Equivalent oxide thickness scaling of Al_2O_3/Ge metal–oxide–semiconductor capacitors with ozone post oxidation*

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Aluminum–oxide films deposited as gate dielectrics on germanium (Ge) by atomic layer deposition were post oxidized in an ozone atmosphere. No additional interfacial layer was detected by the high-resolution cross-sectional transmission electron microscopy and X-ray photoelectron spectroscopy measurements made after the ozone post oxidation (OPO) treatment. Decreases in the equivalent oxide thickness of the OPO-treated Al_2O_3/Ge MOS capacitors were confirmed. Furthermore, a continuous decrease in the gate leakage current was achieved with increasing OPO treatment time. The results can be attributed to the film quality having been improved by the OPO treatment.

Keywords: Al_2O_3 gate dielectric, ozone post oxidation, equivalent oxide thickness, electrical properties

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1. Introduction

Future complementary metal–oxide semiconductor (CMOS) scaling requires the introduction of new channel materials and innovative device structures.[1] Germanium (Ge) has been widely considered as a promising alternative to Si as a new channel material for metal–oxide–semiconductor field-effect transistors (MOSFETs) beyond the traditional device scaling because the carrier mobility of Ge is higher than that of Si and it is compatible with conventional Si integration technologies.[2–4] However, the interface properties of high-*k*/Ge metal–oxide–semiconductor (MOS) devices have been shown to be very difficult to control and stabilize.[5] Consequently, many researchers have tried to create a high-quality interface between high-*k* gate dielectrics and Ge substrates by using passivation layers. One promising solution is to introduce a thin GeO_2 interfacial layer (IL) between the high-*k* layer and the Ge substrate.[6–8] However, during a high-*k* layer growth process (like atomic layer deposition; ALD), the GeO_2 film is inevitably damaged and the final MOS interface is degraded. In order to overcome this problem, a thermal post-oxidation method has recently been proposed to fabricate the high-*k*/IL/Ge gate stacks after high-*k* layer deposition.[9–11] On the other hand, it is widely recognized that equivalent oxide thickness (EOT) scaling is still an important issue in advanced MOS transistors. Therefore, an ultrathin GeO_2 layer is required in Ge MOSFETs to obtain a thin EOT. However, with the conventional thermal oxidation method, it is very hard to obtain a thin, high-quality GeO_2 layer that results in a thin EOT. Recently, a novel plasma post oxidation (PPO) method has been proposed by Zhang *et al.*[12,13] With this PPO method, the EOT could be controlled by tuning the original high-*k* layer thickness and the plasma power. The key point of the PPO method is to pre-grow a thin high-*k* barrier layer before the plasma oxidation, which could make the plasma oxygen ions penetrate the Ge substrate less deeply. Therefore, it might not be necessary to use a plasma oxidation method, which needs complex equipment such as an electron cyclotron resonance (ECR) plasma generator, to achieve this task. Ozone oxidation has been proved to be an effective method to obtain high-quality oxide films and good interfaces for Ge and Si MOS devices at lower temperatures.[14,15] However, it is very difficult to prepare thin EOT oxide films on Si or Ge with direct ozone oxidation.

In this study, we propose a new ozone-post-oxidation (OPO) method for Al_2O_3/Ge MOS devices, aimed at realizing thin EOTs. The electrical properties of the devices are systematically investigated, and the experimental results show that with this OPO method, the Ge MOS interface can be effectively stabilized and no additional GeO_2 interface layer is formed after the OPO treatment.

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2. Experimental details

The OPO treatment was performed under air pressure and at room temperature using the ozone generation equipment made in our laboratory. The power of the UV lamp was 20 W. The fabrication process of the Al_2O_3/Ge MOS capacitors is shown schematically in Fig. 1. First, an n-type Ge wafer with a (100) orientation and a resistivity range of 0.21 $\Omega\cdot$cm$\sim$0.26 $\Omega\cdot$cm was cleaned with de-ionized water, acetone, and cyclic HF-water etching. Next, the wafer was loaded into the deposition chamber to form an ultrathin Al_2O_3 film ($\sim$3.6 nm) on it by using an ALD (Beneq TFS-200) technique. During the deposition process, the wafer was kept at 300 °C.

Trimethylaluminum (TMA) and H_2O were used as the precursors for the aluminum and oxygen sources. To investigate the effects of the OPO treatment on the Al_2O_3/Ge interface properties, the as-deposited samples were treated in an O_3 atmosphere for 2, 3, 4, and 5 min. Samples without OPO treatment were also prepared. N_2 ambient annealing was performed after the OPO treatment for all samples at 400 °C for 30 min in an annealing furnace. In order to investigate the electrical properties of the Al_2O_3/Ge gate stacks, Pt gate electrodes and Au back contacts were fabricated by magnetron sputtering equipment.

The interfacial stoichiometry between the Al_2O_3 films and Ge substrates was examined by X-ray photoelectron spectroscopy (XPS) measurement. The XPS measurement was carried out using a system equipped with a monochromatic Al Kα source (1486.6 eV) for the excitation of photoelectrons. The high-resolution scans were taken at a take-off angle of 45° and a pass energy of 29.35 eV. The peak position of Al 2p was calibrated using the Ge 3d peak of the substrate at 29.4 eV.

The high-resolution cross-sectional transmission electron microscopy (HR-TEM) image of the stacked gate dielectrics was acquired using a JEOL 2010 microscope. The electrical properties of the fabricated MOS capacitors were measured using a precision LCR meter (Agilent 4284A) for capacitance–voltage (C–V) measurements and a semiconductor parameter analyzer (Agilent 4156C) for the current–voltage (I–V) measurements.

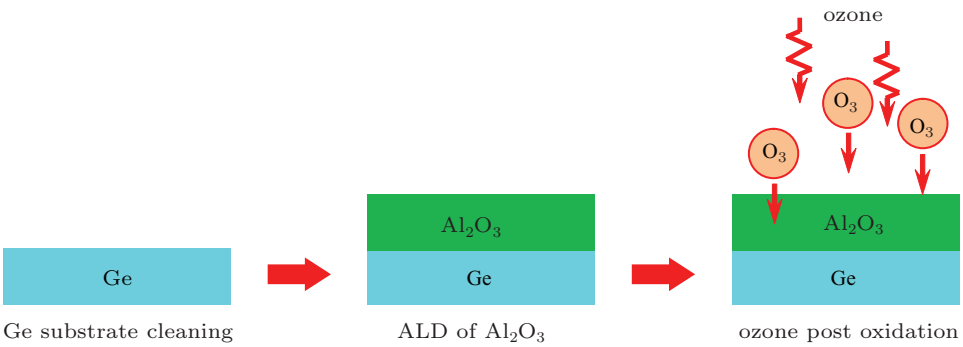


Fig. 1. (color online) The process flow for fabricating a Pt/Al_2O_3/Ge gate stack with an OPO treatment.

3. Results and discussion

3.1. Structure and analysis

Figure 2 shows the Ge 3d and Al 2p core level peaks of the Al_2O_3 (3.6 nm)/Ge structure by means of XPS probing for the as-deposited and 2, 3, 4, 5 min OPO-treated samples. As shown in the figure, except for the Ge^0 component, no Ge-related peak signals can be observed in the XPS spectrum of either the as-deposited or the OPO-treated samples. This indicates either that the Ge substrate was not oxidized after the OPO treatment even for 5 min, or that the amount of GeO_x at the interface is under the XPS's detection limit. It can be found from Fig. 2(b) that the Al 2p spectrum of an as-deposited sample exhibits two split peaks of Al–Al bonding at 73.0 eV and Al–O bonding at 74.1 eV, indicating the coexistence of oxygen-deficient composition and stoichiometric composition in the Al_2O_3 film. As has been reported, an oxygen-deficient layer usually exists at the interface in the Al_2O_3 film that is made by the ALD process, when TMA and H_2O are used as the reactants, due to the hydrophobicity of the HF-last substrate (Si or Ge).[16,17] From the XPS spectra of the OPO treated samples (Fig. 2(b)), we can find that the intensity of the Al–Al bonding feature rapidly decreases, while the intensity of the Al–O bonding feature continues to increase with the increase in the OPO time. This indicates that the OPO treatment can cure the oxygen deficiency in the Al_2O_3 film and finally enhance the average oxygen content of the film.

To more directly understand the impact of the OPO treatment on the interface features of the Al_2O_3/Ge gate stacks, HR-TEM observations were performed. In these samples for the TEM measurement, the OPO treatment was performed after 10 cycles of Al_2O_3 deposition on the Ge substrate, followed by 10 more cycles of Al_2O_3 growth. It can be seen from Fig. 3 that the as-deposited sample is uniform and amorphous with a sharp interface. The physical thickness of the Al_2O_3 layer is deduced to be 3.6 nm. Furthermore, there was no GeO_2 interfacial layer (IL) growth between the Al_2O_3 films and the Ge substrates even after the OPO treatment was performed for

3 min and 5 min.

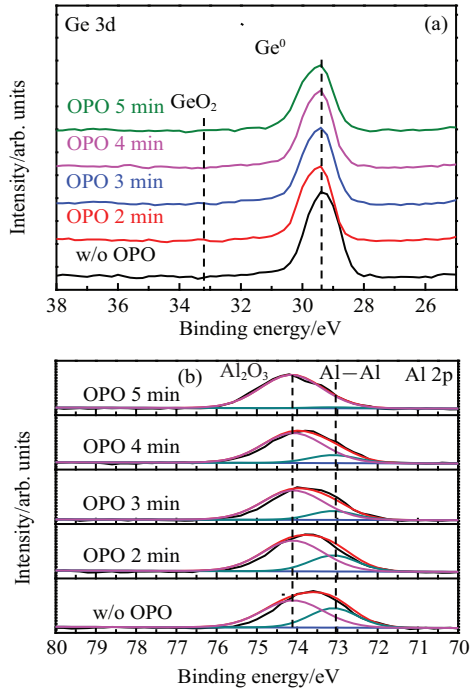


Fig. 2. (color online) (a) Ge 3d and (b) Al 2p XPS spectra of the Al_2O_3/Ge structure before and after OPO treatment.

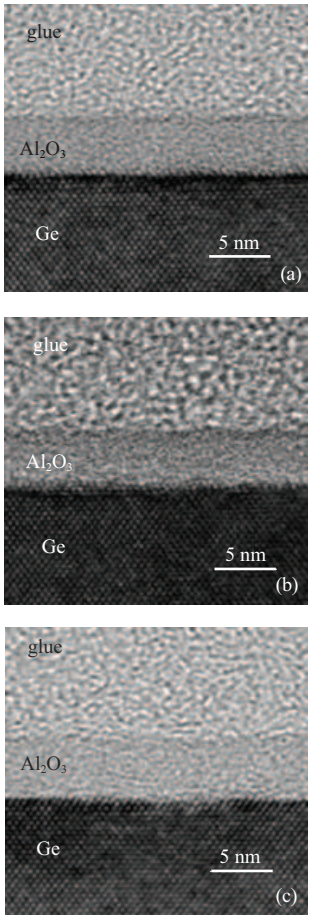


Fig. 3. The high-resolution cross-sectional transmission electron microscopy (HR-TEM) image of ALD-Al_2O_3 on the Ge structure: (a) without OPO treatment; (b) with OPO treatment for 3 min; and (c) with OPO treatment for 5 min.

3.2. Electrical properties

Next, we will discuss the electrical properties of the OPO-treated devices. Figure 4(a) compares the *C*–*V* characteristics of the Al_2O_3/Ge MOS capacitors with different OPO periods and with no OPO. It was found that the sample with no OPO treatment exhibits very poor *C*–*V* behavior. However, the OPO process could significantly improve the *C*–*V* characteristics, which also depend on the OPO time [Fig. 4(a)]. On the other hand, as shown in Fig. 4(b), the EOT value of the capacitor, extracted from the fits of the *C*–*V* characteristics with a Ge-based simulator, decreases from $\sim$ 2.39 nm to $\sim$ 1.79 nm with increased OPO time.

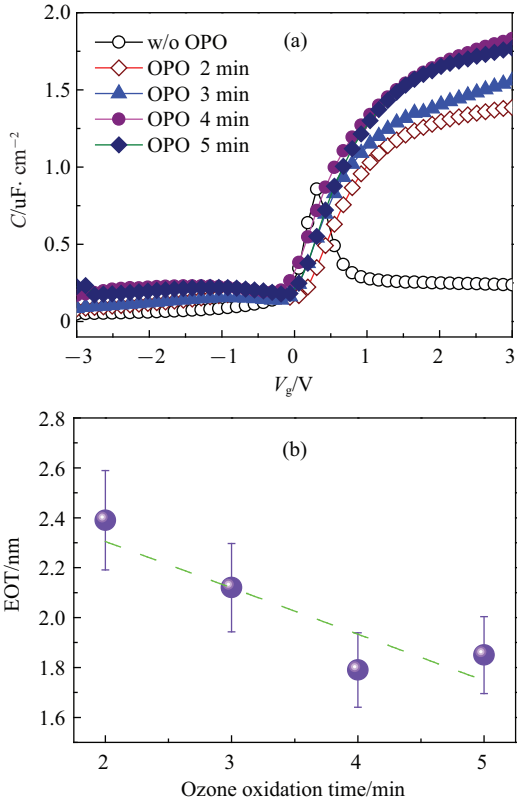


Fig. 4. (color online) (a) The *C*–*V* characteristics (1 MHz) of Al_2O_3/Ge MOS with and without OPO treatment, and (b) the OPO time dependence of the EOT value.

Furthermore, the OPO-treated devices show much lower gate leakage currents than the device with no OPO treatment (Fig. 5). It can be found from the figure that after OPO treatment for 5 minutes, the gate leakage current density is reduced to the order of 10^{-5} A/cm^2@ $V_{FB} + 1$ V.

The main reasons for the reduced EOT and the decreased gate current leakage after OPO treatment might be as follows. The XPS analysis suggests that after OPO treatment, the oxygen-deficient Al_2O_3 was transformed into near-stoichiometric Al_2O_3. As reported in the literature,[16] the leakage characteristic of the near-stoichiometric Al_2O_3 film is better than that of the oxygen-deficient one. Furthermore, the dielectric constant of the near-stoichiometric Al_2O_3 is higher

than the oxygen-deficient one due to its higher density. Consequently, the quality of the Al_2O_3 film is improved after OPO treatment for several minutes, resulting in EOT scaling and the reduced gate leakage current of the Al_2O_3 capacitor. We think that after careful process optimization, a sub-1 nm EOT is achievable with this OPO technology for Ge MOS devices.

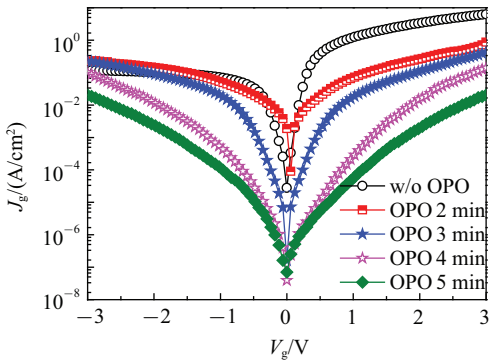


Fig. 5. (color online) The gate leakage currents of Al_2O_3/Ge MOS capacitors after different OPO treatment times.

4. Conclusions

In conclusion, a novel OPO method was proposed to prepare superior Al_2O_3/Ge gate stacks with good electrical properties and low EOTs. Both the EOT and the gate leakage current were reduced significantly with this OPO process, while no significant GeO_2 interface layer was formed. Thus, OPO could be a promising technology for enhancing the performance of Ge MOS devices.

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