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Atomistic Mechanism of the Potassium Ion Electret Used for New Types of Vibration Power Generation Devices

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Abstract

Vibration power generation devices utilizing the potassium atoms in SiO_2 have been recently invented. Therefore, it is important to clarify the property of potassium atoms in SiO_2 for further improvement of the vibration power generation devices. In this study, we discuss a behavior of potassium atoms in SiO_2 by using first-principles calculation. We found that potassium incorporated SiO_2 contains a Si-H bond and an O lone pair. After the removal of the potassium, Si becomes five-fold coordination and a new Si-H bond is generated. As a result, this structure is negatively charged up. It can be utilized in vibration power generation devices.

1. Introduction

Energy harvesting devices attract great attentions because they are inevitable in energy saving society. Many types of energy harvesting devices are proposed such as thermoelectric devices and vibration power generation devices. Recently, potassium in amorphous SiO_2 is applied to create potassium ion electret used for vibration type MEMS power generation device (Fig.1) [1]. The electret is a material that can store electric charge permanently. Thus, it is important to make clear the operating principle of potassium ion electret for practical application of vibration MEMS power generation devices with high efficiency.

However, the mechanism of storing electric charge in SiO_2 of the potassium ion electret is not clarified. In this study, we analyze the structures and the charge states of SiO_2 containing potassium atoms, using the first principle calculation. Moreover, we also clarify the charge accumulation mechanism of potassium ion electret.

2. Method and Model

The calculation was performed by using the VASP (Vienna ab initio simulation package) code [2], which is based on density functional theory with the Perdew–Burke–Enzerhof generalized gradient approximation [3]. The core valence interactions were described by projected-augmented-wave potentials.

In the previous research, potassium-ion-doped SiO_2 is made by thermal oxidation with steam supplied through a KOH solution [1]. So, we made initial structure in the following way. First, we prepared ten supercells of alpha quartz (144 atoms), with a potassium atom inserted into a different site for each supercell. Next, we performed the structural optimizations, and we selected one supercell with the lowest total energy as the initial structure (Fig.2 (a)) for further calculations. By using this initial structure, we inserted a hydrogen atom between a potassium atom and its neighboring oxygen atom (Fig. 2(b)) in the initial structure, and perform the structural optimizations. In the previous research, it is reported that the main source of the electret is likely the oxygen defects accumulating near the Si/SiO_2 interface through the potassium ion migration during charging [1]. Thus, we removed the potassium atom from the structure with a hydrogen. Finally, we performed the structural optimizations of the positively, neutral and negatively charged structures.

3. Results and Discussion

As a result of incorporation of potassium atoms and hydrogen atoms, Si-O-Si bonds of SiO_2 near the hydrogen atom changed into three types of structures (Fig.3). Figure 3(a) describes the structure with three-fold-coordinated Si and an O-H bonds. Figure 3(b) represent the structure with a Si-H bond and an O lone pair. Figure 3(c) gives the structure containing a five-fold-coordinated Si atom with a Si-H bond. The values of ionic valence obtained by Bader charge analysis [4-7] are also given in Fig. 3. These Bader charges indicate that potassium atoms become positive ions. By comparing total energies among the structures in Figure 3, we found that Fig. 3(b) is the most stable. Thus, the potassium incorporation induces generation of Si-H bonds and O lone pairs.

In the previous study, it was reported that the potassium atom in potassium-ion-doped SiO_2 moves to the negative electrode under an electric field and the negatively charged region with low potassium density appears [1]. Thus, we examined which charged structure is stable after removal of the potassium atom from the potassium-ion-doped SiO_2 with a hydrogen atom. The stability can be quantitatively evaluated by the formation energy [8]. The calculated formation energies are shown in Fig. 4. As shown in Fig. 4, the positive charge state was stable when the Fermi energy is lower than 4.7 eV. On the other hand, the negative charge state was stable when the fermi energy is higher than 5.9 eV.

The structures corresponding to the charged states in Fig. 4 are given in Fig. 5. It is observed from Fig. 5 that the O lone pairs structure in Fig. 3(b) changed to the Si-O-Si bond after the potassium removal in both positive and negative charged states. In case of the positively charged state, the hydrogen atom has a bond with an oxygen atom (Fig. 5(a)). From the Bade charge analysis, we found that hydrogen atom behaves as a positively charged ion. On the other hand, in the negatively charged state (Fig. 5(b)), the hydrogen atom bonds with the silicon atom, resulting in the five-fold coordination. The ionic valence of the hydrogen was evaluated to be -0.35 from the Bader charge analysis. This means that. In this case, the hydrogen atom behaves as a negatively charged ion, which

could be the origin of the negatively charged region observed in the experiment [1].

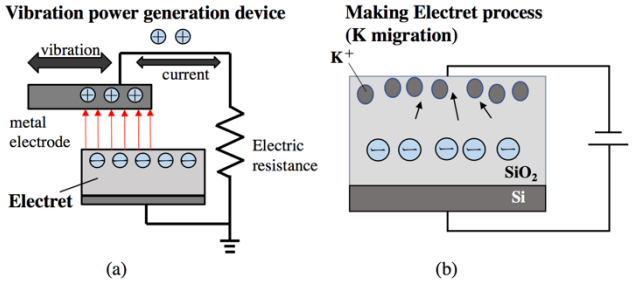

Fig.1(a) Schematic illustration of the vibration power generation devices. (b) Charge storing mechanism of the potassium ion electret.

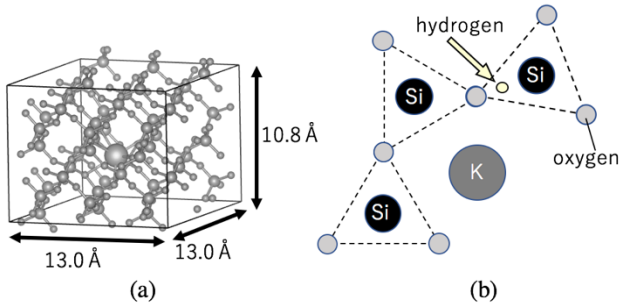

Fig. 2 Calculation models. (a) Initial structure with potassium atom. The largest ball in the center of the structure is a potassium atom. (b) Insertion position of hydrogen atom. A hydrogen atom is placed between O-Si bonds (16 bonds) around a potassium atom. So, we prepare 16 initial structures.

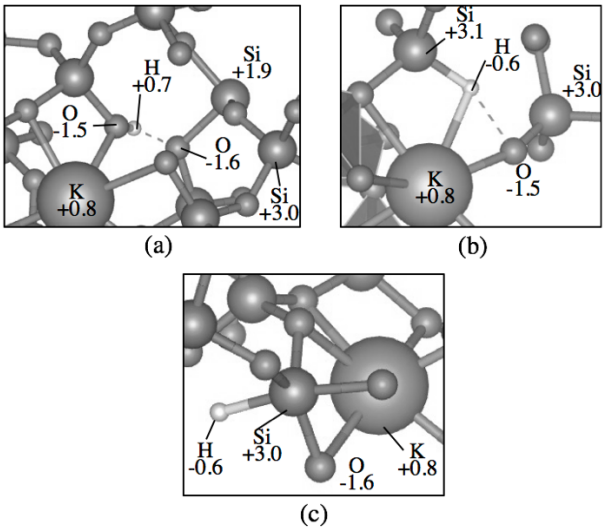

Fig. 3 Calculated structures around a potassium atom. Numbers below the symbol of elements show the charge state of each atoms by Bader Charge analysis.

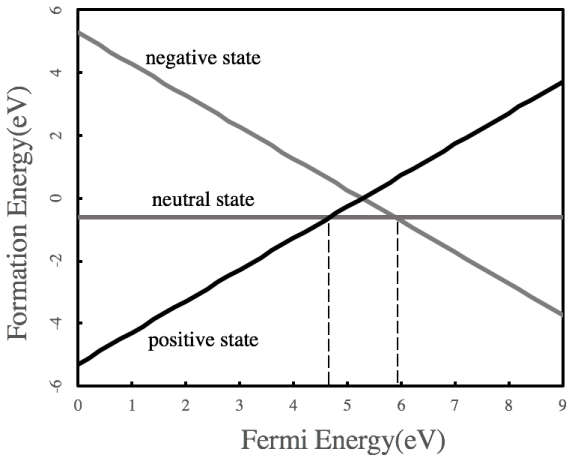

Fig. 4 Formation energy in each charge states after the removal of a potassium atom from Fig. 3(b).

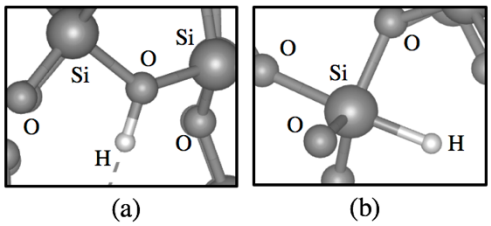

Fig. 5 Calculated structures around a hydrogen atom after removal of a potassium atom from Fig. 3F(b). (a) The structure of positively charged state. (b) The structure of negatively charged state.

4. Conclusions

We investigated the chemical behavior of potassium atoms in SiO_2 used in new devices such as vibration type power generation devices by using first-principles calculation. First, it was found that the potassium atom in SiO_2 supplied electrons to the surrounding SiO_2 and became positive ions. When a hydrogen atom is inserted near the potassium atom, O lone pairs appeared in SiO_2 to store the electrons coming from potassium atoms. Next, we examined the potassium removal. After the potassium removal, SiO_2 changed to a structure that stores electrons resulting in the negatively charged region by forming a five-fold coordinated Si atom with a Si-H bond. This is the charge accumulation mechanism of potassium ion electret.

References

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