Transactions of the Materials Research Society of Japan 26 [4] 1295-1298 (2001)

Cooperative Phenomena in Super-thin Oxide Layer on Metallic Electrodes

K.Eguchi, S.Y.Park, N.Terada and K.Obara

Kagoshima Univ. Korimoto 1-21-40, Kagoshima, Japan
Fax: 81-99-285-8401,e-mail: kozo@eee.kagoshima-u.ac.jp

We present time dependence of transmission electron currents through the surface oxide of titanium substrates in vacuum. The transmission currents were measured as a function of two-dimensional wave number vector, parallel and perpendicular to the surface, by using angle-resolved transmission current spectroscopy in magnetic fields, which was developed by the author. Total transmission currents consist with direct tunneling electron current, reflected electron current and trapped electrons. The behavior of trapped electrons was measured as current noise spectra. The change of surface potential influenced the direct tunneling and reflecting electron currents. After reconstruction of the surface layer due to the energy of incident electrons, periodic current oscillations with long periods were observed. The surface potential due to the trapped electrons interacted with the incident electrons from higher incident angle. This phenomenon suggested the interaction between the electron states in the surface oxide of titanium. These results are applicable for investigating new function for future devices.

Key words: Transmission current, Noise spectra, Titanium oxide, Incident electron

1. INTRODUCTION

So many efforts were done to improve the surface of thin films and many growth techniques have been developed. For example, ion-assisted or electron -assisted film growth techniques were very effective methods to obtain smooth films or hard films.

But the electronic processes at the surface have never been clarified because of the lack of in-situ monitoring techniques for the surface states in the practical circumstance. In order to improve this situations, we developed a new technique using the probability of transmission electron through the surface layer, which was named as angle resolved transmission current spectroscopy in magnetic field (ARTCSM) [1].

The transmission electron currents include the direct transition process due to elastic and inelastic tunneling processes and the indirect transition process by the trapped electrons at the localized states in the surface. The conventional electron diffraction experiments reflect the response of the surface electronic states by the direct transition process. If the localized states exist in the substrate surface, trapped electrons drastically change the spatial dispersion of scattered electrons. This is the big reason for the difficulty when we analyze the surface electronic states of the oxides in the low energy.

In this report, we present a method to investigate the surface electronic states under practical growth conditions. Transmission current was analyzed into the averaged value and fluctuation value (noise). The noise reflects the characteristics of localized state in the surface oxide. In general, although the characteristics of localized states are independent processes, they showed correlated characteristics after special treatment under electron irradiation due to cooperative interactions between localized states.

2.EXPERIMENTAL

The experimental setup was constructed by a hot cathode, a grid system to control the momentum distribution of electrons, and a cylindrical titanium substrate whose size is 25.0$^{\phi}$ × 30.0mm as shown Fig 1 [2].

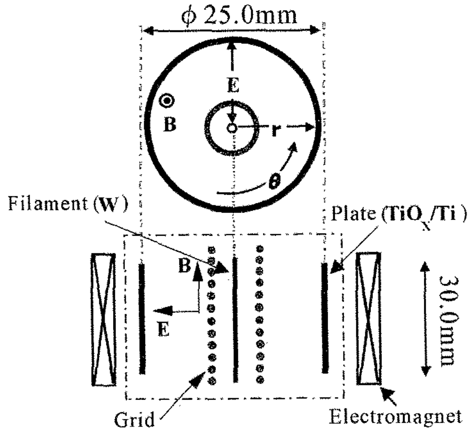

Fig.1 Experimental system (ARTCSM)

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 the axis of the cylinder, respectively. The energy of primary electrons was below 40eV, which is included in the energy range of usual LEED experiments[3]. The background pressure of the vacuum system constructed by a turbo-molecular pump was 1.6× 10^{-8} Torr. To get the stable condition, we must use the good thermal and electrical insulator and needed 2-3 hours to take a proper condition after turn on the switch.

3.RESULT AND DISCUSSION

The transmission probability of an incident electron is dominated by the scattering probability $P(\boldsymbol{k})$ of the electron at surface, where $\boldsymbol{k}$ is two-dimensional wave number vector(k_θ, k_r). These components of the wave number vector are estimated by following equation from magnetic field B and applied voltage V_p as $(k_\theta, k_r) = (eBr_0/2\hbar, (2em_0V_p / \hbar^2 - \hbar_\theta{}^2)^{1/2})$, respectively. Where e, m_0 and $\hbar$ are charge, rest mass of electron and Planck' s constant, respectively. r_0 is radius of the cylindrical substrate.

By using these relations, we can plot any quantity in two-dimensional wave number space. The wave number vector $\boldsymbol{k} = (k_{//}, k_\perp)$ at the surface was approximated by $\boldsymbol{k} = (k_\theta, k_r)$ in vacuum. The transmission current I as functions of magnetic field B and applied voltage V_p was expressed as

$$I(B, V_p) = e\,n\,T \qquad (1)$$

Where n and T are the incident electron density per unit time and the transmission probability from vacuum to the metal substrate, respectively. The magnetic field and the plate voltage were applied in the range of 0 to 68 (G) and 0 to 38.8 (V), respectively. The transmission current was estimated as the average value of 200 data points.

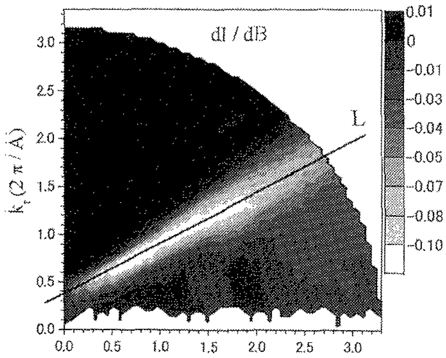

Fig2: Incident angle dependence of dI/dB

Figure 2 shows the incident angle dependence of dI/dB. The line L is explained that transmission current sharply decreased at the critical conditions. This line shows the deviation of electron orbital from the classical situation, which is exactly due to the influence of the surface potential

Figure 3 shows the distribution of current noise density in (k_θ, k_r) space. We denote the current noise as "Noise intensity". Noise intensity was estimated as power of current fluctuation in 200 data points for 8ms.

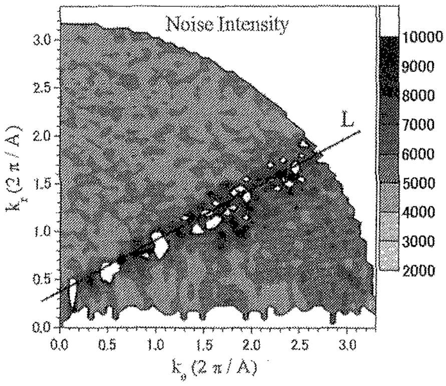

Fig3: The distribution of Noise

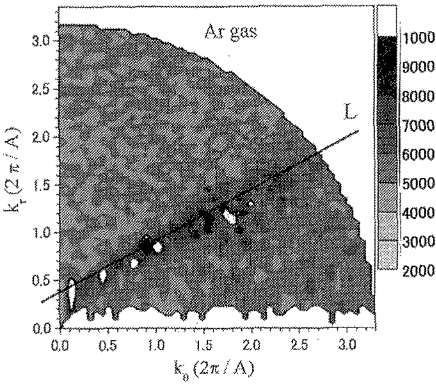

Fig4: The saturation condition of Ar

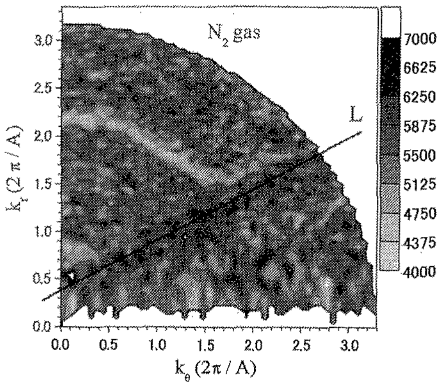

Fig5: The saturation condition of N_2

The transmission current contained the current noise spreading in wide frequency region. In the steady state, transmission current is expressed by the sum of the average value of the current due to the direct tunneling mechanism and the deviations from the average, which were generated by the electron hopping mechanism of trapped electrons [4].

The white area, near line L, shows the area with strong noises like spots that it called the spot-type noises. The intensities of the spot-type noises were much higher than the background noise and located below the critical condition of transmission current as indicated by the line L in Fig.2. The region, where the spot-type noises appeared, coincided with the region of low transmission current density. The generation of trapped electrons is directly related to the decrease of transmission probability of the incident electrons, and then the transmission current decreases because of the increase of repulsive potential generated by the trapped electrons.

These differences of the distribution in k space include important information on spatial correlation of defects. On the other hand, the spot-type noises show the defects coupled with the surface lattice system because the spot in k space is the result of Fourier transformation of periodic distribution in real space. As the strength of the coupling between two bodies is generally a function of the distance between them, we can suppose that the coupling distance between the lattice of the surface and the defects, which generate the spot-type noises in the titanium oxide on the substrate.

In order to investigate the effect of adsorbed atoms on the surface, the N_2 and Ar gas were introduced to the chamber. Immediately after introducing the gas into the system, the current level was decreased compare with the situation before. Especially Ar gas was arrived at saturation level more rapidly than the case of N_2 gas. And then the time for restoration after evacuation for argon exposure was shorter than the case of nitrogen.

Figure 4 and 5 show the distribution of noise density of argon and nitrogen exposures, respectively. The data were measured after evacuating the gas to 10^{-8} Torr, in which the total exposures for Ar and N_2 were 2.0×10^7 (L) and 1.0×10^5 (L), respectively. The concentric configuration of noise in Fig. 5 is induced by the absorbed layer on the surface oxide and a unique feature of adsorbed gas-surface system. Comparing Fig. 4 and 5, we can note that a straight line exists in Fig. 4 but is not observed in Fig. 5. The spot-type noises disappeared and noise intensity decreased in the case of nitrogen exposure. In case of Fig. 4, the spot-type noises distributed along line L, which was the same location as Fig.3, however the intensities and the distance between spot-type noises were different from those in Fig. 3.

These experimental results suggest the chemical bonding with nitrogen atoms and defect sites on the titanium oxide surface. The most effective defects are oxygen vacancies on titanium oxide. We suppose that nitrogen atoms adsorb on the oxygen vacancies and decrease the defect sites on the surface. If the spatial correlation of defect structure existed on surface, the noise distribution in k-space should show the localized structures related to the crystal structure. The spot-type noises near line L distribute with approximately equidistance, as shown in Figs. 3 and 4.

Form equ. (1), transmission current includes the information of transmission probability for surface "barrier". This barrier strongly affects the growth process of on the substrate surface. When we consider the growth process on the surface oxide, the growth front of surface oxide is covered with constituent atoms as a function of coverage, which depends on the experimental parameters. In this case, the transmission probability of an electron to the substrate is the product of the transmission probability in adsorbed layer and that of thin oxide layer on the substrate. The transmission probability in adsorbed layer equal to unit minus reflection probability R due to the adsorbed atoms. Therefore, the transmission probability in the surface oxide becomes [5].

$$T_{\text{oxide}} = (1 - R)(T_t + T_h - T_{\text{trap}}) \qquad (2)$$

In the first step, electron transport current is strongly affected by the electron trapping process as "charging". After trapping electrons in the surface layer, the surface system approaches to the steady state. In the steady state, the direct tunneling and the hopping mechanism dominate the electron transport in the oxide, which show the different time dependence. The direct tunneling process shows a constant transmission current, however, the transmission current due to the hopping mechanism causes the time dependent transmission current.

According to the theory on the electron hopping mechanism, the duration time τ for each electron hopping between two sites with distance r is expressed by following equation at temperature T [10];

$$\tau^{-1} = \nu_p \exp(-\frac{\Delta\varepsilon}{kT}) \cdot \exp(-\alpha r) \qquad (3)$$

Where ν_p, $\Delta\varepsilon$, k and α are phonon frequency, energy difference between two sites, Boltzman constant and parameter for hopping integral between two sites, respectively. By the assumption that the dominant process in the oxide is the process with $\Delta\varepsilon = 0$ near the Fermi level, we can get the simple relation between the correlation time and the distance of hopping as,

$$\tau = \nu_p^{-1} \cdot \exp(\alpha r) \qquad (4)$$

The current fluctuation ΔI is proportional to the number of hopping electrons n_h in the duration τ,

$$\Delta I_\tau = e n_h / \tau \qquad (5)$$

Since the electron hopping process is basically random process of each trapped electron in the surface oxide, the total transmission current includes the hopping events with the wide range of the duration τ. In order to analyze the noise of transmission current, we used the smoothing technique. The power spectrum of current fluctuation was derived as the mean-square of current fluctuation after smoothing the data with the period τ. By changing the period τ in the wide rage, we can get the information of the defect density distribution as a function of the distance r from equ. (4).

Time dependences of transmission current are shown as lines (A) and (B) in Fig. 6, which were measured with the incident energy is 2 eV, the magnetic field is 0 and under 1.6 x 10^{-8} (Torr) for the period 3600 seconds. Figure 6 (A) shows the noise just after exposure in air, and Fig. 6 (B) shows the noise after 40 hours in 1.6 x 10^{-8} (Torr). Apparently, random noise in Fig.6 (A) decreased after long time treatment in high vacuum. This change of time dependence of noise suggests the existence of correlation between individual random processes.

Figure 7 (A) and (B) show FFT spectrum (Fast Fourier Transformation) of the data in Fig.6 (A) and (B), respectively. The frequency of the highest peak in Fig. 7 (A) and (B) were 7.3 x 10^{-4} (Hz) and 9.8 x 10^{-4} (Hz), respectively. In Fig. 7 (A), noise spectrum shows wide distribution, which suggests thermal noise modified by very low oscillation. On the other hand, in Fig.7 (B), there are many higher harmonics of 9.8 x 10^{-4} (Hz) and high frequency noise disappears. These results show the interaction between individual hopping processes, which suggest the cooperative phenomena in the surface oxide.

4. CONCLUSION

Surface electronic structures of titanium surface oxide were investigated by ARTCSM. Distribution of current noise in two-dimensional wave number space showed unique characteristics due to the defects in the surface oxide, which indicated the structure correlated with the crystal lattice structure. The noise distribution in k-space clearly depended on the history of surface treatment. Time dependence of noise showed the existence of the cooperative phenomena in the surface oxide. These characteristics will be a key to investigate new functional devices.

5. ACKNOWLEDGEMENTS

The author thanks to Kazuhisa Mizusako and Imamura Nariaki for helpful discussion and continuous assistance of the experiment.

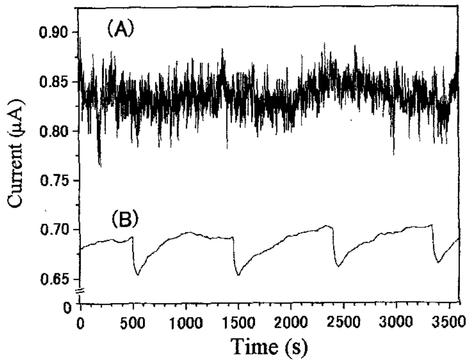

Fig.6: Time dependence of Transmission current

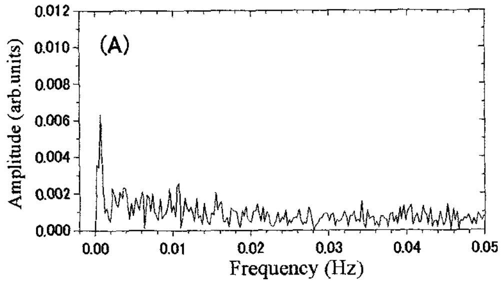

Fig.7: FFT spectrum of (A)

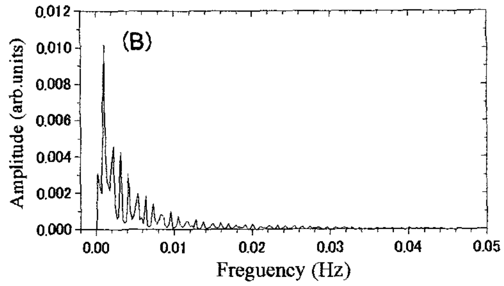

Fig.8: FFT spectrum of (B)

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(Received December 7, 2000; Accepted January 31, 2001)