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Field ion microscope observation of tungsten surface processed in ethanol

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ABSTRACT

An attempt has been made to observe ethanol molecules on tungsten needle by field ion microscope (FIM). An electrochemically polished tungsten needle was dipped in ethanol with and without application of positive bias. FIM images which exhibited elongated spots were obtained with the samples processed with the positive bias. Without the positive bias, the elongated spots were not observed. It was suggested that these spots were originated from the ethanol molecules. Field emission microscopy observations were also conducted to investigate the processed tip surface.

1. Introduction

Field ion microscopy (FIM) is known as one of the techniques for surface structural analysis in atomic scale. FIM has been well-established as a method for analyzing conductive materials, and many brilliant progresses have been reported [1,2]. From the early stage, efforts have been made to image organic molecules [3–9]. Observation of organic molecules is, however, difficult because of many problems. Fabrication of the sharp tip itself with organic molecules is rather difficult. An alternative is to attach organic molecules onto a metal tip, but in this case, it is difficult to form strong bond between the metal and the organic molecule that can stand for the higher electric field applied during the FIM observation. Therefore, Mueller and Rednulic [3], and Graham et al. [4] prepared samples with depositing platinum thin films to embed organic molecules. Iwatsu et al. [5] co-deposited metal atoms and organic molecules to form metal phthalocyanine on the tip surface. Another method to prepare the sample was also reported by above authors: dipping metal needles in *n*-octanol applying a positive bias to the tip [6]. Other works were conducted in various ways to observe organic molecules on metal tips [7–9]. In spite of the above efforts, there are a limited amount of the examples of the observation of the structure of organic materials with FIM [5], and it is still difficult to identify each molecule of organic samples with FIM. Together with the experimental approach, theoretical approach has also been made [10]. The theoretical analysis revealed that the FIM image does not reflect the exact position of the atoms.

To attach organic materials onto metal tips and to observe them with FIM in atomic scale have not fully succeeded. From this background, our work focused on adsorbing organic molecules on metal tips in order to observe each of the molecules on the tip surface with FIM. We report here the results of the FIM observation of tungsten (W) tips reacting with ethanol (C_2H_5OH), which was chosen considering its structural simplicity. As a result, some chemisorption of particles on the tip surface, which may originate from ethanol molecules, was observed in the FIM images. In addition, the analysis of field emission microscopy (FEM) was done in order to investigate the changes of the work function of the tip surface after the reaction, which leads to understanding of the adsorption of the molecules.

2. Experimental procedure

2.1. Experimental setup

FIM observation was performed in a vacuum chamber which was evacuated by a combination of a turbomolecular pump and titanium sublimation pump. The base pressure of the chamber was 10^{-7} Pa. The W tip was mounted on a cold finger cooled by liquid nitrogen. A micro channel plate (MCP) was located at 10 cm away from the tip. Typically, helium (He) gas was introduced in the chamber to a pressure of 2×10^{-2} Pa (calibrated by the relative sensitivity of He) during the observation. The FIM images were recorded by a commercial video camera.

2.2. Experimental procedure

Before observing the FIM images of the processed tip, each tip was observed in order to confirm the initial surface. After the

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observation, the tip was taken out of the chamber and then immersed in ethanol, of which details will be shown below. After the process is over, the tip was installed again in the vacuum chamber, and FIM images were observed. With the same configuration, FEM observation was also conducted after evacuation of He gas to 10^{-6} Pa.

2.3. Processing of tip in ethanol

For the processing, ethanol of 99.5% purity was used as provided and no distillation was done. The tip was immersed in ethanol, in a way similar to that in Ref. [2]. During the immersion, the positive voltage of 10 V was applied to the tip in order to react it with ethanol [6]. The difference between the process shown in Ref. [2] and ours was such that we did not put a cathode in ethanol in order to avoid excess reaction. We prepared three samples: the first one was a control, which was immersed in ethanol without the positive bias to confirm the effectiveness of the applying the voltage (Sample 1), and the others were immersed in ethanol following by applying 10 V for 60 s (Samples 2 and 3). The tip radii of the samples before the process were 12 nm and 14 nm, respectively. These tips were introduced into chamber again, and FIM and FEM observation was done under the above-mentioned conditions.

3. Results

Fig. 1(a and b) show the FIM images of Sample 1 before and after the immersion. The voltages for the FIM observation were both 10 kV. The numbers shown in Fig. 1(a) are Miller indices. There were few changes in the appearance of the images before and after the immersion.

The FIM image of Sample 2 which was processed in ethanol is shown in Fig. 2(a). The required voltage for the FIM observation was 19.5 kV. It was found that the appearance of the image after the process were largely different from that of clean tungsten. Many elongated spots were observed, and almost all the spots were aligned along the radial direction. During the observation, the spots were field-desorbed one by one. Fig. 2(b) shows the FEM image of the same tip after observing the FIM image. The image was observed at the voltage of −2.8 kV. In Fig. 2(a and b) it is seen that the emissive area in FEM image well agreed with the area where the intense signal of FIM image was observed. Fig. 2(c) shows image superposing Fig. 2(a) on the image before the reaction. The position of the (1 1 1) planes in both images was aligned, and there were no modifications of the size of the images. The Miller indices written in Fig. 2(c) shows the facets involved in the areas

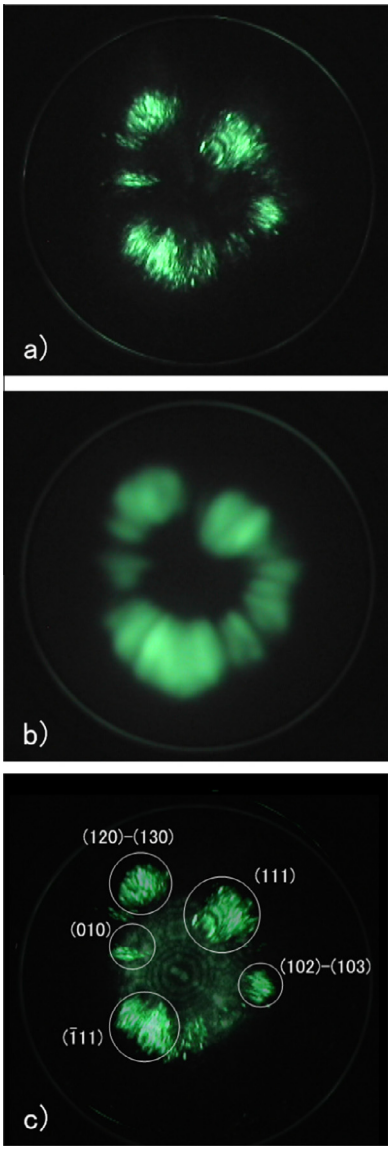

Fig. 2. (a) FIM image of Sample 2 at a voltage of 19.5 kV. (b) FEM image of the same tip, which was observed after evacuating helium gas, at a voltage of −2.8 kV. (c) Superposed image of Fig. 2(a) on the FIM before the reaction. The numbers in the image is Miller indices. In superposing the image, the (1 1 1) planes in both images was aligned, and there were no correction of the size of the images.

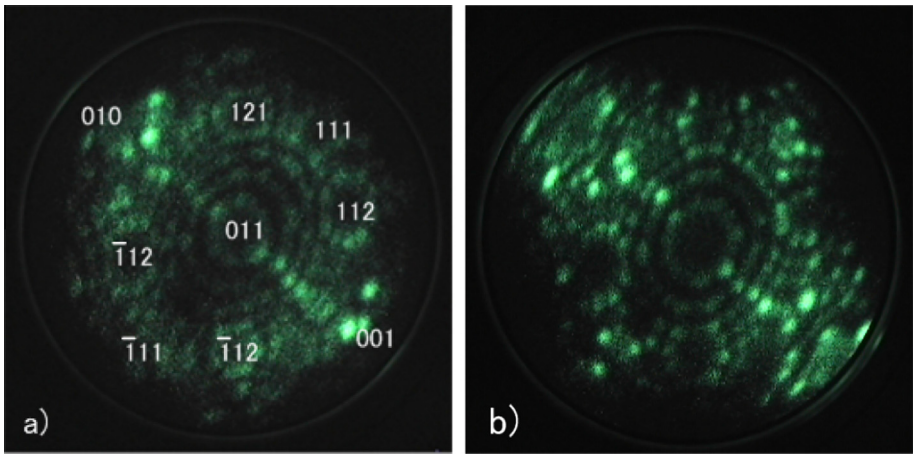

Fig. 1. FIM image of Sample 1: (a) before and (b) after the immersion into ethanol, both of which were observed at a voltage of 10.0 kV.

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