Electron Tunneling through Chemical Oxide of Silicon

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Carrier transport between gold and n^+-Si through chemical oxides of Si was measured for the first time using an atomic force microscope with a conducting probe. It was found from the theoretical calculation of carrier transport in 0.7-nm-thick chemical oxide formed in a mixed solution of H_2SO_4 and H_2O_2 that the carrier transport can be explained as a direct tunneling of electrons through chemical oxide. The contribution of Si-H bonds in chemical oxide formed in hot HNO_3 solution to the electron tunneling was also found.

1. INTRODUCTION

In 1 Gbit dynamic random access memory, for which massproduction will be possible at the end of this century, about 5-nm-thick silicon oxide will be used as a gate oxide in metal-oxide-semiconductor (MOS) field-effect transistors. In such a case the thickness of one monolayer of silicon dioxide corresponds to 6% of gate-oxide thickness. In order to form such an ultrathin oxide of high quality two approaches are possible. One is to control oxide formation on the atomic scale by suppressing the formation of native oxide.[1] The other is to form high-quality thermal oxide at high temperature by transporting oxidizing species through high quality native oxide.

It was found from the measurement[2] of infrared absorption spectra and Si 2p photoelectron spectra that the number of Si-H bonds in chemical oxide formed in a mixed solution of H_2SO_4 and H_2O_2 is negligibly small. It was also found from the measurement[3] of cumulative failure of a MOS diode that chemical oxide formed in a mixed solution of H_2SO_4 and H_2O_2 can function as a passivating film and suppress the increase in surface microroughness, which is caused by the heating of the Si substrate to thermal oxidation temperature in inert gas ambient. However, the carrier transport through this chemical oxide has not been studied yet, probably because it is difficult to prepare defect-free chemical oxide of area on the order of a micrometer squared necessary for the conventional measurement of carrier transport.

It is the purpose of the present study[4] to measure the carrier transport through chemical oxide using an atomic force microscope (AFM) with a conducting probe. Because the contact area of a conducting probe is on the order of a nanometer squared, the effect of defects on the carrier transport is negligible. It is also the purpose of the present study to clarify the carrier transport mechanism through chemical oxide by theoretical calculation.

2. EXPERIMENTAL DETALS

The chemical oxides used for the present study were prepared as follows. First, 200-nm-thick oxide film was formed on a 0.007-0.018 $\Omega \cdot$ cm n-type Si(111) surface in dry oxygen at 1000°C. Second, this oxide was removed with buffered hydrofluoric acid. Third, the resultant silicon surface was treated in 40%NH_4F at 20°C for 6 min to obtain an atomically flat H-terminated Si(111) surface.[5] Then, chemical oxides were formed in a mixed solution of H_2SO_4 and H_2O_2 (H_2SO_4:H_2O = 4:1, abbreviated hereafter as H_2SO_4) maintained at 85-90°C for 10 min or in a solution of HNO_3 (abbreviated hereafter as HNO_3) maintained at 45-60°C for 5 min. The average surface microroughness Ra over the scan area of 60 nm $\times$ 60 nm was found to be as small as 0.1 nm for these two kinds of chemical oxides.

Thicknesses of chemical oxides were determined from the analysis of Si 2p photoelectron spectra assuming that the electron escape depth in chemical oxide is equal to that in thermal oxide. Here, the electron escape depth in the silicon substrate and that in silicon dioxide were determined for silicon oxide films formed in dry oxygen at 800°C by the standard procedure described previously[6] and were 2.7 nm and 3.4 nm, respectively. The thickness of chemical oxide formed in H_2SO_4 and that formed in HNO_3 were 0.68 nm and 0.76 nm, respectively. The conducting probes used for the present study were made of silicon covered with about 10-nm-thick gold films. The atomic force microscope used was SPI3700/SPA300 manufactured by Seiko Instruments Inc. and operated at a repulsive force of nearly 1 nN. Oxide is not formed by applying positive potential to the conducting probe with respective to the Si substrate, while the oxide is formed by applying negative potential to the conducting probe with respect to the Si substrate.[7,8] Therefore, the current-voltage characteristics were measured by applying positive potential to the conducting probe with respect to the Si substrate. The steady-state current through chemical oxide was measured at 2 min after the application of voltage. Current was measured as a function of each voltage at three positions.
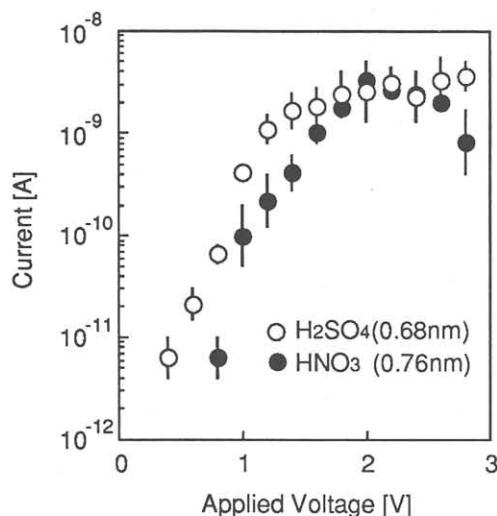
Fig. 1. Current-voltage characteristic measured for chemical oxide formed in H_2SO_4 and that for chemical oxide formed in HNO_3.
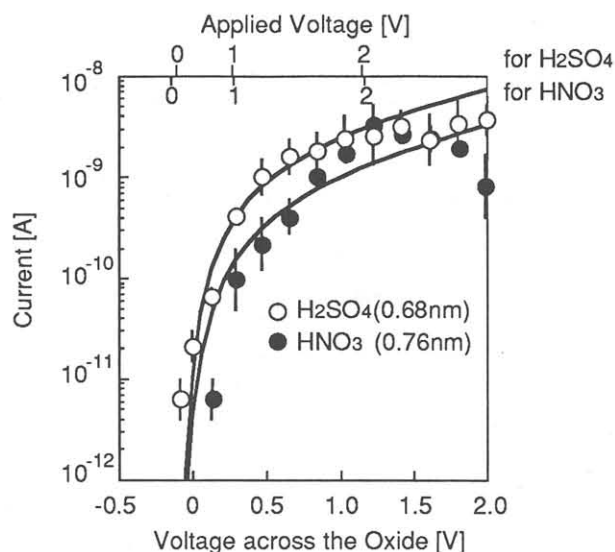

Fig. 2. Solid lines show current-voltage characteristics calculated for the rectangular potential energy barrier for a flat band condition, while open and filled circles show experimental data obtained for chemical oxide formed in H_2SO_4 and that formed in HNO_3 respectively. The horizontal scale at the bottom shows voltage across the oxide, while the horizontal scale at the top shows applied voltage, which includes voltage drop near the surface of Si substrate, for two kinds of chemical oxides. The solid curves are calculated for effective diameter of contact of 5.0 nm.

3. RESULTS and DISCUSSION

Typical current-voltage characteristics observed for gold/chemical oxide of Si/n⁺-Si structure are shown in Fig. 1. Error bars in this figure indicate the range of data measured at three locations of a gold tip. The two kinds of chemical oxides used here were formed in H_2SO_4 and in HNO_3. With an increase in applied voltage, the current increases steeply at a voltage lower than 1 V and then increases slowly at a higher voltage. A smooth change of current as a function of voltage is observed for chemical oxide formed in H_2SO_4, while irregular change of current as a function of voltage is observed for chemical oxide formed in HNO_3.

It is straightforward to show that the tunneling current I_x, which flows from a gold tip to the Si substrate through chemical oxide along the tunneling direction parallel to the x-axis, is given by ,[9]

$$I_x = \frac{Aqm^*}{2\pi^2\hbar^3}\int_{E_c}^{E_s}T(E_x)\int_0^{E_{max}}\{f_s(E+E_x) - f_m(E+E_x)\}dEdE_x.$$

Here, A is the contact area of the conducting probe, q the elementary charge, m^* the electron effective mass, $\hbar$ the reduced Planck's constant, E_x the component of electron energy along the x-axis, E_c the electron energy in the conduction band edge at the Si surface, E_s the electron energy at a vacuum level at the Si surface, $T(E_x)$ the tunneling probability, and $f_s(E+E_x)$ and $f_m(E+E_x)$ the Fermi-Dirac distribution function for electrons in Si and that in gold, respectively. In the derivation of the equation, electron tunneling from the Si substrate to the gold tip and vice versa are considered. Calculation was performed by assuming that the effective value of E_{max} is infinity. For the calculation of $T(E_x)$ the linear increase

in the conduction band edge of silicon oxide is approximated by the stepwise increase of 100 steps, where the width of terraces in the direction of the x-axis is constant. The calculation of $T(E_x)$ for this potential energy barrier was performed under the condition that at each step edge the wave functions of electrons changes continuously. In this calculation, flat band voltage[10] arising from the difference between the work function of Si and that of gold is also considered.

Current-voltage characteristics indicated by solid lines in Fig. 2 are calculated for the rectangular potential energy barrier at a flat band condition. In Fig. 2, the horizontal scale at the bottom shows voltage across the oxide, while the horizontal scale at the top shows applied voltage which includes the voltage drop near the surface of the Si substrate. In these calculations we used the energy discontinuity of 3.15 eV in the conduction band edge at the SiO_2/Si interface,[10] the electron affinity of 4.05 eV for silicon,[10] the work function of 4.70 eV for gold,[11] and 0.32 for the ratio[12] of the effective mass of electrons in the conduction band of SiO_2 to the electron rest mass. If the applied voltage is lower than the flat band voltage, the voltage across the oxide takes the opposite polarity with respect to applied voltage.

It can be seen from Fig. 2 that for chemical oxide formed in H_2SO_4 the tunneling current decreases steeply
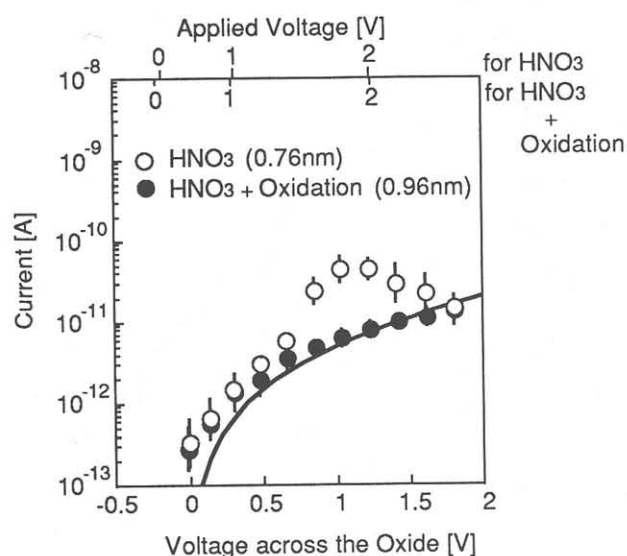
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Applied Voltage [V]

Fig. 3 . Changes in current-voltage characteristics produced by the oxidation at 600 °C in dry oxygen under a pressure of 1Torr for 1min.

when applied voltage approaches or is smaller than flat band voltage. This can be attributed to the increase in the potential energy barrier at the metal/oxide interface caused by the positive flat band voltage and the decrease in electron density in the Si substrate. As can be seen in Fig. 2, for chemical oxide formed in H_2SO_4, implies a high quality of the oxide.

In contrast, large deviation of experimental data from the calculated curve and poor reproducibility of the experimental data above the applied voltage of 2 V are observed for chemical oxide formed in HNO_3. The solid curve in Fig. 3 for chemical oxide formed in HNO_3 is calculated for the effective diameter of contact of 5.0 nm. The observed large deviation and poor reproducibility may be partly correlated with Si-H bonds for the following reason. According to FT-IR-ATR study,[13,14] the number of Si-H bonds in the chemical oxide formed in HNO_3 is 8.4×10^{13} cm^{-2}. Then, an average value of 16.5 is obtained for the number of Si-H bonds which contribute to the carrier transport. Therefore, the Si-H bond affects carrier transport in the chemical oxide, if Si-H bonds can behave as electron traps.[15]

This is confirmed by the disappearance of the peak by oxidizing chemical oxide at 600°C in 1 Torr dry oxygen for one minutes. This disappearance may be correlated with to the desorption of hydrogen followed by the formation of Si-O bonds.

The unknown layer between the Si substrate and a gold tip, if it exists, cannot be identified from the present study. The present current-voltage characteristics cannot be affected by trap creation because the voltage across the oxide is lower than 2V.[16] Also, the present current-voltage characteristics cannot be affected by intrinsic breakdown because the voltage across the oxide is lower than 9V.[16]

4. CONCLUSIONS

Carrier transport in chemical oxide of Si was successfully measured for the first time using AFM. This was achieved by drastically decreasing the cross section for carrier transport. The chemical oxides studied were that formed in H_2SO_4 and that formed in HNO_3. It was found from the theoretical calculation that the carrier transport in chemical oxide formed in H_2SO_4 can be explained as direct tunneling of electrons through chemical oxides, and is affected by the difference between the work function of gold and that of n$^+$-Si if the energy discontinuity in the conduction band edge at the SiO_2/Si interface for chemical oxide is the same as that for bulk SiO_2. Irregular current-voltage characteristics are obtained for chemical oxide formed in HNO_3. This must be correlated with Si-H bonds in chemical oxide.

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