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Reduction of effective dielectric constant of gate insulator by low-resistivity electrodes

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On metal–oxide–semiconductor capacitors, the effective dielectric constant (k_{eff}) values extracted from high-frequency capacitance–voltage measurements were found to decrease when gate electrodes of very low resistivity were used. The equivalent-oxide thickness increase reaches about 1 nm with the low-resistivity electrodes. We examined gate insulators of SiO_2, Al_2O_3, and HfO_2 and gate electrodes of Al, TiN, Au, Cr, and TaN. The equivalent-oxide thickness increase can be prevented by inserting a high-resistivity metal film only 0.3 nm thick between the very low-resistivity metal and the insulator. The present results suggest that k_{eff} is reduced by the screening of ionic insulators with free electrons of the metal due to a quantum effect. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1519736]

In downsized nanometer-scale devices in ultralarge scale integration, quantum effects appear in device operation. For example, the gate capacitance of metal–oxide–semiconductor (MOS) is reduced by the wave function of carriers in a thinned inversion layer or accumulation layer.[1–3] As is well known, direct tunneling currents appear through nanometer-scale insulators. To reduce these currents, high-k [k: relative dielectric constant ($\equiv \varepsilon_r$)] gate insulators are now being intensively investigated.[4–6] In spite of the use of high-k materials, semiconductor technology[7] requires thicknesses of a few nanometers. On this background, we have found a correlation between the effective dielectric constant (k_{eff}) and resistivity of the gate electrodes. To the best of our knowledge, this is the first report of clarified k_{eff}-reduction phenomenon caused by gate electrodes. The equivalent-oxide-thickness [EOT$\equiv k(SiO_2)d(\text{insulator})/k(\text{insulator})$, where d is the physical thickness] increase of about 1 nm was observed when very low-resistivity gate electrodes were used, but EOT of less than 1 nm will be required in the future. We believe that this phenomenon is caused by a quantum effect that appears with the progress of the semiconductor technology trend. Because the metal gate offers several advantages for device performance,[7,8] the k_{eff}-change phenomenon caused by it must be taken into account in future MOS-device technology.

The gate capacitance extracted from the accumulation region of the capacitance–voltage ($C-V$) curve[9] does not show the exact insulator–film capacitance because it includes a reduction due to the interfacial layer of low dielectric constant;[10] an influence from the series resistance, which causes a voltage loss due to sharing between the resistance of the insulator and that of other parts;[11] and an influence from substrate resistivity, which gives a gate-area dependence of the EOT. While the reason for the last factor is unknown, we have found that gate-area dependence disappears when a very low-resistivity silicon substrate is used and clarified that the EOT with a smaller gate area ($<1\times10^{-4}$ cm^2) is the more exact value when relatively high-resistivity substrates are used.

The wafers were (100)-oriented p-type 3–5 Ω cm Si and n-type 0.002–0.003 Ω cm Si. The wafers were cleaned with a H_2SO_4/H_2O_2 mixture, a dilute HF, and a deionized water. SiO_2 films were formed by thermal oxidization at 800 °C in a dry oxygen atmosphere. High-k materials of Al_2O_3 and HfO_2 were deposited on the substrates using an electron cyclotron resonance (ECR) sputtering system with Al and Hf targets and Ar/O_2 gases. The ECR sputtering system can provide high-quality high-k gate insulator films.[12] Postdeposition annealing was performed in a vacuum ($1-3\times10^{-4}$ Torr and $1-2\times10^{-6}$ Torr) at about 600 °C for all samples except that for the temperature-variation study. TiN films were deposited by reactive sputtering with a magnetron sputtering system. By choosing appropriate sputtering conditions, two types of TiN films, gold (G)-TiN and dark brown (DB)-TiN, were formed. The resistivities of the G- and DB-TiN films were about 80 and 750 $\mu\Omega$ cm, respectively. In the DB-TiN film deposition, a little oxygen was added at a very low flow rate. In the thickness-variation study for metal, ECR-sputtered TaN films were used because of their high resistivity and easy controllability in ECR sputtering. TaN films were deposited with a Ta target and Ar/N_2 gases. The resistivity of a thickly deposited TaN film was 2400 $\mu\Omega$ cm. The TiN and TaN films were patterned by chemical wet etching with an evaporated Al mask. Gate electrodes of Al, Au, and Cr were formed by vacuum evaporation with a tungsten-heater boat and a stencil mask. All surfaces of the evaporated films were optically flat. Measured resistivities of these metal films were 7, 5.5, and 130 $\mu\Omega$ cm, respectively. All of the gate electrodes were deposited after postannealing, except for the samples for the trap study. Finally, an Al film was deposited on the back of all samples to form ohmic contacts.

High-frequency $C-V$ curves were obtained at 1 MHz with a root-mean-square voltage of 20 mV and back-and-forth bias sweep. Areas of all gate electrodes were measured using microscope photographs to normalize the capacitance by gate area. The quantum effect due to the accumulation

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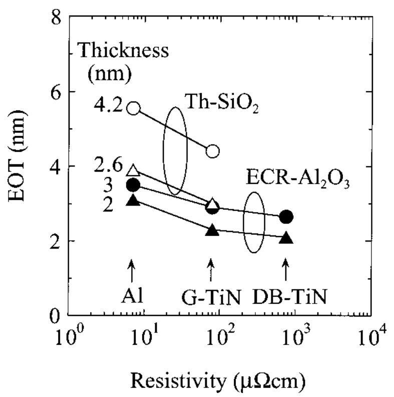

FIG. 1. EOT versus resistivity of gate electrodes obtained from metal/insulator/p-Si MOS capacitors. Gate electrodes of Al, G TiN, and DB TiN and gate insulators of thermally grown SiO_2 and ECR-sputtered Al_2O_3 were employed.

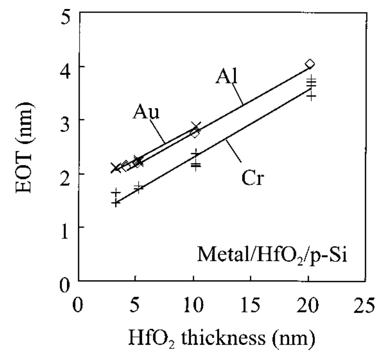

FIG. 2. EOT for vacuum-evaporated Al, Au, and Cr gate electrodes as a function of HfO_2 thickness. Resistivities of these electrodes were about 7, 5.5, and 130 $\mu\Omega$ cm, respectively. Very-low-resistivity substrates were used.

layer was not taken into account in calibrating the measured capacitances. The film resistivity was determined for thickly deposited films (>50 nm).

Figure 1 shows the EOT versus the resistivity of gate electrodes for metal/insulator/p-Si MOS capacitors. The EOT changes with different gate electrode and it decreases with increasing resistivity of the gate electrodes. The results for the thermally oxidized SiO_2 films show that the gate–electrode dependence of EOT is not a special phenomenon in ECR-sputtered insulator films. The lack of data for the DB TiN/SiO_2 is due to poor adherence of the DB-TiN films. The large EOT values for all the ECR-Al_2O_3 plots are due to interfacial-oxide layers formed by annealing in the lower vacuum.

Recently, it has been reported that the Al electrode very easily reacts with high-k insulators, such as hafnium silicate and zirconium silicate but the Au electrode does not.[13] However, we have not observed such an indication for Al_2O_3 and HfO_2. Table I summarizes the EOTs we have obtained with Al, Au, and Al/G-TiN electrodes under various conditions. These data include the samples annealed after G-TiN deposition but the tendency is the same. Furthermore, we have usually obtained very small hysteresis (<20 mV) with the Al electrode, suggesting little reaction with the insulators.

In order to eliminate the slight uncertainty regarding the possibility of damage infliction by the plasma for TiN in the aforementioned experiments, the EOT-change phenomenon was further examined using vacuum-evaporated electrodes of different resistivities. Figure 2 shows the EOT versus HfO_2 thickness. Almost the same EOT was obtained for Al and Au, and much smaller values were obtained for Cr. Since vacuum evaporation with a resistance-heater boat causes hardly any damage to the sample surface, this result apparently indicates that the k_{eff} of the capacitors depends on the resistivity of the gate electrodes. It further shows that the EOT change is caused at all insulator thicknesses.

The thickness of the high-resistivity metal layer required in order to reduce the EOT values was studied using a stacked electrode comprising a low-resistivity metal layer (Al)/high-resistivity metal layer (ECR-sputtered TaN). The result is shown in Fig. 3. It is surprising that TaN film only 0.3 nm thick decreases the EOT. This limits the location of the origin of the EOT increase to near the metal/insulator interface. Additionally, it shows that the ECR-sputtered TaN film was deposited with a uniform thickness on an atomic scale, as suggested from previous reports.[12,14] Moreover, it means that a thick low-resistivity metal film can be used in future MOS devices.

Two possible reasons can be given for the EOT-change phenomenon. One is the effect of traps near the interface and the other is the screening effect of free electrons in the metal. The screening effect is caused by the tail of the wave function of the free electrons because the tail must enter into the insulator due to a quantum effect. To clarify the trap effect, we experimentally obtained the annealing temperature dependence of the EOT and hysteresis with Al/G-TiN(3 nm)/HfO_2(5 nm)/p-Si MOS capacitors. The results are shown in Table II. The hysteresis decreased with increasing postanneal temperature, indicating effective defect reduction by annealing. The EOT change was, however, very small. We therefore believe that the EOT decrease is not due to traps. This is reasonable considering the well-known fact that the number of fast traps (1 MHz) is much smaller than

TABLE I. EOTs we have obtained with Al, Au, and Al/G-TiN electrodes under various conditions.

Si substrate		Measured frequency (Hz)	Insulator		EOT (nm)		
					Gate electrode		
Type	Resistivity (Ω cm)		Material	Thickness (nm)	Al	Au	G-TiN
p	3–5	1 M	HfO_2	5	2.4	2.5	1.7
p	3–5	10 k	HfO_2	5	2.2	2.4	1.6
n	2–3 m	1 M	HfO_2	5	2.2	2.5	1.4
n	2–3 m	1 M	HfO_2	2.7	2.1	2.1	1.1
p	3–5	1 M	Al_2O_3	3	3.3	3.0	2.4

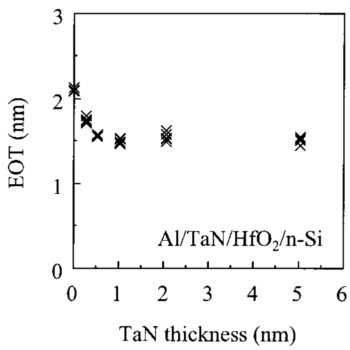

FIG. 3. EOT versus TaN film thickness. The TaN films (2400 $\mu\Omega$ cm) were formed between Al and HfO_2 by ECR sputtering.

that of slow traps in low-frequency (<10 kHz) $C-V$ measurements or quasistatic $C-V$ measurement.

In oxide insulators, a large dielectric constant in the frequency range below infrared appears due to ionic bonds of the metal atoms and oxygen. The metal (δ^+) and oxygen (δ^-) ions move in opposite directions for external field and store large electrostatic energy. If the ions near the metal could not store a large electrostatic energy due to a strong screening effect, the capacitance of an ultrathin insulator must be significantly reduced. For example, if k_{eff} of a 0.25 nm thick layer is reduced to 1, a 1 nm EOT increase must result.

From the standpoint of the screening phenomenon, the results in Fig. 3 mean that the wave function of the free electrons of aluminum is effectively attenuated by the 0.3 nm thick TaN film. It also means that the free electrons of the TaN film can not effectively screen the ion pairs of HfO_2. This coincides with the Thomas–Fermi (T–F) screening length[15] of metals. The T–F screening length can be roughly estimated as ~0.05 nm for the Al film and ~0.4 nm for the TaN film. Since the distance between Hf and O atoms in an amorphous HfO_2 film may be 0.1–0.2 nm, the ion pairs can be effectively screened with Al but not with TaN. This presumption includes a basic hypothesis that the tail of the wave function of the free electrons really shows the screening behavior.

The influence of the screening effect of the tail of the wave function on band-gap energies for metal/semiconductor and metal/insulator interfaces was theoretically studied taking into account of the many-body effect by Inkson and Anderson[16,17] They pointed out that energies of valence-band electrons are raised due to the screening effect and concluded that the band gaps of the covalent semiconductors near the metal are closed and those of ionic semiconductors and insulators are narrowed. They believed that the distance of the band-gap closure from the interface must coincide with the T–F screening length in the metal (1/2 or 1 atom layer). The narrowed band-gap energies of ultrathin Al_2O_3 films on metal substrates[18,19] and unchanged barrier energy of ultrathin SiO_2 films on a silicon substrate[20] have recently been measured and reported. The reported values for metal substrates were very small (3.2–~5 eV for <0.9 nm thick Al_2O_3 films and ~9 eV for a ~3 nm thick film),[18,19] compared to the values predicted by Inkson and Anderson (1–2 eV reduction). Since our capacitance measurements do not directly relate to the band-gap energy, the present results paradoxically provide strong evidence of screening by the tail of the wave function. Note that our results do not depend on insulator thickness. In the frequency region higher than infrared, the k_{eff} change may be different from the present behavior because the dominant contribution would change from ion movement to electron excitations.

TABLE II. Relationship between postanneal temperature and EOT or hysteresis for Al/G TiN(3 nm)/HfO_2(5 nm)/p-Si MOS capacitors.

Postanneal temperature (°C)	Hysteresis (mV)	EOT (nm)
500	122	1.4
600	40	1.5
700	29	1.6

In conclusion, a k_{eff}-reduction phenomenon caused by low-resistivity gate electrodes is presented. The EOT increase reaches about 1 nm. The resistivity dependence of the EOT strongly suggests that the k_{eff}-reduction phenomenon is due to a quantum effect appearing as a result of the progress of the semiconductor technology trend.

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