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Electrical Characteristics and Dynamics of Adsorbed Argon Domain System on TiO_2 Surface due to Angle-Resolved Transmission Current Spectroscopy

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We present time dependence of adsorbed Ar domains on thin titanium oxide in high vacuum just after 150 L argon gas exposure for 0.3 seconds. The kinetics of argon domains on titanium oxide was measured with angle-resolved transmission current spectroscopy in magnetic field (ARTCSM). Transmission current suddenly decreased due to the scattering induced by adsorbed Ar atoms and recovered to the value in the steady state after 1300 seconds from the argon exposure. Dynamic of desorption process of adsorbed argon atoms was detected by characteristics of current noise generated by desorption process of argon atoms. Incident angle dependence of the logarithm of the ration of transmission current just after argon exposure and that in the steady state showed the critical change at 42.6°. This critical behavior is due to the electronic structure constructed with adsorbed argon atoms and thin titanium oxide.

Key words: Ar domain , Transmission current , Titanium oxide, desorption dynamics , Electronic structure

1. INTRODUCTION

In order to develop new devices and functions, it is important to understand the electronic structure of adsorbed layers on functional materials. Titanium oxide is one candidate for such functional materials because of catalytic characteristics. Electronic structures of small system strongly depend on the number of constituent atoms. In general, such small clusters were found in initial state of condensation process or final state of evaporation process. It is, therefore, useful to investigate electronic structures in desorption process of adsorbed atom system. We used argon system because argon atoms adsorbed reversibly. To monitor these phenomena, many kinds of techniques were improved [1,2]. For example, electrons, neutrals and photons were used as indirect probes for monitoring surfaces electronic structures.

But the behaviors of adsorbed atoms at the surface in very wide area have never been understood because of the lack of in-situ monitoring techniques in the practical circumstance. In order to improve these situations, we developed new equipment to investigate surface electric structure, which was named as angle-resolved transmission current spectroscopy in magnetic field (ARTCSM) [3]. By using this technique, monitoring of surface electronic structure in wide area became possible to discuss the surface phenomenon by analyzing transmission current. Transmission current consists of tunneling current and hopping electron current. Tunneling process depends on surface potential and hopping processes depend on localized electronic sates in forbidden band gap. In TiO_2 case, electronic states for hopping processes were supplied from defects near interface.

In this report, we discuss the behaviors of adsorbed argon domains on titanium oxide from electrical characteristics.

2. EXPERIMENTAL

Experimental setup was constructed by a hot cathode, a grid system to control the momentum distribution of incident electrons, and a cylindrical titanium substrate whose size was 25.0^{ϕ} x 30.0 mm as shown Fig 1. Titanium surface was etched by nitric acid rinsed by distilled water, and finally rinsed by ethanol. The surface of the titanium substrate was oxidized in air after chemical treatment. The energy and the momentum of the incident electron were controlled by the applied voltage between the cathode and the substrate and by the magnetic field parallel to axis of the cylinder, respectively. The energy of primary electrons was below 40eV, which is in the energy range of usual LEED experiments [4]. The background pressure of the vacuum system

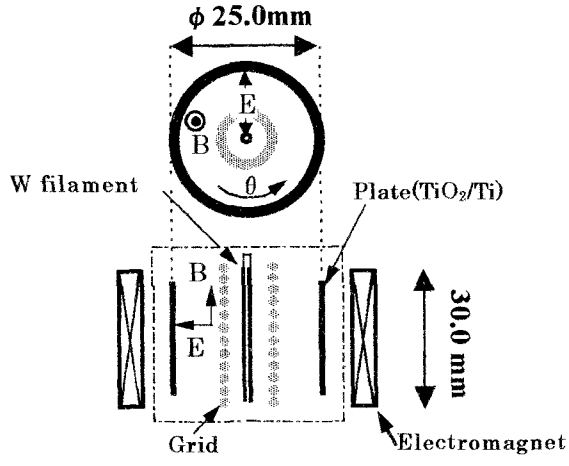

Fig.1 Schematic diagram of experimental system

constructed by a turbo-molecular pomp was 4.0 x 10^{-8} Torr.

Argon gas atoms were introduced in the system by using mass flow controller (MFC). The total exposure of argon gas in each experiment was 1.5 x 10^2 L for 0.3 seconds. After argon gas exposure, desorption processes of adsorbed argon atom system were measured for 1300 seconds at constant temperature, 200 °C. Transmission currents were continuously measured in every 0.1 seconds for the whole experimental period. Incident electron density at the plate surface was below 8 pA/cm^2. Since the effect of impact electron energy was negligible small because of very low electron dose density, desorption process of adsorbed argon atoms was dominated by thermal process.

3. THEORICAL BACKGROUND

Transmission current through the surface oxide includes many information about electronic characteristics of surface oxide as the transition probability of an incident electron. The incident electron was expressed as two dimensional wave number vector (k_θ,k_r), where k_θ and k_r were wave number vectors parallel and perpendicular to the surface, respectively. These components of the wave vector number are estimated by following equation from magnetic field B and applied voltage E as

$$(k_\theta, k_r) = \left(\frac{eBr_0}{2\hbar}, \sqrt{\frac{8meE - (eBr_0)^2}{4\hbar^2}}\right) \quad (1).$$

Where e, m_0, and h are charge, rest mass of electron and Plank's constant respectively. r_0 is radius of the cylindrical substrate.

Transmission current I_0 can express as

$$I_0(k_\theta, k_r) = eNT \quad (2)$$

Where N and T are density of incident electron at TiO_2 surface and transmission probability from vacuum to the metal substrate in unit area and unit time, respectively. The transmission probability can be expressed as the following equation,

$$T = (1-R)(T_{tun} + T_{hop} - T_{trap}) \quad (3)$$

and it consists of reflection process, R, from the surface, tunneling process, T_{tun}, which constructs the fastest component of current, hopping process, T_{hop}, which constructs alternative current, and trapping process, T_{trap}, in surface oxide [5].

If argon atoms were adsorbed on TiO_2 surface, incident electrons are scattered due to elastic and inelastic scattering processes. Component of inelastic scattering process can be expressed as

$$I = I_0 \cdot \exp(-\frac{D}{\lambda}) \quad (4),$$

where D, λ are effective thickness of the potential barrier caused by adsorbed argon atoms and mean free path in adsorbed argon layer, respectively. From this equation, we derived collision numbers as follows [6][7];

$$\frac{D}{\lambda} = \left|\ln\frac{I}{I_0}\right| \quad (5).$$

In the present experiment, the potential barrier thickness is expressed as the averaged value in the whole oxide surface because the current is the quantity due to the integration of each incident electron. We can change the effective barrier thickness from the maximum to near zero by adapting the desorption process.

On the other hand, the mean free path in adsorbed argon layer depends on their electronic structure. Angle-resolved transmission electron current reflects the spatial configuration of electron state density, for example, s-type or p-type configuration.

If adsorbed argon atoms form two-dimensional domains on oxide surface, electronic structure of isolated argon atom should be modified by the result of dipole-dipole interaction in adsorbed argon system. The electronic states of adsorbed argon atoms on oxide surface are not simple because of the defect structures of surface oxide system. As the electronic structure of adsorbed argon atom system interacts with defect cluster system of surface oxide, collision number as shown in equation (5) depends on density of domains.

Alternative component of the current reflects the interaction with adsorbed argon domain system and surface oxide system by electron hopping and trapping processes. Since the surface oxide system

contain the intrinsic defect density in it, characteristics of current noise depend on their own defect cluster system. If current noise density depends on the desorption process of adsorbed argon system, its characteristics reflect the time dependence of domain structures, if current noise density did not depend on time, argon atoms adsorbed independently.

Magnitude of noise intensity reflects the size of fluctuating domains. As shown in equation (2), since the current noise is proportional to the transmission probability of hopping and trapping processes, we can consider the magnitude of current noise density as the quantity proportional to the collision cross section of domain system.

4. RESULT AND DISCUSSION

Figure 2 shows the transmission current and pressure, incident electron=35eV and perpendicular to the surface. Sampling interval was 0.1 seconds. After measuring the value at the steady state of transmission current, region A as indicated in Fig.2, in high vacuum, 4.2 x 10^{-8} Torr, we injected argon gas by 1.5 x 10^{2} (L) for 0.3 seconds. Transmission current sharply decreased to 30% of the initial value (steady state) just after the injection of argon gas (B in Fig. 2). After evacuation of argon gas, transmission current returned to the steady state after 1300 seconds. In this process, unique current noise generated by argon-oxide interaction was observed as indicated by C→D in Fig. 2.

Current noise in the recovery process to the steady state (B → D in Fig.2) includes all contributions for alternative current. Basically, as current noise is due to the summation of each electron process, current noise was expressed as the magnitude of current fluctuation at unit time and unit area for one electron as follows;

(3)

$$i_{noise}(t) = i(t)/i_{av} \qquad (6).$$

Where $i(t)$ and i_{av} are transmission current at time t and averaged current of 200 samples. We analyzed

(4)

the alternating current by FFT, but there weren't any periodic characteristics in the result. It is that the origin of generation of current noise is independent process for time. We, therefore, evaluate the magnitude of current noise as effective value in constant period as follows;

$$I_{noise} = \sqrt{\frac{1}{N}\sum_{j=1}^{N}(i_j - i_{av})^2} \qquad (7).$$

Where N is the number of sampling of data.

Figure 3 shows recovery time dependence of effective values of current noise at incident electron energy, E=8eV, 9eV, 35eV, respectively. Incident angle of electron was fixed at θ =52.8°. In Fig3, although effective values of current noise seem to be depend on the incident electron energy, its effect was negligible small because of very low dose intensity. Therefore, characteristic in Fig.2 should be understood as time dependence of surface defect structures modified by adsorbed argon domain systems. These data are typical examples for magnitude of current noise, not continuous data series. Important point to interpret noise intensity is that noise intensity will be proportional to the density of defect sites in the surface oxide if it does not depend on time.

In Fig3, only the result at E= 9eV showed time dependence on time and its value connected from the low noise vale to the high noise value, 0.004< Effective Value < 0.02. The magnitude of effective values of noise increased with time increasing. We thought that this process was responsible to the kinetics of surface argon domain system which interact with each other. Because the noise mechanism in our experiment includes hopping and trapping of incident electrons, surface potential fluctuates if adsorbed argon make defect clusters on oxide surface.

The features of the curve at E=9 eV were related to the following physical condition which occurred on oxide surface. At the initial state of adsorption. The defect sites on oxide surface were

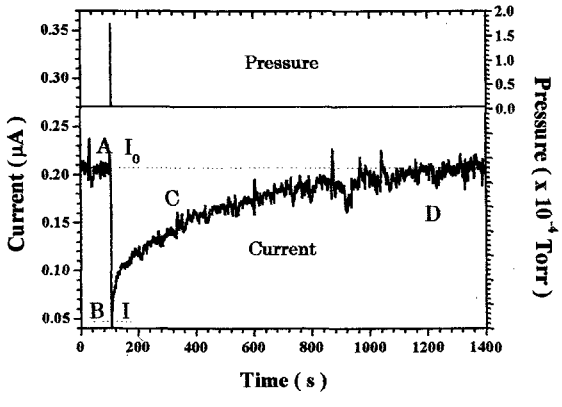

Fig.2 Time dependence of transmission current of thin titanium oxide after 150 L argon exposure. Energy of incident electron is 35 eV and incident angle is perpendicular to the oxide surface.

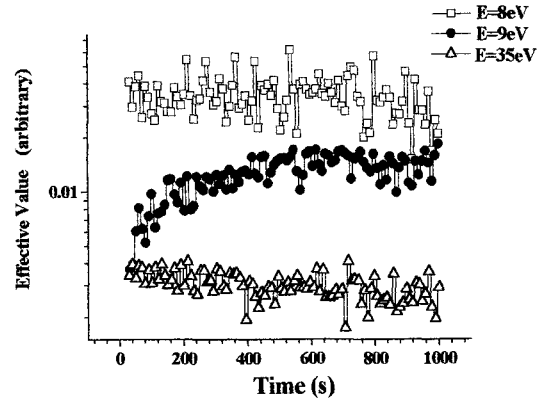

Fig. 3 Time dependence of current noise intensity after argon exposure. Time dependence of current noise suggests the interaction with argon-oxide system.

almost covered with argon atoms. In such situation, adsorbed argon can hardly diffuse because of rare vacancy sites, therefore the amount of noises becomes small. However, with time increasing, argon domain becomes easy to diffuse because of argon desorption, as the result of this process, the amount of noises increased with time increasing. That is, argon domain at the surface changes surface potential by the processes of diffusion and desorption. So noise analysis in the present experiment is one of effective methods to know the characteristics of argon domains at the surface.

Next, we consider the effective potential thickness formed immediately after argon gas exposure. Effective potential thickness was deduced from equation (5). In equation (5), mean free path in argon layer, λ, depended on incident electron energy (E). Metasatable electron states of argon below 16 eV were observed. If we do the experiment under the conditions with E= constant and constant incident angle to the surface (θ), we can understand the result of collision frequency derived from equation (5) as the change of the effective potential thickness.

Figure 4 shows incident angle dependence of D/λ at incident energy 35 eV. D/λ was constant up to 42° and did not depend on time. This characteristics suggest s-type configuration of electron wave function of barrier system due to argon atoms. On the other hand, the characteristics of D/λ above 42° strongly depended on time. The characteristic after one month from sample preparation, (1), showed increase of D/λ. This increase of D/λ decreased as shown in curve (2) at two days from curve (1), and decrease of D/λ strongly depended on the incident angle. Finally, D/λ decreased as increasing incident angle. In these three curves, the critical point for the change of D/λ did not depend on time. This is the reason why the origin of angle dependence is related to the electronic structure of adsorbed argon atoms. Decrease of potential barrier shows the increase of surface reactivity because electron transfer is essential mechanism for all surface reaction processes.

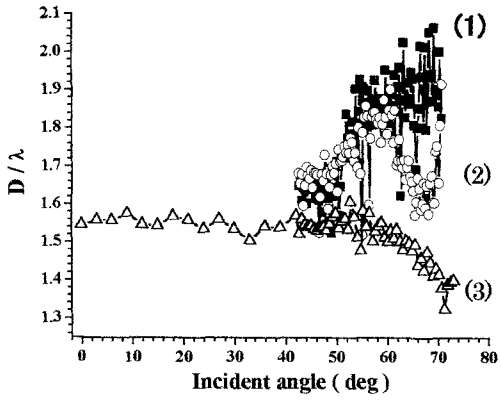

Fig. 4 Incident angle dependence of collision frequency, D/λ , in adsorbed argon system. (1) after 1 month from sample preparation, (2) after 2days from curve (1), and (3) after 3 months from sample preparation.

One physical reason for the decrease of D/λ is the existence of conduction band due to argon clusters. This situation was observed solid argon layers. Conduction band of argon domains will be formed as the result of the interaction between argon and surface oxide system. These drastic changes suggest the electronic structure induced by any kind of structural transformation of atom system of surface oxide.

5. CONCLUSION

The time dependence of argon domains on titanium oxide was investigated with transmission electron current spectroscopy. Time dependence of transmission current after argon exposure showed kinetics of adsorbed argon domain system. Time dependence of current noise suggested the existence of domain-domain interaction which were correlated to the desorption process of argon. Angle dependence of collision frequency, D/λ, showed the existence of the change of surface potential due to argon-oxide system. These characteristics show that surface electronic system related to the adsorbed argon atoms was detectable with angle-resolved transmission electron spectroscopy.

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