Current-voltage Characteristics of Water-adsorbed Imogolite Film

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Electric current flow was observed through imogolite film when imogolite ($(HO)_3Al_2O_3SiOH$) was exposed to water molecules and connected to external electrodes. Current flow was due to the bound water on the surface of imogolite. Current flow increased as the pH of the water decreased. The current-voltage (I-V) measurements from a field effective transistor (FET) using H_2O/imogolite film revealed that the current carrier in H_2O/ imogolite had p-type characteristics, *i.e.* the carrier was probably H^-. The possible mechanism for current transportation in imogolite/water was also suggested in this paper.

Key Words : Imogolite. Field effect transistor. pH. I-V character

Introduction

Imogolite is a naturally occurring hydrous aluminosilicate found in soil of volcanic origin polymer with a chemical formula of $(HO)_3Al_2O_3SiOH$.[1] It forms hollow tubes with an external diameter of 2 nm with typical lengths ranging from about 400 nm to several micrometers. The tube walls consist of curved gibbsite-like sheets with SiOH groups on the inside and AlOH groups on the outside. According to our previous results,[2] imogolite behaved like an insulator under vacuum. Upon the adsorption of several gases and organic compounds such as O_2, N_2, Ar, benzene, ethanol and pyridine, current flow through imogolite was not observed. It was only under water exposure that the current was observed. These results suggest that current carriers were formed on the surface of imogolite after adsorption of water molecules.

Surface hydroxyls of imogolite have the ability to lose or gain protons from aqueous solution and hence to change the surface charge. At low pH values, the net charge of the surface is positive and becomes negative at very high pH values. This can be shown by the following two chemical reactions:

$$\equiv AlOH + H^+ \Rightarrow \equiv [AlOH_2]^+ \qquad K_{a,1}$$
$$\equiv AlOH \Rightarrow \equiv AlO^- + H^+ \qquad K_{a,2}$$
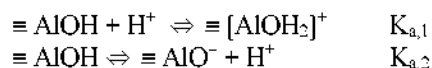
The pH value where the net charge is zero. *i.e.*, when $[AlOH_2]^+ = AlO^-$, is called the pH of point-of zero charge (pH(PZC)). For pure imogolite this pH is about 9 or maybe even somewhat higher.[3] Below a pH = 9 the positively charged surface species $[AlOH_2]^+$ predominates. This species is believed to have a role in surface conduction.

In this paper, we report the surface conduction properties of imogolite dipped in various aqueous solutions with pH values of 7, 5, and 3. These conditions create different $[AlOH_2]^+$ concentrations below the pH(PZC) condition. Current-voltage curves (I-V curves) are measured by connecting imogolite film to two gold electrodes. Further, a field-effective transistor (FET) using water/imogolite is constructed to determine the carrier type, *i.e.*, p- or n-type for this system.
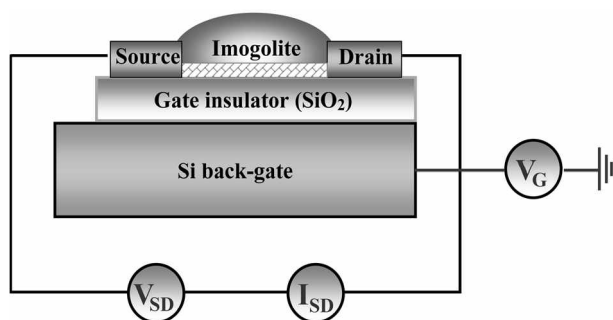
Experimental Section

Imogolite was synthesized with orthosilicate and hydroxyl-aluminum in a low pH solution by the method developed by Farmer *et al.* and Wada *et al.*[4,5] The bonding and wiring structures of the synthesized imogolite were confirmed by IR, TEM. and XRD. The synthesized imogolite was dispersed by sonification in weak acidic water and then spread as a film on a silicon substrate.

To obtain the I-V curve. gold electrodes were formed on both ends of imogolite film by magnetic sputtering in order for the distance between electrodes to be 1.5 mm. The current-voltage was measured with an ampere meter (Keithley 2400) after liquid water was dropped onto the imogolite film. We also constructed an FET using water/imogolite. Imogolite contacted with an insulator material SiO_2 (18 nm thickness), which was deposited on a highly doped silicon back gate by magnetic sputtering (Figure 1).

Results and Discussion

Figure 1 depicts the schematic layout of the FET architecture device used to measure the I-V curve of water-adsorbed imogolite film. Under vacuum imogolite showed no electrical conductance. It is quite plausible that imogolite is an insulator with a wide-bandgap since the outer and inner sides of imogolite tube, *i.e.* alumina and silica. are both wide-bandgap insulating materials. However. when imogolite was exposed to water molecules inside a vacuum chamber. current flow was observed as reported in our previous report.[2] It was believed that current passes through the water molecules adsorbed on imgolite surface.
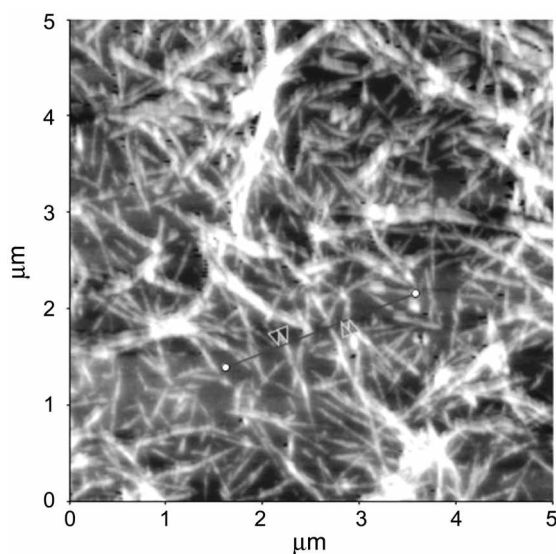
Our strategy in this experiment was to observe the effect of the pH of the adsorbed water molecules on conductance. This was necessary to use water drop having different pH values as shown in Figure 1. Each Au electrode was connected with the water drop. Therefore, the measured current with ampere meter, I_{SD}, contained the current through bulk water molecules as well as the current through water molecules adsorbed on imogolite. It was necessary to distinguish
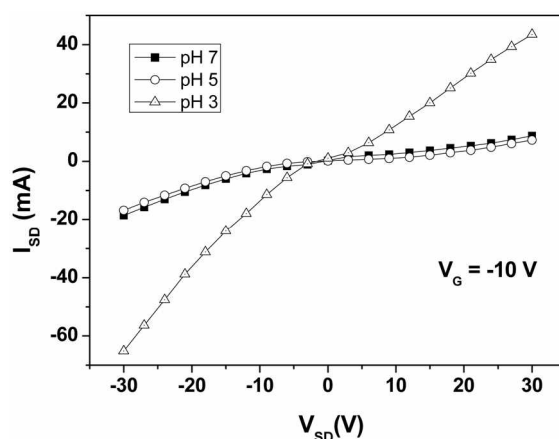
Figure 1. Schematic of experimental set-up used to measure I-V curve of water adsorbed onto imogolite film.

Figure 3. I-V curves of water adsorbed on imogolite film at pH = 7, 5, and 3 at V_G = 10 V.

between the effect of adsorbed and bulk water molecules on current flow. To measure the current through only the bulk water molecules. we made the device only without the imogolite film at the same condition. The measured I_{SD} with the imogolite film between the electrodes was always higher (20-150 times) than the I_{SD} without the imogolite film at the same experimental condition. For example, the I_{SD} at pH = 7, pH = 5, and pH = 3 were measured 177, 272, 7170 μA. respectively, with the existence of imogolite film. On the while, the corresponding I_{SD} values without the film were much lower and to be 6.47, 11.6, and 56.0 μA. The former value was the summation of two current values, *i.e.* the current passing through the water molecules adsorbed on imogolite and the current passing through the bulk water molecules. It appeared that the protons in the bulk water play a smaller role in the transport of current compared to the water molecules bounded on the imogolite surface.

Figure 2 is an atomic force microscopy (AFM) picture of the imogolite sediment after dispersion on Si substrate. The sediment consisted mainly of fibers, which were aligned in bundles. This imogolite sample was thought to contain a significant amount of impurities such as proto-imogolite.

Figure 2. AFM image of imogolite sediment obtained by centrifugation of the as-prepared imogolite.

allophane. since fine granular morphology suggested an allophane structure.

Figure 3 shows the I-V (I_{SD} *vs* V_{SD}) curves of the imogolite film dipped in water drop at different pH values. For comparison under the same conditions. we used the same imogolite device to compensate for experimental error. A slight change in current was observed when the pH was decreased from 7 to 5. However, the current increased 2-3 times at pH = 3. It is difficult to explain these current values since there are no published data on the conduction of water molecules adsorbed onto imogolite. In 2006. Lee *et al.*[6] measured conductivity of polypyrrole-coated imogolite by varying the thickness of polypyrrole.

In 1991. Wehrli *et al.*[7] studied the surface protonation of the different crystallographic planes of kaolinite. Kaolinite is a clay mineral consisting of an extended sheet of two constituents: a silica-type layer of stoichiometric composition $(Si_4O_{10})^{4-}$ and a gibbsite-type layer $(OH)_6\text{-}Al_4\text{-}(OH)_2O_4$.[8] Its gibbsite structure is similar with the surface structure of imogolite. They examined the pH-dependent protonation of the hydroxyl groups at the basal gibbsite. and proposed that at pH < 5 Al-OH-Al groups at the gibbsite surface are protonated and dominate the overall weathering process of kaolinite. Their computed values of proton density at the gibbsite of kaolinite at pH = 7. 5. and 3 were about to 0. 0.2. and 1.8 μmol/m^2, respectively. In their calculation. the saturation point of protonation was determined to be 2.0 μmol/m^2. The observations made by Wehrli *et al.* can provide some explanations for our results in Figure 3. Assuming that a similar protonation occurred on the imogolite surface at pH = 3. most of surface species of imogolite would be covered with positively charged $[AlOH_2]^-$. Furthermore. this species is responsible for the surface conduction observed in Figure 3.

In order to determine the carrier type of current in the water/imogolite system. we measured the voltage-current at pH = 3 by varying the gate voltage (V_G) with the setup shown in Figure 1. FET devices using water/imogolite exhibited p-type characteristics as shown in Figure 4. When the V_G was changed from +10 V to −10 V. the current
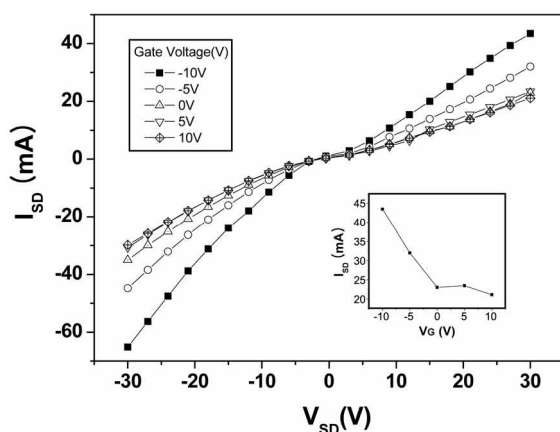
Figure 4. I-V curves of water/imogolite FET device at pH = 3 at various gate (V_G) voltages ranging from −10 to 10 V. Inset is a I_{SD} versus V_G plot recorded on the same device at V_{SD} = 30 V.
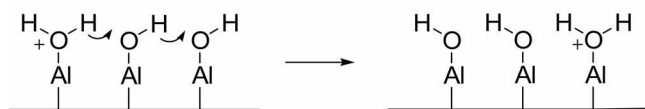
Scheme 1. Suggested mechanism for current transportation in the imogolite/water system.

increased gradually from 21 to 44 mA at V_{SD} = 30 V. (Inset of Fig. 4) The shape of the I-V curves implies that water/imogolite device behaves like a semiconductor with a band gap in the magnitude of 5-7 eV judging from the flat line around V_{SD} = 0 V. The total resistance of this device, which included contact resistances, was calculated to be 1.3 kΩ for V_G = 0 V.

Interestingly, similar behavior has been observed in the layered structure of vanadium pentoxide hydrate ($V_2O_5 \cdot nH_2O$). It had higher electrical conductivity than of anhydrous orthorhombic V_2O_5.[9] In 1983, Barboux *et al.*[10] studied the conductivity of this material in H_2O vapor and investigated the relationship between the changes in conductivity of $V_2O_5 \cdot nH_2O$ with increasing H_2O vapor pressure. They concluded that the increase in conductivity was due to the H^+ in this material. Uchida and Kittaka[11] extended this study by investigating the electrical properties of $V_2O_5 \cdot nH_2O$ by measuring the impedance as a function of H_2O vapor pressure.

The imogolite/water system at pH = 3, in which most of the imogolite surface was believed to be covered with $[AlOH_2]^+$ species, showed p-type semiconductor characteri-

stics. Even though it is not clear what species are to the actual current carriers, a proton (H^+) is thought to be a plausible candidate. In other words, current transfer would occur by the effective motion of a proton, which would be involved in the formation and destruction of bonds through a long chain of hydroxyl groups adsorbed onto imogolite. Therefore, the mechanism for current transportation in imogolite/water system is suggested in Scheme 1.

Conclusion

Electric current flow was observed through imogolite when imogolite (($HO)_3Al_2O_3SiOH$) was exposed to water molecules. The current flow was believed to be due to the bound water on the surface of imogolite. Higher current flow was observed as the pH was decreased. According to the results from the FET measurements by varying the gate voltage, we suggest that current carrier was probably a proton (H^+) moving through imogolite surface. The interaction of H_2O with electrical conditions of imogolite is an interesting subject for further study, since this property might elucidate new properties of the material.

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