In-Situ Monitoring of Oxide Ion Induced Breakdown in Amorphous Tantalum Oxide Thin Film Using Acoustic Emission Measurement

Takashi Tsuchiya*, Kaita Ito, Shogo Miyoshi, Manabu Enoki and Shu Yamaguchi

Department of Materials Engineering, The University of Tokyo, Tokyo 113-8656, Japan

An acoustic emission (AE) measurement was employed under DC bias applied condition to investigate breakdown behavior of highly resistive tantalum oxide thin film induced by redox reaction of oxide ion and its resultant generation of oxygen gas. Above dc bias of 14 V, AE event with strong components around 400 kHz and below 100 kHz was detected only once just after the bias was applied. On the other hand, a number of AE events were intermittently observed at 20 V, where the resistivity of the film drastically dropped. The behavior indicates oxygen gas was generated at the bottom electrode interface and released due to forming of a blister as large as several hundreds of micrometers.


(Received May 28, 2014; Accepted July 2, 2014; Published August 8, 2014)

Keywords: nanionics, redox reaction, acoustic emission

1. Introduction

Controlling of ionic behavior, including not only migration but reduction and oxidation (redox) reaction, in thin film have been considered as one of key issues in a range of nano electronic devices, since an ion migration becomes evident under intense electric field.1–4) For an ionic behavior in bulk materials, conventional electrochemical method usually helps us to understand detail of the electrochemical property, to say conductivity, transport number of ionic carrier, faradaic impedance at electrode/electrolyte interface, and so on. On the other hand, it is not straightforward to investigate electron/ion mixed conduction in thin films which consists of an electronic conductivity under strong influence of Poole–Frenkel, or F-N mechanism,5) where a small signature of ionic conduction can easily be hidden. Thus, novel approach for the detection of ionic behavior in nano space is regarded to be of much importance.

Here, we report an in-situ monitoring of nano ionic behavior by means of an acoustic emission measurement, which has been used as a probe for destruction, deformation, or corrosion of materials by detecting elastic waves generated in various environments under stress.6–9) Recently, AE monitoring technique was employed to investigate some of ferroelectric materials and proved its excellent sensitivity for domain switching, micro cracking, and phase transition under dc bias applied condition.10–13) Meanwhile, no report is found for an in-situ observation of an ion migration or redox reaction in nano ionic materials. In the present study, AE monitoring of oxygen gas evolution behavior under DC bias applied condition was performed to detect redox reaction in an amorphous tantalum oxide (α-TaOx) thin film, which is considered as one of most promising material for nano ionic type switching device including atomic switch and atom transistor.1,2)

2. Experimental

The two electrode set up for in-situ AE measurement is shown in Fig. 1. All the layered thin films were fabricated on silicon substrates with the dimensions of 7 × 12 mm by a reaction RF sputtering technique. An α-TaOx thin film of 200 nm thickness was sputtered onto Ru working electrode (WE) with 99.9% purity by a reaction sputtering method with D2O + Ar + O2 gas mixture with the flow rate of 0.6 + 3.8 + 15.6 sccm at room temperature.14) D2O was added to the gas in order to increase protonic defect by hydration reaction in sputtering process.15) D/Ta ratio was estimated as 0.72 by Rutherford back-scattering spectroscopy (RBS) analysis. The counter/reference electrode (CE/REE), which consists of Au and carbon thin films, with the dimensions of 2 × 3 mm was deposited to 6 nm total. In all the sputtering processes, the substrate temperature was kept at room temperature. The direction of the polarization is expressed as positive when the Ru working electrode is positively (anodically) polarized. A high sensitivity AE sensor (M304A, Fuji ceramics corp.) with head amp was used to detect even small amplitude AE events. While various DC bias was applied to the cell, AE signals were monitored by the AE sensor attached onto the silicon substrate of the cell by an epoxy adhesive. A diameter of the AE sensor is 3.5 mm. The resonant frequency of this sensor is about 250 kHz. Output signal from AE sensor was continuously sampled by the continuous wave memory.
A (CWM) system with 10 MHz frequency, bipolar 5 V range and 12 bit resolution and stored into hard disk drives. AE events was detected from the recoded waveform with a threshold voltage of 11 mV which is slightly above the noise level of 1.4 mV RMS with high pass filter of 30 kHz.

3. Result and Discussion

3.1 Electrochemical measurement and FE-SEM observation

The DC bias dependence of current through the cell is shown in Fig. 2(a). The present authors previously reported in-situ observation of redox reaction in a-TaOx thin film via hard X-ray photoemission spectroscopy, and that proton and oxide ion take part in the reaction.15) Especially, proton and oxide ion current have considerable contribution to total current in hydrated a-TaOx thin film, whereas Poole–Frenkel conduction of electron is dominant in dry a-TaOx thin film.5) Even if it is hydrated sample, however, ionic conduction is very small under low electric field region. Total resistivity, which includes resistivity for both ionic and electronic carrier, is over than several hundred mega ohms, so that observed current is suggested to be quite small, as seen in the figure. On the other hand, current becomes several hundred nA order above 14 V.

Average current value under each DC bias is shown as Poole–Frenkel (PF) plot in Fig. 2(b). Under influence of PF effect, the electric-field stimulated electron emission from a deep donor level increases carrier density with the increase of an electric field through the relation between the electronic current flux, J, and applied electric field, E, expressed as, 

\[ J = \sigma_0 E \exp\left(\frac{-q\varphi_i - n\sqrt{qE/\pi\varepsilon}}{\kappa T}\right) \]

where \( q \), \( n \), \( \sigma_0 \), and \( \varphi_i \) denote elementary electric charge, a constant which takes the value between 1 and 2 depending on the donor trap concentration, the low field conductivity independent of \( E \), and coulomb potential barrier of the donor state, respectively.5) The best fitting results (indicated by black line), assuming relative dielectric constant as 21 which is obtained by AC impedance spectroscopy, and parameter \( n \) as 2, still show much smaller bias dependence than the experimental result. According to the fittings, the increment in current above 14 V is not attributed to PF conduction of electron, thus ionic current enhanced under large electric field is suggested to overlap onto small electronic current by PF conduction. Moreover, not only an enhancement of ionic current under intense electric field, also an increase in electronic carrier caused by an electrochemical reduction of the film due to oxygen gas evolution at anode side interface, may take place. Evolved oxygen gas generates large inner stress and finally form blister at the interface, since the film is dense and gas-tight. The FE-SEM images in Figs. 2(c) and 2(d), which were observed after 20 V was applied, clearly show the formation of blisters observed as a dark contrast gap with more than 1 µm in height. This evidences a formation of
gas with mobile and negatively charged ions. Accordingly, oxygen gas evolution at the bottom electrode interface is suggested. The same behavior was observed at Pt/Gd doped CeO$_2$ oxide ion conductor interface.17) It is noted that no blisters were found by the FE-SEM observation after 18 V was applied, as shown in Fig. 2(e). The sharp dependence on DC bias voltage is discussed on the basis of AE measurement.

3.2 Acoustic emission measurement

Wavelet-transform (WT) spectra and AE waveforms of the AE signals detected under 14 V to 20 V of DC bias applied conditions are shown in Figs. 3(a)–3(j). Observed AE signals consist of two components in the frequency region of around 400 kHz and below 100 kHz as shown in Figs. 3(a)–3(e). Note that a frequency region around 250 kHz is prominent for all DC bias applied conditions, due to an effect of resonance.

Fig. 3 (a)–(e) Wavelet transform (WT) spectra and (f)–(j) AE waveform of AE signals under various DC bias conditions. (a), (f) $E = 14$ V, (b), (g) $E = 16$ V, (c), (h) $E = 18$ V, (d), (i) and (e), (j) $E = 20$ V. The saturation observed in Fig. 3(i) is due to overload of the signal.
characteristic of the AE sensor. The bias dependence of amplitude of AE events is shown in Fig. 4. The AE amplitude gradually increased as DC bias increased from 14 V to 20 V. The smallest AE amplitude observed in this study is 19.8 mV, which is far above the threshold voltage, indicating very steep increment in AE amplitude between 12 V and 14 V. Based on the electrochemical property of the cell, shown in Figs. 2(a) and 2(b), the increase in AE amplitude well synchronizes with an emergence of ionic current under an intense electric field. According to the feature of AE, electrochemical property, and SEM images, the AE observed in the study is attributed to a blister formation, or micro-crack generation by oxygen gas evolution at anode side interface due to electrochemical oxidation of oxide ion. With a certain amount of oxide ion conduction and gas-tight structure, an inner stress is induced at WE/α-TaO₃ interface by the partial pressure of oxygen, \( P_{O_2} \), which is modulated following Nernst equation in an equilibrium state expressed as

\[
4F \varepsilon_{\text{app}} = R T \ln \frac{P_{O_2(\text{WE})}}{P_{O_2(\text{RE})}},
\]

where \( F, R, \) and \( T \) are Faraday constant, gas constant, and absolute temperature, and WE and RE are assumed as ion blocking and reversible electrode, respectively. Below the threshold bias voltage, which is determined by the strength of mechanically weak site at WE/α-TaO₃ interface, an accumulation of oxide ion occurs whereas a precipitation of oxygen gas, in other words oxidation of oxide ion, is suppressed. An inner stress reaches high enough to break weak site and oxidation of oxide ion continuously proceeds above the threshold bias, resulting in evolution of oxygen gas accompanied with formation of blister. The threshold bias voltage of blister formation is under the influence of kinetics of oxide ion behavior, which is suggested to be critical especially at low temperature as room temperature where chemical equilibrium of oxygen gas is hardly attained in a short period.

As also shown in Fig. 4, the total number of AE events observed in 300 s for each bias condition indicates considerable difference between 14 to 18 V and 20 V that only one AE event was observed at just after the bias is applied for 14 to 18 V while AE events were intermittently observed for 20 V averagely 0.36 events in a second with occasional interval of several tenth seconds. In 20 V applied condition, oxide ion flux is large enough to maintain oversaturation of oxygen in spite of continuous blister formation, resulting in an intermittent appearance of AE signals. On the other hand, recover of oversaturation after oxygen gas evolution is very slow due to small oxide ion flux below 20 V, resulting in small number of AE observed in 300 s. Absent of blister in FE-SEM observation after 18 V is applied (shown in Fig. 2(e)) is due to very small number of blister.

In summary, in-situ monitoring of oxide ionic behavior in α-TaO₃ thin film under an intense electric field was successfully demonstrated by means of acoustic emission measurement. As a conclusion of the present study, even if its transport number is very small, a certain amount of oxide ionic conduction surely makes \( P_{O_2} \) difference, which causes redox reaction inside the thin film with both structural destruction and electric breakdown. The result indicates further application for investigation of extended range of ionic behavior in nano-electric devices that is hardly detected by conventional electrochemical methods.

Acknowledgements

The present study was financially supported by the Japan Science and Technology Agency (JST)/CREST “Atom Transistor Project”.

REFERENCES