

## Atomic Force Microscopy on Imogolite, Aluminosilicate Nanotube, Adsorbed on Au(111) Surface

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Natural imogolite and its adsorption structure were studied on a Au (111) substrate by tapping- and non contact (NC)-mode atomic force microscopy (AFM). When the length of the imogolite tubes was over 2–3 micrometers, a tangled structure was observed. In contrast, when the length was shortened to 1  $\mu\text{m}$ , a layered structure consisting of well-ordered imogolite tubes was formed. When the length was shortened further, imogolite tubes dispersed on the substrate. These results indicate that the adsorption structure is influenced by the interaction between imogolite tubes depending on their length, suggesting the controllability of the structures of this material. The structure of a single imogolite tube itself is also discussed.

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### 1. Introduction

Imogolite is an inorganic aluminosilicate nanotube discovered in volcanic ash soil as a natural material.<sup>1)</sup> The inner and outer walls of the imogolite tube are formed by gibbsitelike sheets with SiOH and AlOH groups, respectively (Fig. 1). This material has attracted considerable attention because of the functions derived from its small tubular structure, and methods for its chemical synthesis have been developed. According to previous studies,<sup>2)</sup> the experimentally obtained diameters of natural and synthesized imogolite tubes are 2.1–2.3 nm and 2.5–2.8 nm, respectively. The diameter obtained by simulations is 2.62–2.89 nm, which is close to the value of the synthetic tubes. The reason for the difference in natural and synthetic diameters has not yet been clarified.

Since imogolite has a hollow tubular structure that has a high surface-to-volume ratio, it exerts significant effects on ion exchange and water adsorption in soil.<sup>3)</sup> For the application of these functions, imogolite tubes have been studied as a heat exchange material, a fuel storage medium and an effective desiccant. The synthesis of new nanomaterials by changing the hydroxyl groups of imogolite to other functional groups has been proposed.<sup>4)</sup> For such applications, analysis of the adsorption structure of imogolite tubes on a substrate is of great importance as is the clarification of the structures themselves.

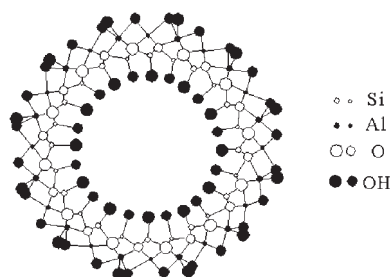


Fig. 1. Schematic image of imogolite. Larger circles of atoms represent front side ones.

Imogolite tubes have been studied thus far by atomic force microscopy (AFM), transmission electron microscopy (TEM) and secondary electron microscopy (SEM).<sup>1,3,5–7)</sup> In the electron microscopy studies,<sup>5,6)</sup> imogolite tubes were hung on a grid mesh, and the analysis of the structure of imogolite itself was the final goal. In the AFM studies, imogolite tubes were observed on a glass substrate studies. However, only random adsorption structures were observed, and any well-ordered structures of imogolite tubes were not found on the substrate. The difference in the molecular length did not affect the adsorption structure. The diameter of the observed single imogolite tube, 20–30 nm, could not be discussed either, because the apparent size of small structures is influenced by the curvature radius of the AFM cantilever, and it is difficult to determine the precise size by AFM.<sup>5–7)</sup>

In this study, imogolite tubes adsorbed on a Au(111) substrate were observed by tapping-AFM in air and by noncontact-AFM (NC-AFM) in ultrahigh vacuum. It was revealed that the adsorption structure depends on the tube length. When the molecular length was over 2–3 micrometers, tangled imogolite tubes were observed, while a layered structure consisting of well-ordered imogolite tubes was formed when the length was shortened to 1  $\mu\text{m}$ . When the length was shortened further, imogolite tubes dispersed on the substrate. These results suggest that the adsorption structure of the imogolite tubes can be controlled by changing the interaction among tubes or between tubes and the substrate. The structure of a single imogolite tube was studied by NC-AFM. Adsorption of particulate solids onto the imogolite outer surface was also confirmed.

### 2. Experimental

Natural imogolite tubes were dissolved in distilled water and dispersed by ultrasonication. The aqueous solution was then dropped on a Au(111) substrate deposited on a clean mica surface and dried for one day in air at room temperature. In this study, tapping AFM and NC-AFM measurements were carried out at room temperature in air and under ultra high vacuum conditions, respectively.

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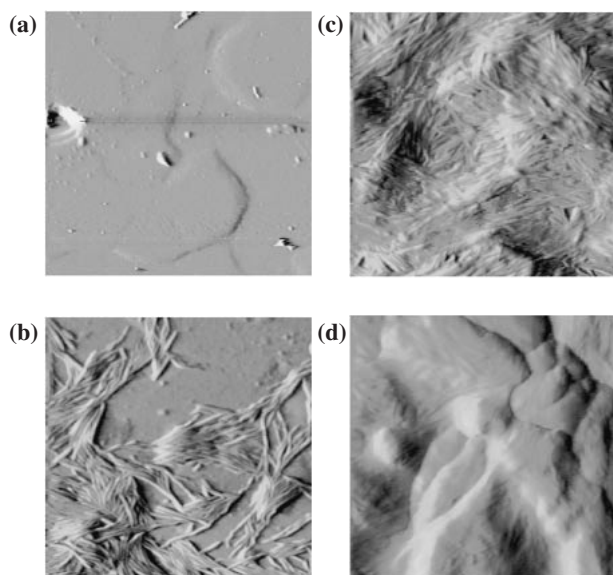


Fig. 2. Tapping-AFM images of imogolite tubes on Au(111) ( $1000 \times 1000 \text{ nm}^2$ ) substrate: (a) outside, (b) at edge of, and (d) around center area of thin layer formed by droplet; (c) image obtained between (b) and (d).

### 3. Results and Discussion

#### 3.1 Adsorption structure of imogolite tubes

On a sample surface prepared by the procedure described, a half-transparent thin layer corresponding to the size of the original droplet of the imogolite solution remained. Figure 2 shows a tapping-AFM image of this surface. A clean Au(111) surface structure was observed outside the thin layer as shown in Fig. 2(a). In contrast, the surface was very rough at the central area of the thin layer, and three-dimensional islands of dense deposit were observed [Fig. 2(d)]. From the center to the edge of the thin layer, the roughness of the surface decreased and thread-like structures were observed [Fig. 2(c)]. Around the edge of the thin layer, the density of the deposit decreased and each thread on the surface was clearly observed [Fig. 2(b)]. These threads were considered to be the imogolite tubes, the structure of which is discussed later.

In order to investigate the adsorption structure of imogolite tubes, we observed the sample surface around the edge of the thin layer by tapping AFM. The length of the imogolite tubes was changed by controlling the duration of ultrasonification carried out before adsorption.<sup>7)</sup> For the imogolite tubes of  $1 \mu\text{m}$  length, the formation of a well-ordered layer structure was observed for the first time.

With a short ultrasonification time, tangled imogolite tubes were observed as shown in Fig. 3(a). Thick bundles of threadlike structures branch into thinner bundles as shown in the magnified image [Fig. 3(d)]. In the area of the thick bundles, threads intertwine with each other. It was also observed that some bundled threads follow the grain structures on the substrate. These results indicate that imogolite is a soft material in contrast to the carbon nanotube, suggesting the possibility of flexible structural control of this material on the nanoscale. Since threads were bundled, the length of each molecule could not be determined; however, the length of the observed bundles was over 2–3 micrometers.

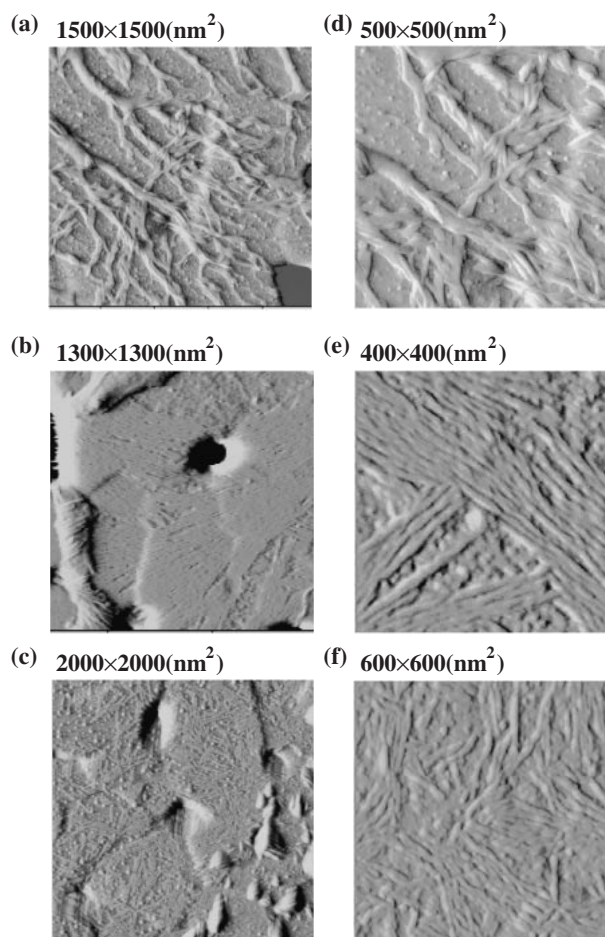


Fig. 3. Tapping-AFM images of characteristic adsorption structures around edge of thin layer formed by droplet: (a) tangled molecular, (b) well-ordered layer, and (c) dispersed structures. (d), (e) and (f) are magnified images of (a), (b) and (c), respectively.

When the imogolite tubes were shortened to  $1 \mu\text{m}$  with further ultrasonification, a flat layered structure consisting of domains was observed [Fig. 3(b)]. As shown in the magnified image [Fig. 3(e)], well-ordered imogolite tubes were observed in each domain. These threads are equally spaced and have the same width as that of the thin branches observed in Fig. 3(a), and no further branching was observed. Thus, we concluded that the threads in Fig. 3(e) are single imogolite tubes. The placement of these domains was independent of the steps, grain boundaries, and crystal orientation of the Au(111) substrate surface. Even when the layers overlapped, threads were well-ordered in each layer. These results suggest the existence of a strong interaction among threads in a layer.

For the molecules of shorter length [Fig. 3(c)], a flat structure similar to that in Fig. 3(b) was observed. However, contrary to the well-ordered structure in Fig. 3(b), short imogolite tubes  $\sim 0.1 \mu\text{m}$  long dispersed, as shown in the magnified image [Fig. 3(f)]. In some places, longer threads exhibited the local formation of an ordered layer structure. These results indicate that the adsorption structure is strongly influenced by the length of imogolite tubes, namely, the change in the tube-tube interaction. Since the substrate structure has no effect on the adsorption site and orientation of the short imogolite tubes, the interaction between

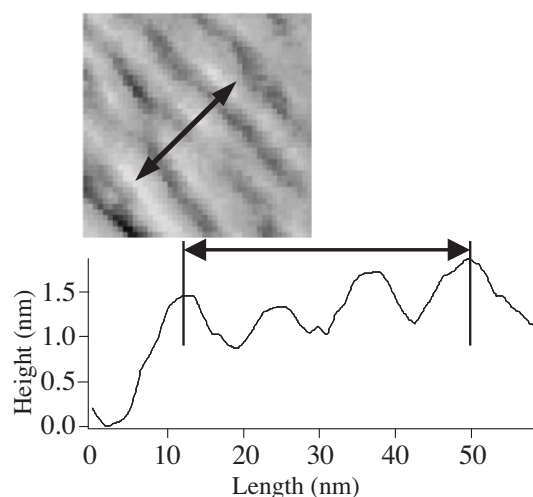


Fig. 4. Magnified tapping-AFM image of well-ordered layer structure and its line profile.

imogolite tubes and the substrate is weak in this case. It is noteworthy that the structural change shown in this study was not observed in the case of the glass substrate.<sup>7)</sup>

### 3.2 Structure of single imogolite tube

The diameter of a single thread observed in Figs. 2 and 3 was 20–30 nm, which is significantly larger than the value predicted by the theory, 2.1–2.3 nm. Although the observed height by tapping AFM was 2–3 nm, the actual diameter cannot be determined from this value alone. In this section, we consider this point in detail.

In the AFM experiment, objects of apparently larger width are generally observed, caused by the influence of the curvature radius of the AFM cantilever. As the size of the object becomes 2–3 nm, as in this study, this effect becomes particularly prominent. This is one reason why the molecular structure was not discussed in previous AFM studies.

In order to determine the diameter, we investigated the layered structure shown in Fig. 3(b). In this figure, the threads in the domain are equally spaced and well-ordered. Since an attractive interaction between the tubes causes this structure, these threads are supposed to contact each other. Therefore, the diameter of the thread can be obtained by measuring the interval between the ordered threads. Figure 4 shows a magnified image of the ordered threads and its cross section along the arrow in the image. The averaged interval between the threads was 10–15 nm, which is 5–8 times larger than the theoretical value of the imogolite diameter. In order to see the details, we carried out NC-AFM on this material.

An NC-AFM image of a single thread and its cross section are shown in Figs. 5(a) and 5(c), respectively. The observed surface is very rough (2–3 nm) as shown in the cross section, and a spiral pattern can be seen. In order to emphasize the local corrugation, the differential image of Fig. 5(a) is shown in Fig. 5(b). The pitch of the spiral in Fig. 5(b) is approximately 5 nm, which is much larger than the periodicity expected from the atomic structure of the imogolite tube. It is also notable that granular adsorbates with a diameter of  $\sim 5$  nm exist near the thread as shown in

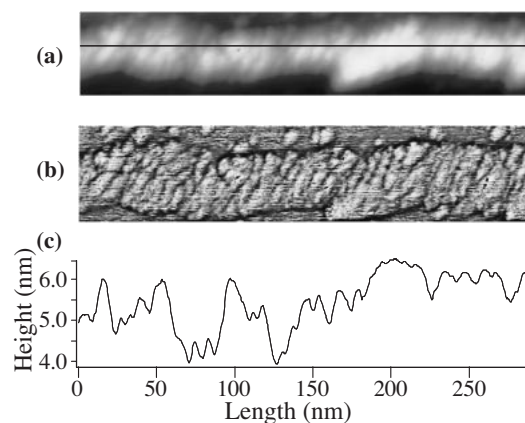


Fig. 5. NC-AFM images of single imogolite tube and its line profile: (a) height-image, (b) differential images, and (c) cross section along line in (a).

Fig. 5(b). The adsorbates were also observed in other areas on the substrate.

From these results, the imogolite tube may be covered by the granular adsorbate, resulting in the observed large diameter. The material may be a fragment of flattened imogolite tubes on the substrate due to their softness, which is under examination.

Since the intermolecular interaction between imogolite tubes should be influenced by the adsorbates on the molecular surface, variation in the adsorbate may be another possibility to control the ordering of the imogolite tubes.

## 4. Conclusions

Natural imogolite, one of the smallest inorganic tubes, was adsorbed on a Au(111) substrate and observed by AFM. It was revealed that the adsorption structure depends on the tube length. For tubes with a length of 1  $\mu\text{m}$ , a well-ordered structure was observed for the first time. The diameter of the observed imogolite was 10–15 nm, which is 3–6 times larger than the theoretically predicted value. Adsorption of some granular substance on the outer surface of imogolite, resulting in an observed larger diameter, was also confirmed. Details of the adsorbate are under investigation.

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