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Electrochemistry Communications 4 (2002) 1–4

electrochemistry communications

www.elsevier.com/locate/elecom

Trapping of transient processes in aluminium oxide thin films in a voltage pulse experiment

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Received 13 September 2001; received in revised form 10 October 2001; accepted 10 October 2001

Abstract

An experimental setup is presented that allows the trapping of transient states in potentiostatic and potentiodynamic experiments. The setup is suitable for electrochemical experiments as well as for dielectric investigations. The system stops an experiment by triggering at a predefined current level after a minimum time of the voltage pulse. The advantage of this device is demonstrated by means of a voltage pulse annealing procedure for a metal–insulator–metal (MIM) contact with an anodically prepared aluminium oxide film as insulator. The setup significantly increases the stability against a breakdown of the anodic oxide film. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Current transients; Dielectric films; Aluminium; Tunnelling; Electrochemistry; MIM

1. Introduction

In electrochemistry and dielectrics, the trapping of transient states is of interest. This allows the investigation of a system in a well-defined state, using methods that are otherwise too slow.

Transient states may proceed the breakdown of thin oxide films [1,2]. Breakdowns are characterised by current levels that are significantly higher than the steady-state currents at that time [3]. Nevertheless, the current might be only a local maximum since the absolute current value can be higher directly after a voltage pulse due to capacitive charging. This current does not attack the film at all [4]. One needs a device that limits the current in a certain time range, but allows the current to exceed this limit during the capacitive charging.

2. Experiments and results

Fig. 1 shows the current transient of a cathodic breakdown in a double-logarithmic presentation on a high purity aluminium sample (99.95%) covered by an 4.5 nm thick aluminium oxide film in pH 6.0 acetate buffer. Four regions can be distinguished in this transient. After capacitive charging (A) the current decreases down to a local minimum (B) due to relaxation processes [5,6]. The current then increases again during the cathodic breakdown (C) before it reaches the constant value of stationary hydrogen evolution (D).

The time to breakdown (taken as the point of inflection in section (C) of the current transient) varies significantly if the experiment is repeated under the exact same conditions [7]. This indicates a statistical variation of the breakdown process which was also discussed by Boksiner and Leath [8].

Thereby, the experiment cannot simply be switched off after a predefined time. To trap the experiment at a certain stage the switch off must be triggered by the current level. Problems arise experimentally when current measurements at short times (Fig. 1, sections (A) and (B)) activate the switching off procedure too early. Hence, a more sophisticated setup has to be used, that prevents the system to enter the prohibited experimental conditions which are indicated by the dashed rectangle in Fig. 1.

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PII: S1388-2481(01)00260-0

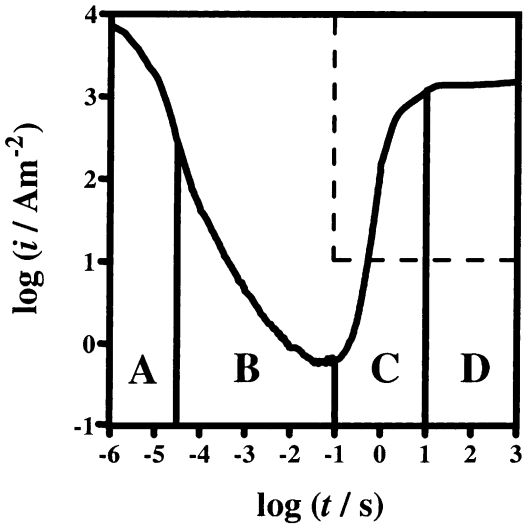

Fig. 1. Current transient of a potentiostatic breakdown of Al_2O_3 film ($d = 4.5$ nm) on Al after a potential jump to $E_{HESS} = -2$ V (hydrogen electrode same solution), 25 °C, acetate buffer pH 6.0: (A) charging of the oxide capacity; (B) dielectric relaxation = metastable area; (C) cathodic breakdown of the oxide film; (D) stationary hydrogen evolution. The dashed rectangle in the upper right part indicates prohibited experimental conditions.

Fig. 2 shows the experimental setup developed here. All logical information such as trigger and status information are represented by transistor transistor logic (TTL level). Herein the logical 0 is represented by a 0 V level and logical 1 by a 5 V level, both against ground.

Timer 1 defines the maximum length of the experiment and starts the experiment by triggering the pulse generator and a logarithmic clock generator. The pulse generator supplies a voltage to the potentiostat. The potentiostat polarises the sample to the potential of interest and reports the current to a fast current converter. Each time this fast current converter gets a trigger signal from the clock generator, it converts the actual current into a proportional voltage which is recorded in a transient recorder. The fast current converter system is an auto-ranging system that allows the measurement of currents between 2 A and 100 fA using 15 different measurement ranges. The logarithmic clock generator starts with a 1 MHz sample rate in the beginning, and is reduced by a factor of 10 for each decade in the time domain [9]. This system is necessary since the file size that is recorded after 10 ks at a sampling rate of 1 MHz would occupy several Gigabyte. Rather than starting with a low sampling rate, the data points are logarithmically distributed over time. This represents much better the dynamics of the system that are very high in the beginning and decrease with time. As a result, the data points appear almost equidistant in the double logarithmic presentation.

To extend this system the current output is monitored simultaneously by a differential amplifier, which converts the current into a proportional voltage. This voltage is then compared by an analogue comparator with the voltage output of a reference current source. If this comparator recognises that the measured current exceeds the reference value, it sets a bit. This bit can be stored in a JK-MS flip-flop (JK-Master–Slave, see textbook of electronics) which works as a digital sample and hold device. Timer 2 triggers after a preselected time and the second JK-MS flip-flop will store the signal.

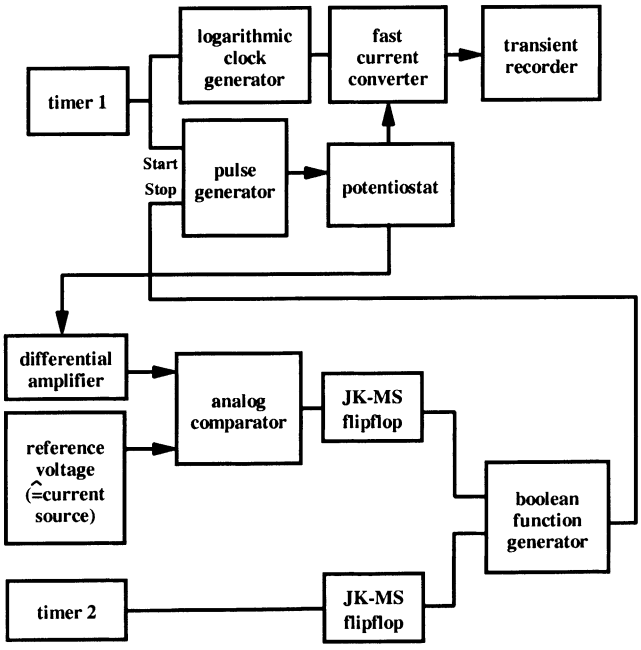

Fig. 2. Schematic diagram of the electronic setup used. Connections with arrows indicate analogue signal flows, line connections indicate digital connections (TTL level). Details are described in the text.

Both signals are used as input signals for a Boolean function generator. This generator allows the choice of Boolean functions for a given set of input variables. When considering a simple AND function, the generator will trigger the stop of a pulse port in the pulse generator when t is larger than t_2 and i is larger than i_{critical}. Hence, the current can be very high in the beginning, but it cannot exceed a certain value after a predefined time. This means that the box in the upper right corner of Fig. 1 will not be reached. If the experiment of Fig. 1 is repeated with the switching system described above the current will decrease down to its minimum at the end of section (B). For example, if after 100 ms the system is activated to prevent currents higher than 1 mA, this will correspond to a current density of 10 A m^{-2} for a sample with an area of 1 cm^2 or 10^{-4} m^2. The current increases up to that value and the voltage pulse experiment is stopped. As a result, the state of the system is arrested.

3. Application and discussion

In Fig. 3, the applicability is demonstrated on a metal–insulator–metal (MIM) contact where the oxide has been formed anodically [10]. For the first 100 μs, the capacitance charging of the MIM capacitor dominates the current before the level of steady-state tunnel current is reached. After about 10 ms, a sudden steep increase in current is observed. This is the beginning of the breakdown process. Without a switching system the current increases up to a maximum value that is limited only by the contact resistance of the metal films. The oxide film is destroyed, the sample has then a permanent short circuit.

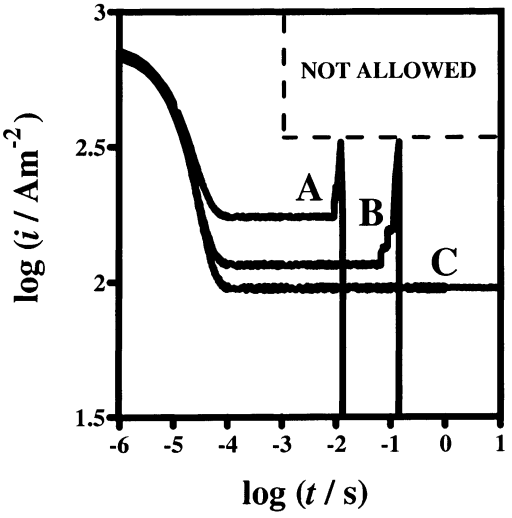

Fig. 3. Subsequent current transients of voltage steps to 3.5 V on a MIM contact (30 nm Al/4.5 nm Al_2O_3/20 nm Ag) using the described switching system: (A) highest tunnel current and shortest time to breakdown; (B) partially annealed sample with lower tunnel current and longer time to breakdown; (C) completely annealed sample with lowest tunnel current and increased breakdown stability.

Using the new system, the pulse is stopped if a critical current is exceeded. This is indicated by the sudden decrease in current after reaching the limit. If the same experiment is repeated with the same sample, the current transient looks similar at the beginning. The charging is almost identical to the first transient indicating that capacity and contact resistance remain unchanged. However, the significant smaller tunnelling current demonstrates that a different state was trapped in the second experiment. In this case, it takes about 10 times longer until the breakdown process starts. The current increases to the same limit and the experiment is interrupted again. A different state is trapped as seen in the third current transient. The charging is identical again, the tunnel current stabilises on an even lower level. This time the sample remains stable during the whole pulse experiment. The different tunnel currents prove that different states were trapped at the end of each experiment.

It is not trivial to monitor these entrapped states. Electrochemical impedance spectroscopy without bias voltage shows almost no differences in capacity and resistance. On the other hand impedance spectroscopy can not be performed at high voltages were the sample is metastable and a stationary method as impedance spectroscopy is to slow. Differences in the resistance of the same sample after pulse treatment can be clearly monitored for intermediate voltages. Here, the lowered number of defects in the oxide which serve as centres for resonance tunnelling results in a lower tunnel current or a higher impedance, respectively.

The unchanged capacity on the other hand indicates that film thickness and structure remains. But the breakdown field strength increases obviously from the virgin aluminium oxide to the voltage pulse treated ones.

This setup can be easily adapted to other experiments. For example galvanostatic and potentiodynamic experiments can be extended to prevent them from exceeding critical experimental conditions.

Acknowledgements

The authors wish to thank M. M. Lohrengel and M. Schramm for making available the logarithmic rate generator and the analogue comparator.

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