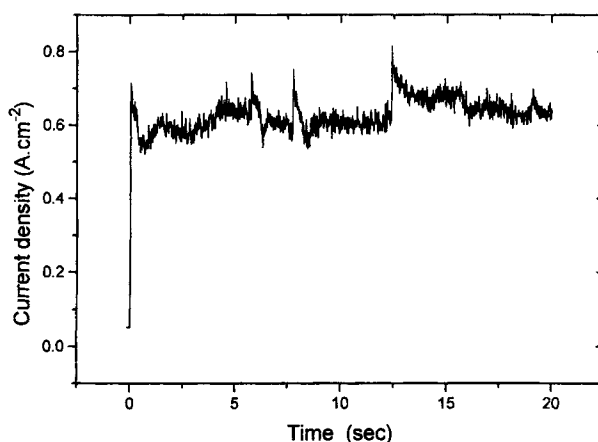


Figure 6. Sustained oscillations as a function of time obtained by applying step voltage 6 V for *n*-type silicon in 0.1 M (+ 0.9 M NH_4Cl solution) fluoride media at pH 4.0, in presence of $[\text{Ru}(\text{bpy})_3]^{2+}$ complex, rotation rate 600 rpm, initial voltage 2 V.

The frequency also varied with the fluoride concentration—it increased with the fluoride concentration being increased. Here, both the pH and fluoride concentration were kept constant throughout the measurements. Also light intensity was kept constant at about 50 mW cm^{-2} . It can be seen from figure 4 that the amplitude and frequency of oscillations varied with time. It disappears at step voltage larger than 2 V. Figure 5 shows sustained oscillations for 10 min obtained under white light illumination. The effect of adding $[\text{Ru}(\text{bpy})_3]^{2+}$ complex on the current-voltage characteristic was also studied. The I–V characteristic was the same as that of dye-free solution but with some enhancement of the photocurrent. The presence of the ruthenium complex also resulted in redox stabilization of Si optoelectrode via electron transfer process based on remarkable interfacial interaction between the reducing species and the

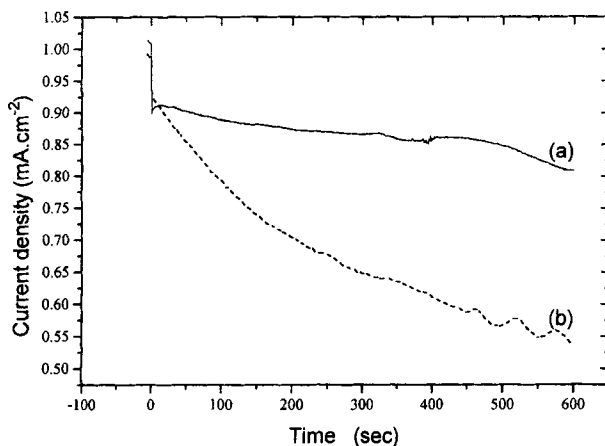


Figure 7. Normalized transient photocurrent of illuminated *n*-silicon in 0.1 M (+ 0.9 M NH_4Cl solution) fluoride media at pH 4.0 in (a) presence and (b) absence of $[\text{Ru}(\text{bpy})_3]^{2+}$ complex, rotation rate 600 rpm, initial voltage 0.001 V; step voltage 0.599 V.

photoelectrode. In the presence of Ru complex, a stabilization of photocurrent is observed as indicated in figure 6. Figure 7 shows the time dependence of photocurrent for *n*-Si electrode in fluoride medium in (a) presence and (b) absence of $[\text{Ru}(\text{bpy})_3]^{2+}$ at 0.6 V. Other Ru complexes of different structures and different redox efficiencies show similar behavior. It is seen that within 10 min the photocurrent produced by photooxidation of $[\text{Ru}(\text{bpy})_3]^{2+}$ is of remarkable stability. This demonstrates clearly that the used complex redox system stabilizes the illuminated Si electrode by an efficient electron transfer process in which the positively charged ruthenium complex acts as reducing agent by a tunneling mechanism. It seems reasonable to suggest that electron transfer mechanisms are apparently sufficiently fast and efficient to neutralize photogenerated positive charge carriers, in the surface of the photoanode, thereby leading to both the inhibition of corrosion of the semiconductor surface as well as to the prevention of periodic build-up and decay of space charge within the superficial oxide layer. A large fraction of these holes become involved in parallel side reactions leading to a corrosion of the Si photoelectrode in the absence of the redox stabilizing systems.

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