

Control of Adsorption and Desorption of Oxygen on TiO₂ Surface by Atomic Force Microscope

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The adsorption of oxygen on the TiO₂ surface is accelerated by applying -3.0 V in O₂ atmosphere. The spatial distribution of adsorbed oxygen atoms is confirmed from AFM topographs and conductivity maps. The current vs voltage characteristics after uv irradiation are altered by the photodesorption of oxygen.

Key words: AFM, TiO₂, oxygen adsorption, photodesorption

1. INTRODUCTION

The manipulation of atoms on solid surfaces by a scanning tunnel microscope (STM) has attracted a considerable attention from viewpoint of an application of nanolithography. The spatial resolution of a feature on solid surface was of order of a few microns [1-4]. The principle of the nanolithography by STM is based on field-assisted reactions on the solid surface. Thus, the mechanism of the field-assisted surface reactions must be revealed in detail for improving the spatial resolution. In STM however an electric field was not varied in the wide range during scanning although current vs voltage (I-V) characteristics were measured at a fixed position as in the case of current imaging tunneling spectroscopy[5]. In contrast, an atomic force microscope with a conducting cantilever (AFMC) can observe not only a topograph but also a map of the surface conductivity of a solid surface[6]. In AFMC, an electric field is varied in a wide range, so that the depletion or accumulation layer can be formed at a selected position of the semiconductor surface. The adsorption of oxygen on the surface of an n-type oxide semiconductor was accelerated in the accumulation conditions, and the desorption of oxygen occurred in the depletion condition under the uv illumination[7]. In the present work, I-V characteristics at an interface of the TiO₂ and a cantilever have been measured in the dark and under uv illumination. The adsorption of oxygen on the TiO₂ surface is attempted under the accumulation condition in the dark. The effects of uv illumination on the adsorbed oxygen are studied from current vs voltage characteristics under uv illumination.

2. EXPERIMENTAL

For preparation of an n-type TiO₂, the single crystalline TiO₂ (110) 10×10×1 mm in dimensions was reduced at 800 °C for 4 h in 2% H₂ atmosphere.

An In metal was deposited on a rear surface of the TiO₂ crystal for making an ohmic contact. Measurements of a topograph and a conductivity map were carried out by an atomic force microscope (SPI 3800N SEIKO). The TiO₂ crystal was placed in an ambient controlled chamber into which ultraviolet light was introduced through a SiO₂ fiber. The laser light detecting the distortion of a cantilever was passed through a glass filter (Y-50) which cut off light of 500 nm or less, in order to eliminate uv light for the irradiation of the TiO₂ surface. A light source was a high pressure-mercury lamp of 100 W. Light consisting mainly of lines at 365 nm was supplied by passing light of the mercury lamp through a filter (UV-D36B) which was transparent around 360 nm. A conductive cantilever was Au-coated Si₃N₄ (a force constant 0.18 N/m and a resonance frequency of 25 kHz). For measurements of I-V characteristics, a bias voltage was swept from -4.0 to 8.0 V at a sweep rate of 0.6V/s, where a positive voltage was defined when the TiO₂ was positively polarized with respect to the cantilever. AFM topographs and maps of the surface conductivity were taken by a contact mode in which a repulsive force of 0.18×10^{-9} N was maintained during scanning.

3. RESULTS AND DISCUSSION

A magnitude of current was dependent on the situation of the surfaces of the TiO₂ and the cantilever. In a specific case, no current was frequently detected in the range of -3.0 to 3.0 V. Under this situation an application of a large positive voltage led to no changes in current vs voltage (I-V) characteristics, whereas an application of -10 V resulted in an abrupt appearance of current. The abrupt appearance of current was observed in either O₂ or Ar atmosphere. Figure 1 shows an AFM topograph of the TiO₂ surface after an application of -10 V for 10 s at several positions of the TiO₂ surface. As seen in Fig. 1, some upheavals formed on the TiO₂ surface. Figure 2

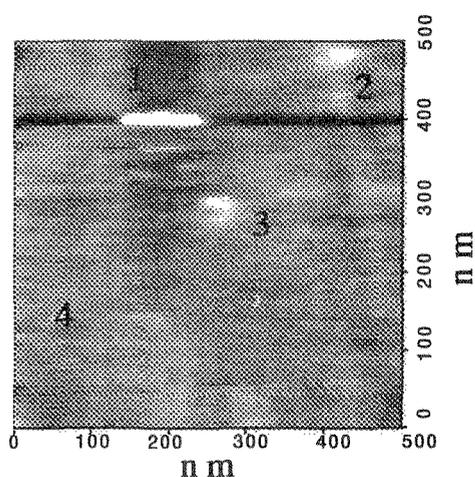


Fig. 1. AFM topograph of TiO_2 surface after a voltage of -10 V has been applied.

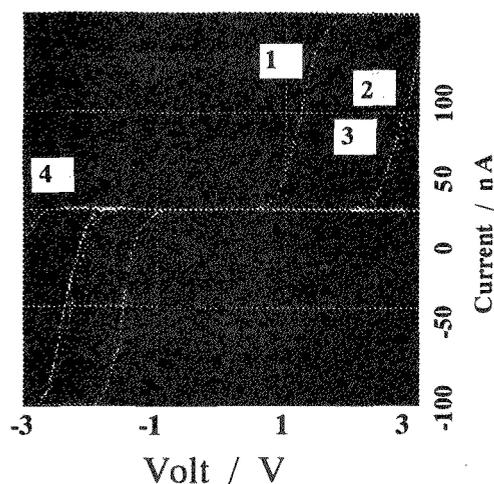


Fig. 2. Current vs voltage characteristics at positions of 1, 2, 3 and 4 denoted in Fig. 1.

shows I-V characteristics at several positions of the TiO_2 surface shown in Fig. 1. Curve (1) is I-V characteristic at the large upheaval which are denoted by the position number (1). A large current is observed at a voltage > 1.0 V and < -1.0 V. Curves of (2) and (3) are the I-V characteristics at the small upheaval denoted by the position number (2) and (3). Current flows at a voltage > 2.0 V and < -2.0 V. Curve (4) is I-V characteristic at the TiO_2 surface where no upheavals are formed. No current is observed at a positive voltage. The I-V curve (4) is typical of the Schottky junction between TiO_2 and Au of the cantilever. The curves (1), (2) and (3) are I-V characteristics expected for a junction of metal / insulator / semiconductor (MIS). Such breakdown of the rectification characteristic was observed at the TiO_2 surface on which Au was deposited by vacuum evaporation. Accordingly, these upheavals on the

TiO_2 surface are assigned to Au films. The deposition of the Au films occurs only at a large negative voltage of -10 V. This suggests that the Au films are deposited by field-assisted evaporation: Au^+ ions are emitted from the cantilever by an electric field across the gap between the TiO_2 surface and the cantilever, and then accelerated Au^+ ions are deposited on the TiO_2 surface [8]. An application of -10 V for a short period gives rise to the evaporation of Au atoms, and the cantilever surface may be cleaned. As a result, a proper I-V curve may be achieved as seen in the curve 4.

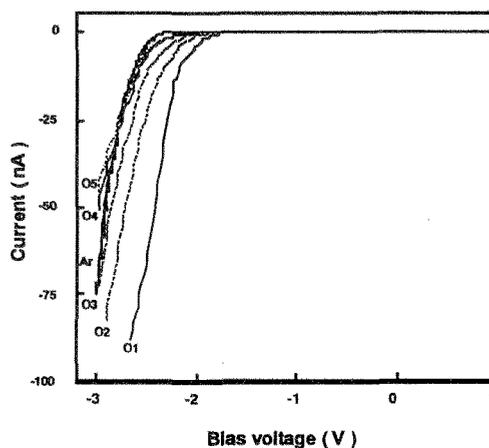


Fig. 3. I-V characteristics at interface of TiO_2 and cantilever in Ar or O_2 atmosphere. O1, O2, O3, O4 and O5 are I-V curves after an application of -3.0 V for 0, 5, 10, 15 and 30 min.

For suppression of the Au deposition, the adsorption and desorption of oxygen were carried out in the range of -4.0 to 8.0 V. I-V characteristic at a position of the TiO_2 surface in Ar atmosphere is shown by a dotted line in Fig. 3. An appreciable current flows at a negative voltage less than -1.5 V, whereas no current flows at a positive voltage. The I-V characteristic is typical of the Schottky junction; an applied potential is mainly dropped in the space charge layer of the TiO_2 rather than across the gap between the TiO_2 surface and the cantilever. The I-V characteristic in Ar atmosphere remains unchanged after the TiO_2 has been kept for 30 min at -3.0 V. Similarly, no changes in I-V characteristics are observed in Ar atmosphere after an application of -2.0 , -1.0 , 1.0 , 2.0 and 3.0 V for 30 min.

An ambient gas was changed from Ar to O_2 after the cantilever was moved out from the TiO_2 surface, and then the cantilever was again approached the TiO_2 surface for measuring I-V characteristics. A position of the TiO_2 surface in contact with the cantilever was not coincident with that in Ar atmosphere. In Fig. 3, a solid line denoted by a symbol O1 is I-V

characteristic for the first sweep. A magnitude of current is larger than that in Ar atmosphere. The difference is mainly ascribed to a variation in surface conductivity as will be seen in a map of the surface conductivity. In Fig. 3, solid lines denoted by symbols, O2, O3, O4 and O5 are I-V characteristics after an application of -3.0 V for 5, 10, 15, and 30 min. It should be noted that the I-V characteristics are drastically altered with a period of an application of -3.0 V; current at a negative voltage decreases remarkably up to the application period of 15 min, but a change in current is slight from 15 to 30 min. Thus, the decrease in current is almost completed until 15 min.

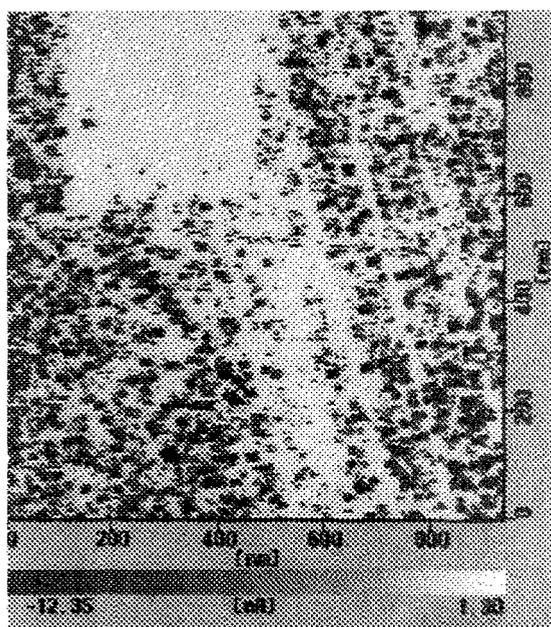


Fig. 4. A map of conductivity at -2.0 V.

A possible surface reaction at room temperature is the adsorption of oxygen molecules: Oxygen molecules are adsorbed on the TiO_2 surface by capturing electrons in the conduction band of the TiO_2 and consequently negatively charged chemisorption states, O^- , are formed in the band gap of the TiO_2 surface. The negatively charged surface states are well known to be responsible for an increase in the barrier height at the TiO_2 -Au interface, leading to the decrease in current at a negative voltage[9]. Besides an influence on the barrier height, the adsorbed oxygen molecules can interrupt the overlaps between the wavefunctions of Au and Ti atoms, and thus electron transfer from the conduction band of the TiO_2 to Au is hindered. Such an effect of adsorbed molecules is meaningful in STM,[10] but is not so important in the present work because a tight contact between the TiO_2 and the cantilever is attained under a repulsive

force.

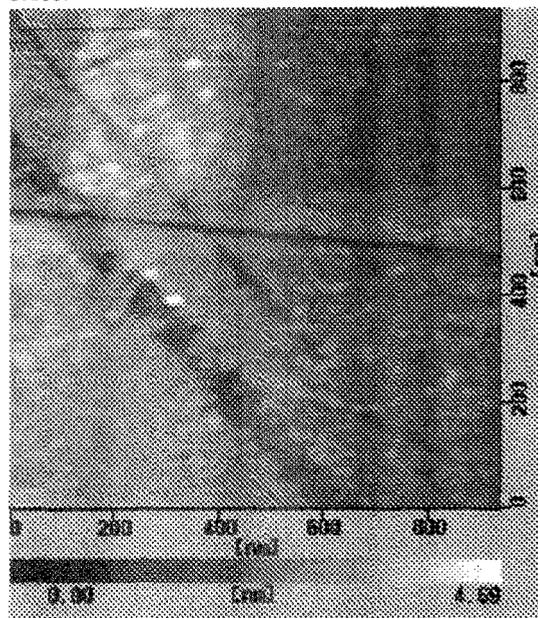


Fig. 5. AFM topograph taken simultaneously with a conductivity map shown in Fig. 4.

A possible explanation for the acceleration of oxygen adsorption at a bias voltage of -3.0 V is related to the current flow at the TiO_2 -Au interface. In AFMC, current of a few ten nA corresponds to a high current density because a contact area is very narrow. The high current density is responsible for the excitation of the lattice vibration at a local site, leading to the acceleration of oxygen adsorption[11]. However, this explanation is not relevant because a change in I-V characteristic is very slight after a bias voltage of -2.0 V has been applied for 30 min to an another surface position where current of 20 nA flowed at -2.0 V (results are not shown here). An alternative explanation is due to the modulation of the electron density at the TiO_2 surface by an electric field: As mentioned above, the electrical properties of the TiO_2 -Au interface are typical of the Schottky junction, although a narrow gap exists between the TiO_2 and the cantilever. In the Schottky junction, the electron density at the TiO_2 surface increases with increasing a negative voltage, and thus a rate of oxygen adsorption which is proportional to the electron density at the TiO_2 surface is accelerated by increasing a negative voltage[7].

We attempted to observe a map of the surface conductivity by the following procedures: First, an area of 200×200 nm was scanned at -3.0 V in O_2 atmosphere at a very low scanning frequency of 0.5 Hz. It took 30 min for the scanning a whole area of 200×200 nm where large current of ca. 100 nA

flowed during the scanning. Subsequently a scanning area was expanded to 1000 × 1000 nm and a map of the surface conductivity was taken at -2.0 V. The obtained map of the surface conductivity is shown in Fig. 4. A noticed feature of the surface-conductivity map is that zero conductivity appears in the area of 200 × 200 nm which has been scanned at -3.0 V. The zero conductivity area is clearly distinguishable from other area where current of 13 nA or less flows. As mentioned above, the decrease in current by applying -3.0 V reflects on the adsorption of oxygen on the TiO₂ surface. Consequently, the map of the surface conductivity suggests that the adsorption of oxygen occurs selectively on the area of 200 × 200 nm which has been scanned at -3.0 V. Of course, a small amount of oxygen molecules is probably adsorbed on the other area, because the desorption of oxygen by uv irradiation is insufficient at zero bias voltage[7].

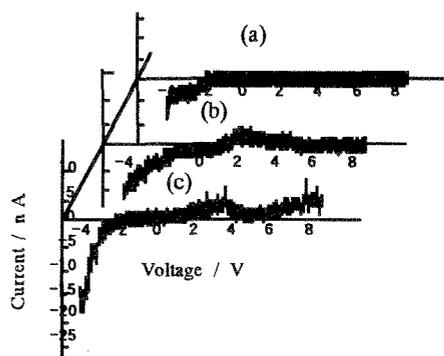


Fig. 6. Current vs voltage characteristics in the dark before (a) and after (b) uv illumination. (c): under uv illumination.

An AFM topograph of the area of 1000 × 1000 nm which was taken simultaneously with the map of surface conductivity is shown in Fig. 5. In the AFM topograph, there are scars and valleys on the TiO₂ surface which are mainly produced by etching in a HCl solution. Such surface roughness is one of the reasons of the nonuniform surface conductivity shown in Fig. 2. In spite of a slight surface roughness, an apparent upheaval by 2 nm is observed at the area of 200 × 200 nm. The upheaval of 2 nm is extremely large compared with the size of an adsorbed oxygen molecule itself, so that the upheaval is ascribed to another attractive force, rather than a real topographic change. A reasonable origin of the attractive force is attributed to negative charges of adsorbed oxygen molecules, O₂⁻, which are also responsible for the increase in the barrier height at the TiO₂-Au interface[12]. An AFM topograph taken

at 0 V is same as in Fig. 5, and remains unchanged for a few days in Ar atmospheres. Thus, desorption rates of oxygen are fairly low at room temperature in the dark. The stability of the pattern due to the oxygen adsorption both in dark and under uv illumination will be discussed elsewhere.

To reveal the mechanism of photodesorption of oxygen on the TiO₂ surface, I-V characteristics at the interface of the TiO₂ and the cantilever were measured in Ar atmosphere under uv illumination. In Fig. 6, curves (a) and (c) are I-V characteristics before uv illumination and under uv illumination, respectively. Curve (b) is the I-V characteristic in the dark after uv irradiation has been performed at 10 V for 1 min. A noticed feature in Fig. 6 is that current flows even at a positive voltage under uv illumination. The positive current is in part ascribed to the electron injection from the Au to holes photogenerated in the valence band of TiO₂. The I-V characteristic after uv irradiation is apparently different from that before uv irradiation: A magnitude of current at a negative voltage is larger compared with that before uv illumination. This implies that the barrier height at the TiO₂ and Au interface is reduced by uv illumination. Observations of AFM-topographic changes caused by the photodesorption are in progress.

4. REFERENCES

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