

## Abstract for Ph.D. Thesis

Electrochemical lithiation/delithiation process of single crystalline silicon substrate

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From the view points of social problems such as the environmental issues and stable supplies of electric energy, introduction of renewable energy and construction of the distributed energy system are required. In order to effectively use energy, energy storage and its standardization should be required, and then, it is essential to introduce the power storage system. Among the various storage systems, lithium (Li)-based secondary batteries such as Li-ion battery, which are widely used as a current power storage system, and Li-air battery, which is expected to be the next generation battery, are attracted the great attention and widely studied. Silicon (Si) is considered as a promising anode material for the Li-based secondary batteries because of its high lithiation capacity. However, there are several problems such as significant volume expansion/contraction due to lithiation/delithiation of Si, which causes degrading of the anode and then, leads to reduce cycle characteristics and coulombic efficiency. In the aqueous solution system, atomic level understanding is progressing by fundamental studies using single crystal electrodes. On the other hand, for the Li-based secondary batteries, which use non-aqueous solution, atomic level understanding about mechanism of the electrode reaction is not enough because only material developments have been focused. It is very important to understand the interfacial structure and electronic state of the electrode in atomic level, and to feedback them to material development.

This thesis consists of 6 chapters to report the investigations of the structure, composition, and electronic state of electrochemically lithiated/delithiated single crystalline Si substrate, which is atomically flat and defined the structure, in order to understand the mechanism of the lithiation/delithiation process of Si.

In chapter 1, as an introduction, Li-ion battery, Li-air battery, and  $\text{Li}_x\text{Si}_y$  alloy were reviewed and the purpose of this thesis was clearly described.

In chapter 2, the fundamentals and principles of the measurements, such as scanning electron microscopy (SEM), soft X-ray emission spectroscopy (SXES), and surface X-ray diffraction (SXRD), used in this thesis were described.

In chapter 3, the structure, composition, and electronic state of the electrochemically lithiated/delithiated Si(111) were investigated. It was found that four electrochemically lithiated Si layers were formed on the Si(111) substrate. Based on the results of the SXES combined with SEM, the composition and the electronic states of those four lithiated Si layers were site-selectively obtained. It was found that the four layers were the crystalline  $\text{Li}_x\text{Si}_y$  (c- $\text{Li}_x\text{Si}_y$ ) phase, the amorphous  $\text{Li}_x\text{Si}_y$  (a- $\text{Li}_x\text{Si}_y$ ) phase, the mixed phase of c-Si and a- $\text{Li}_x\text{Si}_y$ , and the mixed phase of c-Si and Li atom from the top layer. The shape of c- $\text{Li}_x\text{Si}_y$  phase was a  $\mu\text{m}$ -sized three-fold symmetric triangular pyramid, which reflects the atomic arrangement of the Si(111) surface, and the XRD patterns using synchrotron radiation (SR) revealed that the crystal orientation is in the

same direction as the Si(111) substrate. Based on these results, the structural change during the lithiated/delithiated Si process was discussed using the results of *in situ* SXRD measurement.

In chapter 4, the structure, composition, and electronic state of the electrochemically lithiated/delithiated Si(100) were investigated. It was found that four electrochemically lithiated Si layers were formed on the Si(100) substrate as well as in the case of Si(111). It was found that the c- $\text{Li}_x\text{Si}_y$  and a- $\text{Li}_x\text{Si}_y$  formed as well as the Si(111). It was clarified that the c-Si and Li atom mixed phase was transferred to a- $\text{Li}_x\text{Si}_y$  when the amount of Li reached to a certain concentration. Based on these results, the structural change during the lithiated/delithiated Si process was discussed using the results of *in situ* SXRD measurement.

In chapter 5, the lithiation anisotropy of the Si(111) and the Si(100) substrates was discussed. It was suggested that Li diffusion rate in the Si(100) substrate was faster than that in the Si(111) substrate. It is considered that the difference of atomic arrangement of the 2nd outermost Si layer, as shown in Fig. 1, affects the Li diffusion rate. The vacancy site in the 2nd outermost Si layer of Si(111) is smaller than that of Si(100), indicating that Si(100) has much more space for Li diffusion than Si(111).

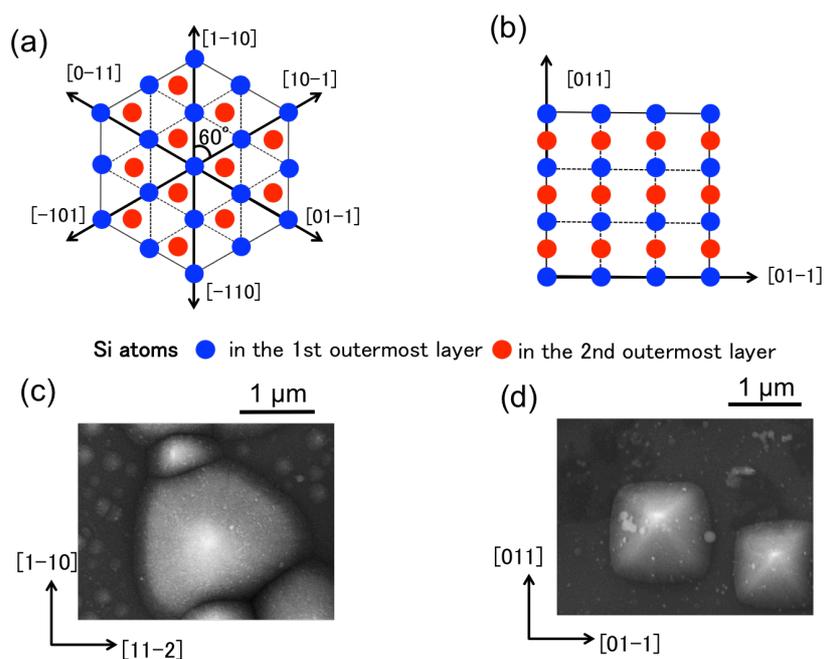


Figure 1 The surface atomic arrangement of the (a) Si(111) and (b) Si(100).  $\text{Li}_x\text{Si}_y$  alloy which formed on the (c) Si(111) and (d) Si(100).

In chapter 6, this thesis was finally summarized. It was demonstrated that both the Li insertion and Li diffusion process and the structure of the formed  $\text{Li}_x\text{Si}_y$  alloy were strongly dependent on the atomic arrangement of Si. Based on the atomic level analysis results of this thesis, it is expected the further development of the Si anode for the Li-based secondary batteries.