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# AFM Observation of Self-Assembled Monolayer Films on GaAs(110)

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Atomic force microscope images and X-ray photoelectron spectra confirm that the self-assembled monolayer (SAM) films of octadecanethiol (ODT),  $CH_3(CH_2)_{17}SH$ , are formed on the cleaved GaAs (110) surface in an ethanol-diluted ODT solution. However, there exist circular depressions in the surface whose area increases with immersion time, indicating that the trace of water in the solution may oxidize GaAs followed by removal of ODT molecules. The oxidation in pure ethanol is faster than that in ODT solution, showing that the SAMs prevent GaAs from oxidation.

### **1. INTRODUCTION**

Self-assembled monolayer (SAM) films consist of organic molecules spontaneously adsorbed onto substrates. Since SAMs are energetically-favored and ordered, these films exhibit uniform and robust structures of nanometer-scale thickness. Moreover, these films show a wide range of surface physical and chemical properties, distinctly different from the bare substrate materials. In principle, SAMs can provide "designer" surfaces by selecting molecules formed on the substrates. Therefore, SAMs have been of intense interest in the past few years, but actual examples of highly organized films have been limited almost exclusively to those formed on oxide and coinage metal substrates.<sup>1)-7)</sup> Recently, it has been reported that the SAMs of alkanethiols could be formed on the GaAs (001) surface.<sup>8)</sup> However, there still exist many problems in SAMs such as nanometer size defects 9), surface oxidation, film non-uniformity. In order to overcome these problems, it is necessary to clarify the formation mechanism and properties of SAMs from the atomistic/molecular point of view. Atomic force microscope (AFM) provides a good mean to investigate SAMs on the molecular scale resolution.

Here, we fabricate ODT  $CH_3(CH_2)_{17}SH$ , SAMs on the GaAs (110) surface and observe the films by using AFM. In this paper, we shall show their AFM images and compare them with the results from X-ray photoelectron spectroscopy (XPS).

## 2. EXPERIMENTAL

We used cleaved GaAs (110) (Zn doped,  $1-2.5 \times 10^{19}$  cm<sup>-3</sup>) surface as the substrate for SAMs since it exhibited an atomically flat surface. In order to avoid oxidation during film formation, the substrate was cleaved in a 1.0 mM ODT solution in ethanol and the solution was preserved in an argon purged flask to prevent ODT mol-

ecules from oxidation. After keeping the samples for a certain period of time, the wafers were rinsed with pure ethanol solution for 5 min and dried with pure argon gas.

The films were imaged with a commercial AFM in both contact and non-contact modes using a 20 µm scanner. All the films were observed within 3 hours after taken out from the solution. In the case of contact mode, both normal and lateral deflections were detected by an optical beam deflection method with a four-segment photodetector to observe topographic and frictional force, respectively. A silicon nitride cantilever with a spring constant of 0.09 N/m was used. Typical force was set to be less than 0.5 nN to minimize the modification of film surfaces. In the case of non-contact mode, a silicon cantilever with an average spring constant of 19 N/m was used. Typical modulating amplitude and frequency were of the order of 20 mV and 137 kHz, respectively. We found that the non-contact mode of operation provided more consistent and accurate data on the depression depth of the films. This is reasonable since in the contact mode, the AFM tip presses on the surface with a certain force resulting in erroneous height values from the topographic images. No damage to the films was observed even after multiple scans with both AFM modes.

XPS measurements were also performed to investigate the composition and chemical bonding of the surfaces before and after the ODT immersion. The samples were immediately introduced into the loadlock chamber after taken out from the solution in order to avoid oxidation of the surfaces. The spectra were obtained with 250 W of Al- $k\alpha$  X-ray using a cylindrical sector field analyzer, with a base pressure of less than  $5 \times 10^{-10}$  Torr. XPS spectra were acquired by setting the work function of the specimen to 4.5 eV.

#### **3. RESULTS AND DISCUSSION**

We measured at least four images with sizes larger



Fig.1 AFM images of ODT monolayers immersed for a certain period of time, (a) as cleaved GaAs (110) surface, (b) 2 days, (c) 13 days, (d) 20 days, (e) 29 days, and (f) 2.5 months immersion. Straight lines in the figures denote that atomic steps exist on the cleaved GaAs (110) surface. In (b)-(e), dark spots are depressions of SAMs.

than 1 µm<sup>2</sup> for each sample to ensure real surface features. Figure 1 shows typical AFM images of the surfaces after different immersion time. Figure 1 (a) is an AFM image of a freshly cleaved surface and exhibits atomic steps with a height of 0.2 nm, i.e., monolayer height of GaAs. Figure 1 (b)-(e) show the images for the surfaces immersed in ODT solution. In these images, step-like structures originated from the monolayer steps of the GaAs substrate which are still visible. It is found that the area of circular depressions (10-300 nm in size) increases with immersion time. However, these circular depressions have surprisingly a constant depth of 1.3±0.3 nm (indicating a close packed, tilted ODT monolayer). These features have been observed with scanning tunneling microscopy in other systems.9) After a prolonged immersion time (Fig.1 (f)), the surface has no longer any clear depression, but monolayer steps of substrate are still visible. These observations indicate that SAMs are really formed on the GaAs (110) surface and the depressions may come from the desorption of ODT molecule from the surface due to either the degradation of the solution or the trace of water in the solution.

In the non-contact mode, we observed almost the same images as those in the contact mode and the measured depths of the depressions are approximately 1.4 nm except smaller sizes. (The depth measurements are somewhat inaccurate due to the finite apex of the AFM tip in the case of small depressions.) These values are in good agreement with the thickness of SAMs estimated from a molecular model, where no substrate reconstructions occur and the ODT molecules selectively chemisorb on the As atoms to form a centered  $2\times 2$  close-packed arrangement, tilted 57.4 ° with respect to the surface normal.<sup>10</sup>

We also performed lateral force microscopy (LFM) measurement to ascertain SAMs on GaAs (110), which is shown in Fig. 2. The frictional force is four times larger (about 10 nN  $^{11,12}$ ) on the depressions than on the flat parts of the surface (SAMs). The frictional force reflects the physical and chemical properties of the surfaces, i.e., difference of composition and chemical binding between these two regions.

The surface chemical bonding and compositions were examined for two cases by using XPS, (a) a surface immersed in pure ethanol solution for one day and (b) one immersed in ODT solution for two days. The results are shown in Fig. 3. In the case of (a), the As  $2p_{3/2}$  spectrum is split into two peaks assigned as metal and oxide at 1322.4 and 1325.6 eV, respectively.<sup>13)</sup> Ga  $2p_{3/2}$  spectrum is composed of metal peak at 1116.5 eV and oxide peak at 1117.6 eV, but only one peak is observed due to the small



Fig.2 An LFM image of SAMs on GaAs (110) which was immersed in ODT solution for 29 days, the same sample as Fig. 1 (e).



**BINDING ENERGY (eV)** 

Fig.3 Typical photo-electron spectra on p-type GaAs (110). (a) after immersed in pure ethanol solution for one day, (b) after immersed in ODT solution for two days.

binding energy shift and natural width of X-ray source. O 1s peak (531.0 eV) is also appeared, while no C 1s peak is detected. On the contrary, in the case of (b), no oxygen peak is observed even after two days immersion in the ODT solution, while a carbon peak appeared at 285.0 eV. The full width at half maximum of Ga  $2p_{3/2}$  spectrum decreases, indicating very little oxidized component of gallium. From the above results, we can conclude that ODT molecules spontaneously chemisorb on As atoms of GaAs (110) surface before oxidation.<sup>10)</sup> This means that SAMs play an important role in preventing oxidation of the GaAs surface. However, we could observe no sulfur peaks due to ODT molecules. It is partly because transition probability of sulfur photoelectron is limited and this peak piles up on the large and broaden Ga 3s peak. Another reason is that sulfur atoms exist at the interface between GaAs substrate and long molecules of ODT (2.6 nm), and therefore sulfur photoelectrons attenuate through the molecules.<sup>10</sup> When immersed in ODT solution for two months, oxygen and oxide peaks appeared, while carbon peak decreased. This indicates that ODT molecules desorb from the GaAs surface and the bare GaAs surface is oxidized.

## 4. CONCLUSIONS

We observed octadecanethiol SAMs on GaAs (110), and investigated their desorption mechanism using AFM and XPS. The AFM results reveal that there exist characteristic depressions with nanometer size in SAMs which increase in both size and number with immersion time. The XPS studies revealed that no detectable oxygen except carbon exist on the SAMs covered surface, while significantly less carbon and oxygen exist on the bare GaAs substrate. For the SAM immersed longer period, e.g., 2 months, the carbon signal decreased while oxygen increased. We concluded that the SAMs are formed on GaAs (110) surface where surface oxidation was less, and that the depressions observed in AFM images are due to the oxidation of the substrate in the degraded solution and resulting desorption of ODT molecules.

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