Mem. SR Center Ritsumeikan Univ. No. 25, 13-16 (2023)

Photo-induced Lithiation in Silicon Semiconductor

Nur Chamidah[1], Toyonari Yaji[2], Yuki Orikasa[1]

1) *Department of Applied Chemistry, Graduate School of Life Sciences, Ritsumeikan University, 1-1-1 Nojihigashi, Kusatsu 525-8577, Japan*
2) *Research Organization of Science & Engineering, Ritsumeikan University, 1-1-1 Nojihigashi, Kusatsu, 525-8577, Japan*

A significant technological improvement is expected for storing light energy by converting it into electrical energy. Even though energy-converting devices from light energy to electrical energy, solar cells have widely developed, both energies cannot be stored in their own form. One of the attractive technologies is converting light energy directly to chemical energy, which can be stored like lithium-ion batteries. When there is an energy difference in Fermi level between electrode and electrolyte, light energy induces ion transfer at the electrode/electrolyte interface. However, the fundamental studies of the photo-induced charge-transfer reaction are lacking, and this technology has not been used practically. In this study we investigate the photo-induced lithiation using silicon semiconductors (both p- and n-type) as electrode in a lithium-ion battery system. Under light irradiation without electrochemical driving force, the photo-induced current is clearly observed. Si K-edge X-ray absorption spectroscopy reveals the formation of lithium-silicon alloyed phase after the light irradiation.

1. Introduction

Converting light energy into electricity is a technology with great potential to satisfy the growing of global energy demands. Solar cell is a common device that utilizes this technology to convert light energy into electrical energy that can be used immediately or to be stored in energy storage devices for future use. However, the latter case including two steps of energy conversion in the basic solar cell leads to low efficiency during device-to-device transfer. The efficiency of energy conversion could be significantly enhanced if it were feasible to convert light energy directly into chemical energy instead of using the two-step process currently employed. Apparently, a photo-ionic concept that supports this direct light energy conversion process has been proposed by H. Tributsch in 1983 [1], before the commercialization of lithium-ion batteries. When there is the energy difference of Fermi level between a semiconductor electrode and electrolyte, light energy induces ion transfer at the electrode/electrolyte interface [1]. Recently, the photo-induced delithiation reaction of $LiFePO_4$ lithium-ion battery cathodes has been reported by employing dye-sensitized material under light irradiation [2]. The study implies that light energy forms the electron-hole pairs with the holes aiding the chemical conversion.

To realize devices based on photo-induced energy conversion, it is essential to develop materials specifically for the anodes. Silicon semiconductor becomes a promising candidate to be utilized owing to its narrow band gap (ΔE_g Si = 1.1 eV) and huge theoretical specific capacity (~4200 mAh g^{-1}), which is almost 11 times of the commercial graphite anode [3,4]. Silicon has been widely investigated as an anode material for high-energy lithium-ion batteries [4–6]. Diffusion properties of lithium ion into silicon anodes has also been intensively studied [7–9] however, its application to the photo-induced chemical reaction has not been understood. We have studied the photo-assisted electrochemical reactions using silicon single crystals and reported that the kinetics of lithium alloy electrochemical reactions are enhanced by light energy in both p-type and n-type silicon semiconductors [10]. In this study, we investigate the possibility of lithium alloying reaction occurring solely through the influence of light energy in the absence of any electrochemical driving forces. The lithium alloying state of the light-irradiated samples is analyzed by silicon X-ray absorption spectroscopy.

2. Experimental

Preparation of Silicon Electrodes

Silicon p-type (p-Si) and silicon n-type (n-Si) single crystal wafers were cut into 20 × 20 mm and taken into several pretreatments before it used as the electrodes. The first step was to remove the organic contamination on the surface of the materials using piranha solution. Piranha solution was prepared by mixing the sulphuric acid (H_2SO_4, 96%) with the hydrogen peroxide (H_2O_2, 60%) by the ratio of H_2SO_4: H_2O_2 = 2:1 (v/v (%)). The silicon single crystal was dipped inside the piranha solution for 30 minutes. The next pretreatment step was the removal oxide compound at the surface of the silicon single crystal. This process was carried by immersing the silicon single crystal in hydrofluoric acid (HF, 46%) for about 1 hour. Ultrapure water was used to rinse the sample thoroughly after each treatment.

Experimental Setup

In this experiment, the three electrodes battery system was used for each photochemical measurement. The reference electrode (RE) was placed parallel to the counter electrode (CE) side by side, leaving some gap for the working electrode (WE) at the backside of the cell directly irradiated by light. Lithium metal was used as RE and CE, p-Si and n-Si were used as the WE. A titanium sheet current collector was used to cover the working electrode material. $LiClO_4$ in propylene carbonate was used as the electrolyte because it is more stable under air and heat exposure. The construction of the photochemical measurement setup is shown in Fig. 1.

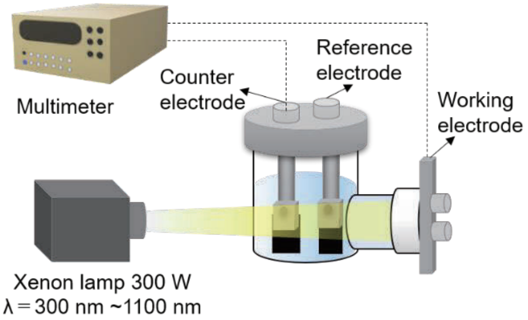

Fig 1. Photo-electrochemical measurement setup. The reference electrode was placed parallel to the counter electrode leaving the gap for working electrode at the backside of the cell to be irradiated by light. Three electrodes were connected to digital multimeter.

Photocurrent and X-Ray Absorption Spectroscopy Measurements

In this research, Xenon Lamp 300W was used as the light source since it produces constant light intensity that is suitable for the primary measurement. The wavelength range of Xenon lamp extends from 300 nm to 1100 nm, which is shorter than 1127 nm corresponding to an energy of 1.1 eV. Xenon lamp energy could cover a range that includes energy higher than 1.1 eV. As the light irradiated the photochemical cell, those three electrodes in the cell were connected to the digital multimeter instruments in series. The photo-charge measurements include three steps of data: (1) before light irradiation for 1 hour, (2) under light irradiation for 24 hours, and (3) after the light irradiation for 1 hour. After the measurements, the chemical state changes of silicon were investigated by performing X-ray absorption spectroscopy (XAS) measurement. The irradiated silicon samples were washed with dimethyl ether and saved into a transfer vessel without exposure to air. The XAS measurement were conducted at BL-10 in Ritsumeikan University SR Center. The data was collected in fluorescence mode.

3. Results and Discussion

3.1. Photocurrent Measurement

Half-cell measurement of silicon in the photochemical cell under light irradiation was performed to examine the generation of photocurrent. The photocurrent has a main correlation with the current response of the cell when it is irradiated by light. Therefore, we focus on measuring the current response of the irradiated cell and opted to exclude the voltage response to maintain the clarity of our work. The measured current during the light irradiation is shown in Fig. 2 (a) for p-Si. The area between the dashed lines corresponds to the time range of the light irradiation, resulting in the current generation. When the light starts to irradiate the photochemical cell, the current increasing is detected. It increases up to 1.1 mA for the p-Si during the irradiation. Meanwhile, in Fig. 2 (b) which

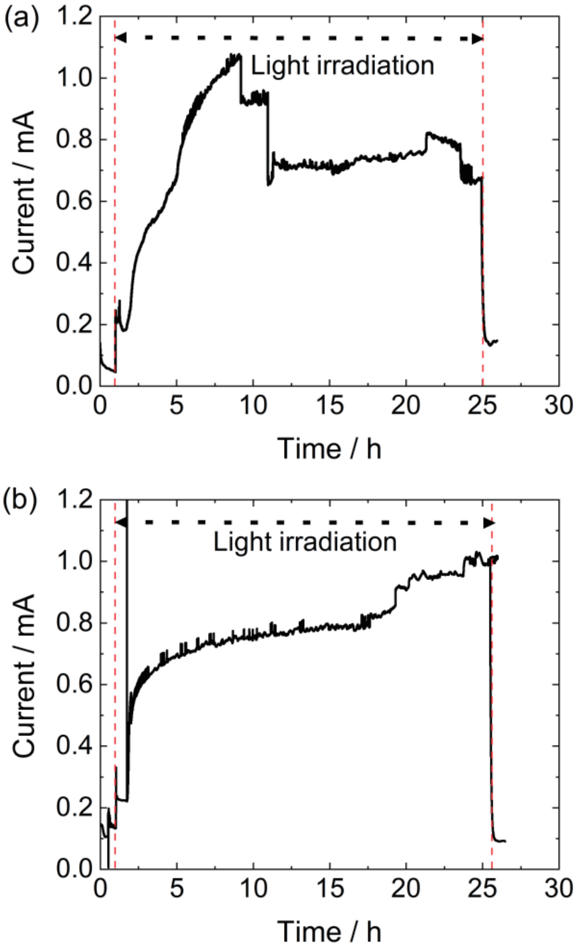

Fig 2. Photocurrent response of (a) p-Si and (b) n-Si under light irradiation for 24 hours.

corresponds to the photocurrents profile of n-Si under light irradiation, shows a gradual increase of the photocurrent up to 1 mA. The currents drop significantly when the light exposure is stopped. By this measurement, we confirm that light irradiation itself induces the photocurrent. The detailed mechanism has not been understood, but the light energy causes electrons and holes in the silicon, inducing the charge-transfer reaction at the electrode/electrolyte interface. In addition, photocurrent was observed regardless of p-Si or n-Si.

3.2. X-ray Absorption Spectroscopy Measurements of Silicon After Light Irradiation

The results of Si K-edge XAS measurement for p-Si and n-Si at the initial stage and after the light irradiation are shown in Fig. 3 (a) and 3 (b), respectively. The result shows that the spectrum of silicon after light exposure is entirely distinct from the initial state. The white line peak at 1840 eV, which corresponds to the native peak of silicon [11], is broadened and the edge energy is shifted towards lower energy. The pattern of the spectrum profile agrees with the typical spectrum change during the lithium insertion into the silicon electrode [7,10]. These results support that the photo-induced current causes lithiation in silicon electrodes. The observed current indicates that the electrons are flowing within the circuit, which also triggers the charge transfer between the electrodes. Thus, the chemical state of silicon is changed by lithiation.

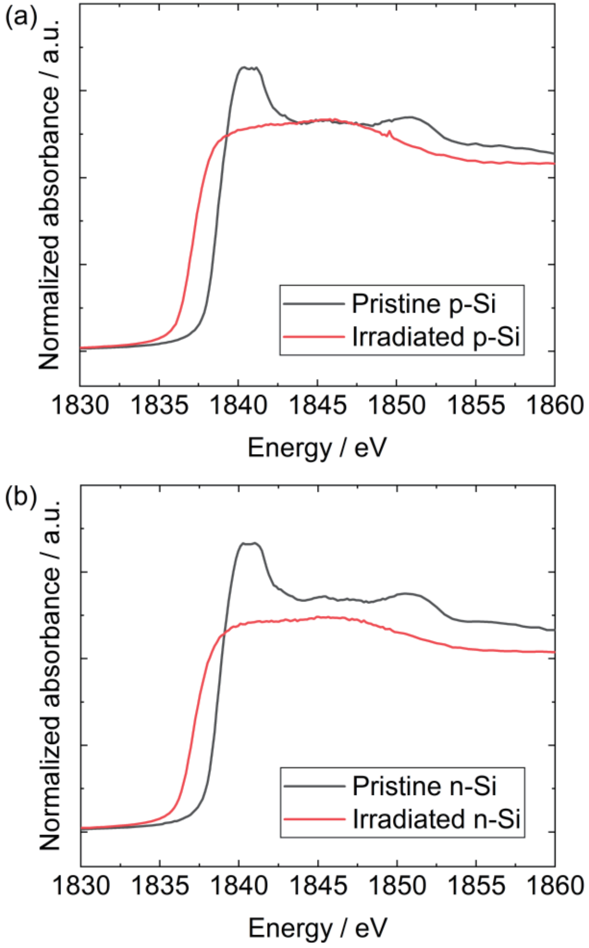

Fig 3. Si K-edge XANES of (a) p-Si and (b) n-Si single crystal before and after light irradiation in the photochemical cell.

3.3. Discussion

By considering the photo-ionic mechanism in semiconductor [3], when the light is irradiated to a semiconductor electrode, and if the energy is higher than the bandgap of Si (ΔE_g Si = 1.1 eV), the electrons will be excited to the valence band leaving holes on the conduction band (Fig. 4). In p-Si, the excited electrons accumulate at the surface of the silicon by the band-bending of the electrode and electrolyte interface then induces the insertion of Li-ions on the electrolyte. However, in our study, n-Si also enables the photo-induced lithium-alloying reaction. This implies the band bending at the electrode/electrolyte interface is not the dominant factor.

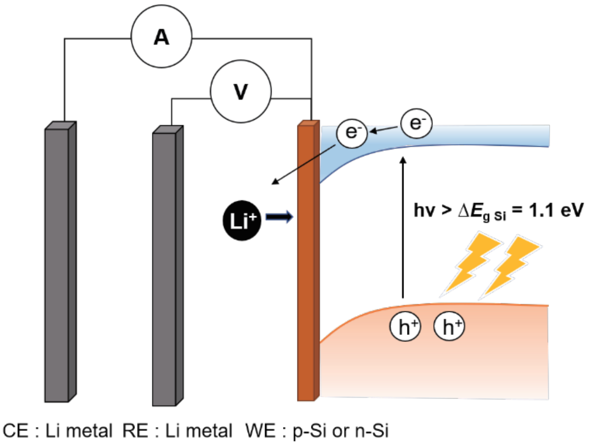

Fig 4. Photo-ionic process at semiconductor/ electrolyte interfaces. When the irradiated light energy (hv) has energy higher than the band gap energy of Si, the energy is absorbed by the material and excites the electrons from valence band to the conduction band, inducing ion transfers between electrode and electrolyte.

4. Conclusions

The photo-chemical conversion of light energy into chemical energy has been investigated by analyzing the photo-induced reaction of lithium into silicon semiconductors. P-Si and n-Si semiconductors were selected as the electrode materials to establish the photocurrent evaluation setup using lithium-containing organic electrolyte by the light irradiation. The photo-induced current is dramatically increased in silicon semiconductors once the light is irradiated to the electrodes. The photo-induced currents are observed in both p-Si and n-Si. The lithium alloying reaction of silicon by light irradiation is confirmed by the results of Si K-edge XAS measurements.

Acknowledgement

The part of this work was supported by Ritsumeikan Global Innovation Research Organization, Ritsumeikan Advanced Research Academy, and The Science Research Promotion Fund in Promotion and Mutual Aid Corporation for Private Schools of Japan.

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