Formation of Metal Nano Layer using Tunneling Current through Thin Oxide Film in the Electrolyte–Oxide–Silicon System

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ABSTRACT

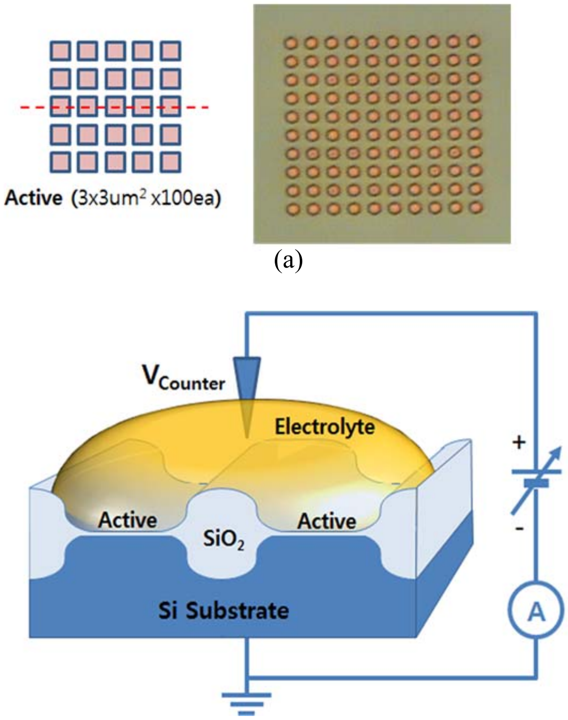
Tunneling current in the Electrolyte–Oxide–Silicon (EOS) system is relatively under-covered in the study of the EOS system. In this work, we report the experimental study to form metal nano particle or layer on the oxide by the tunneling current of the EOS system and compared it with the Electrolyte–Metal–Oxide–Silicon (EMOS) system and the Metal–Oxide–Silicon (MOS) system. The experimental results show the stable electronic characteristics in contrast with those of the raw EOS system by controlling the H^+ density in the oxide. We show that the proposed technique can selectively deposit extremely thin metal layer on the active sites in a self-alignment manner.

Keywords: tunneling current, electroplating, MOS, Electrolyte-Oxide-Silicon, metal nano particle

1 INTRODUCTION

In recent years, there have been many attempts to utilize the semiconductor device in the electrolyte such as an Ion-Sensitive Field-Effect Transistor (ISFET) and Electrolyte–Oxide–Silicon (EOS) for biomedical and industrial applications. In the EOS system, tunneling current through the gate insulator has been considered as an undesirable factor causing reliability issues such as gate insulator degradation and interface state generation [1-3].

In this paper, by controlling the tunneling current through the insulator layer, we propose a technique to effectively form metal nano-particles (or film) on insulator. Hereafter called the method as 'tunneling electroplating'. Typically, the conductive films on the surface of SiO_2 are deposited by physical method using sputter deposition process or chemical method using Chemical Vapor Deposition (CVD). Since a metal film deposited on SiO_2 does not adhere well or forms lumps because of the deference of the surface energy, it is difficult to make a uniform nano sized metal layer on SiO_2 surface. On the other hand, the tunneling electroplating method can selectively deposit extremely thin metal layer even on the non-planar active area such as the trench structure and FinFET structure.



(a)

(b)

Fig. 1. (a) Illustration of the active area and the photomicrograph of LOCOS processed silicon (b) Schematic showing the EOS system when tunneling electroplating is performed in an electrolytic solution of $HAuCl_4$

For the demonstration, we have applied the proposed the tunneling electroplating to the conventional EOS device repeatedly. From our measurement, we show that the EOS device is converted to the Electrolyte-Metal-Oxide-Silicon (EMOS) device which means that Au nano-particles are successfully formed on the tunneling oxide. Moreover, in this paper, we report that the thin conductive film on the surface of EOS system protects the penetration of the H+ ions to the oxide, thereby stabilizing the resultant EMOS system..

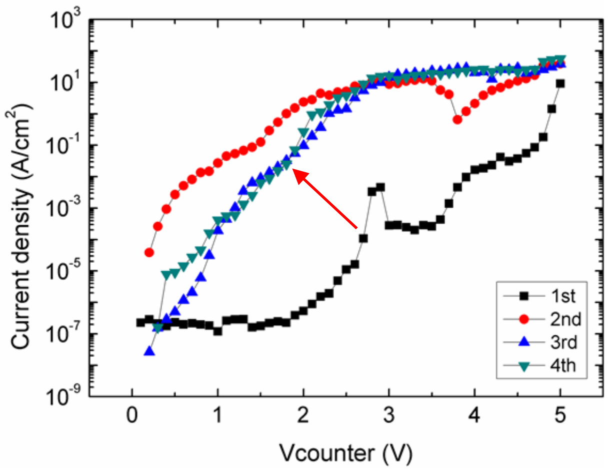


Fig. 2. Current density versus counter electrode voltage measured the tunneling current for several times through the oxide film in EOS system

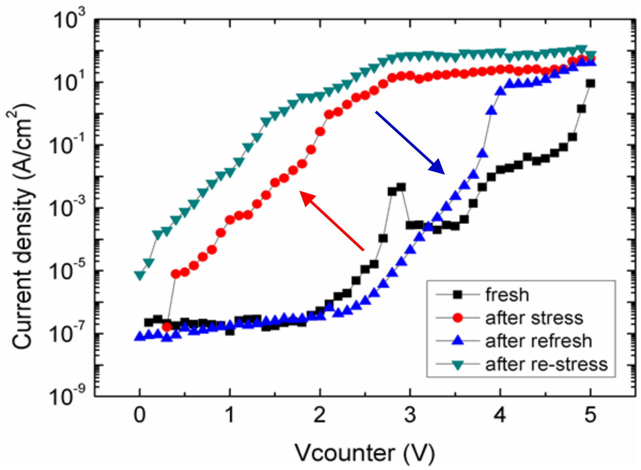


Fig. 3. Current density versus counter electrode voltage measured the tunneling current after application the stress voltage with positive bias (red arrow) and the refresh voltage with negative bias (blue arrow)

2 EXPERIMENT

The schematic view of the experimental set-up is shown in Fig. 1. We use the N-type Si wafer for the substrate with the orientation [100] and the resistivity of 0.001 Ω·cm to minimize the surface depletion at the Si-SiO_2 surface. For the insulator in the field area, the 400nm thick oxide was made by the LOCal Oxidation of Silicon (LOCOS) process [4] and it can be suppressed the local field crowding by increasing the oxide thickness smoothly at the active and field oxide boundary. The arrays of 100 active areas with the area of 3 by 3um and the 6nm thick oxide are formed by the high temperature furnace. The electrolyte is composed of $HAuCl_4$ solution (1wt %) and 0.1M HCl to form the metal particle on the surface.

We measure the current-voltage characteristics using Agilent 4156C semiconductor parameter analyzer. The gold counter electrode immersed in the electrolyte with 0.5mm diameter is used to apply voltage ($V_{counter}$) and we measure the tunneling current repeatedly to determine the tunneling current characteristics of the EOS system as shown Fig. 1. For the investigation of surface of the EMOS system, we use the non-contact mode of Atomic Force Microscope (AFM) machine (XE-150 by Park systems)

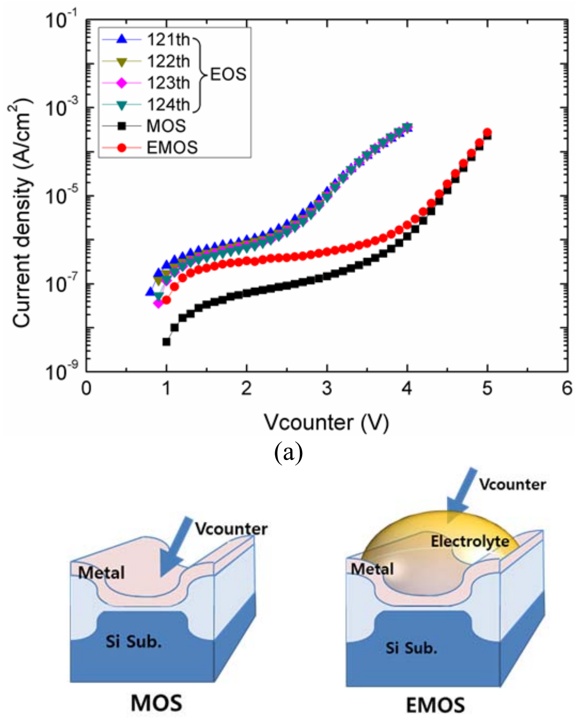
3 RESULT AND DISCUSSION

In order to see the current-voltage characteristics of the EOS, we sweep the counter electrode voltage from 0V to 5V for several times and measure the tunneling current through the oxide film as shown in Fig. 2. The experimental results show huge difference between the first application of the gate voltage (the first sweep) and the subsequent sweeps after. From the second $V_{counter}$ sweep, the tunneling current increases dramatically over whole range of the measurement voltage. After the first sweep, we found that H_2 gas bubbles are generated on the active sites by the microscope. The electrons tunneling through the oxide from the silicon substrate make the hydrogen bubbles by reduction of H^+ ions on the SiO_2-electrolyte interface. The H_2 bubble on the SiO_2 disturbs the formation and the adhesion of Au particle to surface during the metal electroplating.

Once the current density increases by positive voltage, the current-voltage characteristics are maintained for subsequent sweeps. It can be explained as follows; when the positive voltage is applied to the counter electrode, H^+ ions located at the interface of SiO_2 and the electrolyte enter into the oxide layer in the active region. It has been known that that the H+ ions can moves freely in the oxide via the hopping process [5]. The mobile H^+ ions enhance the electric field of the oxide by the Poisson effect and thus the effective oxide thickness decreases. As the result, the tunneling current increase as shown in Fig. 2. As the result, the oxide quality has been degraded due to the H^+ penetration.

We speculate that the enhanced oxide tunneling current after the positive electrode sweep generates the massive H_2 bubble at the oxide/electrolyte interface. For this reason, $V_{counter}$ sweep of degraded oxide should be prevented for further electroplating process.

In order to recover the degraded oxide (red circle), we apply the 'refresh' voltage with negative bias ($V_{counter}$ sweep from 0V to -4V) and measure the tunneling current in the counter electrode from 0V to 5V as shown in Fig.3. The current level after the negative bias of gate is recovered to the original one (blue triangle), which infers that the trapped H^+ ions in the oxide are extracted to electrolyte during the negative voltage on the counter electrode. When we sweep the counter electrode voltage from 0V to 5V in succession, the same process of the oxide degradation by H^+ penetration occurs (green inverted triangle).



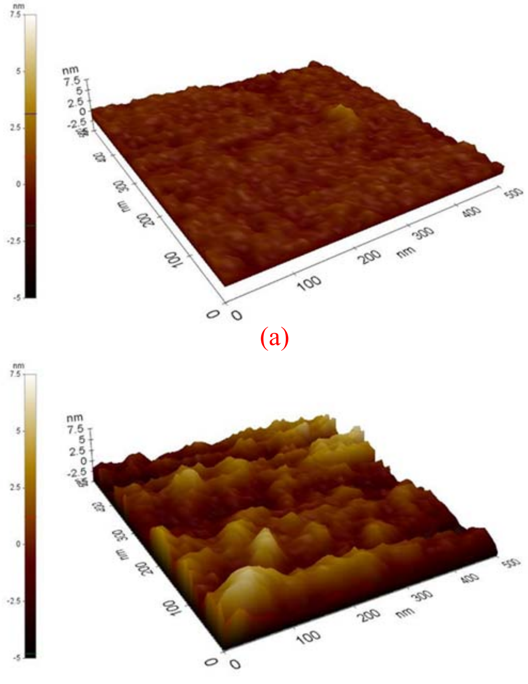
(a)

(b) (c)

Fig. 4. (a) Current density versus counter electrode voltage measured the tunneling current of EOS system after repetition of the tunneling electroplating cycle (The number means the count of the cycle performed) and comparison with MOS and EMOS system (b)(c) schematic showing MOS and EMOS structure with thick metal layer processed by e-gun evaporation on the oxide

Therefore, we propose cycling the positive (stress phase) and negative (refresh phase) bias alternately during the electroplating process to prevent leakage current due to H$^+$ in the oxide. During the positive bias sweep (stress phase), the Au metal nano particles are formed by the reduction reaction with the tunneled electrons at the surface of SiO$_2$/electrolyte. During the negative bias sweep (refresh phase), the H$^+$ ions are extracted from the oxide layer to the electrolyte.

After repetitions of this cycle over one hundred times, current-voltage characteristics of the EOS system is obtained as shown in Fig. 4(a). Unlike the current characteristics of the initial status (black square in Fig. 2), the tunneling current settles down to the smooth curve. This infers that the thin metal layer has been formed successfully during the positive biased on the counter electrode and the irregularity of the reduction reaction occurring in the SiO$_2$/electrolyte interface disappears. Once the metal layer is formed at the interface, the additional migration of the H$^+$ into the oxide is effectively blocked. Therefore, the tunneling current of the EOS system with thin metal layer shows the stabilized characteristics subsequent application of the positive voltage.



(a)

(b)

Fig. 5. AFM images of the oxide surface topology in this experiment (a) before tunneling electroplating cycle (b) after tunneling electroplating cycle

For the sake of comparing the measurement result with the tunneling current of conventional structures, we prepare both the Metal-Oxide-Silicon (MOS) device and the EMOS device as shown in Fig 4(b) and (c), respectively. Each device has the 200nm thick metal layer on the oxide fabricated by the e-gun evaporation process. For the EMOS device, same solution of the previous EOS system is used and the Au electrode is immersed in the solution. The current-voltage characteristics of the conventional MOS and EMOS device are shown Fig. 4 (a) also.

In the MOS device, the gate leakage current in the low voltage and high bias voltage is caused by the direct tunneling and the Fowler-Nordheim (FN) tunneling mechanism, respectively (refer black square in Fig. 4(a)). The EMOS device shows similar characteristics with the MOS device (refer red circle in Fig. 4(a)). However, the current-voltage characteristics with high bias voltage in the EOS system after tunneling electroplating are different from that of the conventional the EMOS and MOS system. A significant increase of current, mostly in the regime of direct tunneling current, is observed. This result is similar with a Stress Induced Leakage Current (SILC) [6, 7] found in the conventional MOS structure. Therefore, we conclude that the penetrated H$^+$ ions are responsible for the oxide degradation during the tunneling electroplating process.

The formation of the metal layer is confirmed by the AFM image as shown in Fig. 5. Before the tunneling electroplating, a relatively flat surface can be observed as shown in Fig. 5(a). After the tunneling electroplating, the roughness of the surface increase significantly as shown in Fig. 5(b). Hence, it can be verified from these images that the metal particle layer is successfully fabricated on the oxide surface.

4 CONCLUSION

We have proposed a new technique, called the tunneling electroplating, to obtain the EMOS with the metal nano layer utilizing tunneling current in the EOS system. As the voltage sweep cycle applies repeatedly, we could obtain stable electronic characteristics in contrast with those of the raw EOS system by controlling the H^+ density in the oxide. Since the proposed technique can selectively deposit extremely thin metal layer on active sites in a self-alignment manner, it can be readily used for fabrication of the various devices with the metal layer as the sensor channel for the bio- or photo-sensor applications.

5 ACKNOWLEDGEMENT

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