Improved Electrical Properties of Germanium MOS Capacitors With Gate Dielectric Grown in Wet-NO Ambient

J. P. Xu, P. T. Lai, *Senior Member, IEEE*, C. X. Li, X. Zou, and C. L. Chan

***Abstract*—Wet-NO oxidation with or without wet NH_3 pretreatment is used to grow GeON gate dielectric on Ge substrate. As compared to dry NO oxidation, negligible growth of GeO_x interlayer and, thus, a near-perfect GeON dielectric can be obtained by the wet-NO oxidation. As a result, MOS capacitors prepared by this method show greatly reduced interface-state and oxide-charge densities and gate-leakage current. This should be attributed to the hydrolyzable property of GeO_x in water-containing atmosphere.**

***Index Terms*—GeO_x interlayer, Ge MOS capacitors, GeON, wet-NO oxidation.**

I. INTRODUCTION

GERMANIUM MOSFETs with high-κ gate dielectrics (ZrO_2 [1], HfO_2 [2]–[5], and Al_2O_3 [5]) have received more and more attention for the future high-speed CMOS technology due to the much higher carrier mobilities of Ge than Si (two times higher for electrons and four times higher for holes). However, since the deposition of high-κ material usually occurs in an oxidizing ambient [6], [7], germanium substrate could be oxidized to form the water-soluble and unstable germanium oxide (GeO_x) [8], [9]. To overcome this problem, various processes were used to improve the interface quality, including NH_3 surface treatment [2]–[5], to form a GeO_xN_y interlayer, and Si interlayer technique with several monolayers of Si grown between the dielectric and the substrate by SiH_4 surface annealing [10], [11]. However, nitrogen incorporation in the former method may not be sufficient to fully passivate the dangling bonds on the Ge surface and prevent its oxidation, while the thickness of the Si interlayer in the latter method has to be accurately controlled to prevent parasitic Si channel, thus increasing the processing difficulty. In this letter, a novel process is proposed to fabricate high-quality GeO_xN_y gate dielectric by oxidizing Ge in an NO plus water-vapor atmosphere. As a result, the growth of the GeO_x interlayer is effectively suppressed, and high-quality GeO_xN_y bulk and GeO_xN_y/Ge interface with low oxide charge and interface-state densities and greatly reduced gate-leakage current are obtained. This should be due to the water-soluble property of GeO_x in the wet ambient. For comparison, Ge MOS capacitors are also prepared in dry NO ambient. Obvious differences in electrical properties between the wet and dry NO-oxidized samples can be observed.

TABLE I
OXIDE CAPACITANCE AND THICKNESS, OXIDE-CHARGE AND INTERFACE-STATE DENSITIES, AND FLATBAND VOLTAGE OF THE SAMPLES EXTRACTED FROM 100-KHz HF C–V CURVE

Sample	C_{ox} (pF)	t_{ox} (nm)	Q_{ox} (cm^{-2})	D_{it} at midgap ($cm^{-2}eV^{-1}$)	V_{fb} (V)
DNOG	46.1	12.1	-1.32×10^{12}	1×10^{12}	0.412
WNOG	60.6	9.2	-5.72×10^{11}	6×10^{11}	0.171
WNH3NOG	65.8	8.4	-5.55×10^{11}	5×10^{11}	0.158

II. EXPERIMENTS

MOS capacitors were fabricated on (100)-oriented n-type Ge substrate with a doping concentration of 2.65×10^{16} cm^{-3}. The wafers were cleaned using trichloroethylene and acetone followed by cyclic HF (50:1 diluted HF solution) dip with DI water rinsing to remove Ge native oxide [2]. Thermal oxidation at 550 °C was carried out in dry or wet-NO ambients (denoted as DNOG and WNOG samples, respectively). Another sample (WNH3NOG) was prepared first by wet NH_3 pretreatment for 2 min and then by wet-NO oxidation at 550 °C. For a better evaluation of the performance of the GeON dielectric and the growth of the GeO_x interlayer, a relatively long oxidation time of 20 min was used to produce a thicker film (8.4–12.1 nm, as shown in Table I). Then, the WNOG and WNH3NOG samples received a wet N_2 anneal, while the DNOG sample had a dry N_2 anneal, all for 5 min at the same temperature. The wet NO, NH_3, and N_2 atmospheres were realized by bubbling pure NO, NH_3, and N_2 gases through deionized water at 95 °C with a flow rate of 250 ml/min for NO and NH_3 and 500 ml/min for N_2. Al was thermally evaporated and patterned as the gate electrode of the MOS capacitors with an area of 7.85×10^{-5} cm^2. Finally, a thermal anneal was carried out in forming gas (H_2/N_2) ambient for 20 min at 300 °C.

High-frequency (HF, 100 kHz and 1 MHz) capacitance–voltage (C–V) characteristics were measured at room temperature using HP4284A precision LCR meter. Oxide capacitance (hence, oxide thickness), flatband voltage, and oxide-charge

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Manuscript received January 23, 2006; revised March 6, 2006. This work was supported by the National Natural Science Foundation of China (NSFC) under Grant 60576021, and the Research Grants Council (RGC) of Hong Kong Special Administrative Region (HKSAR), China, under Project HKU 7142/05E. The review of this letter was arranged by Editor C.-P. Chang.

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Digital Object Identifier 10.1109/LED.2006.874124

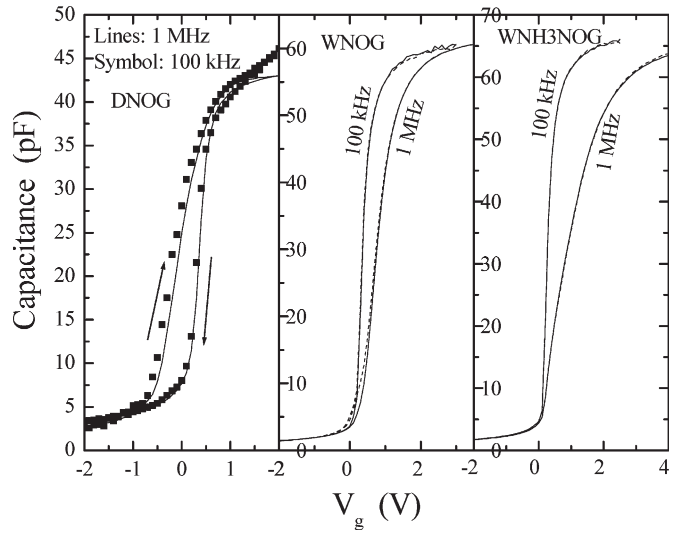

Fig. 1. Typical high-frequency *C–V* curves of the samples under dark condition at room temperature, swept in both directions at frequencies of 1 MHz and 100 kHz, respectively. Area of capacitor is 7.85×10^{-5} cm^2. (a) DNOG sample, (b) WNOG sample, and (c) WNH3NOG sample.

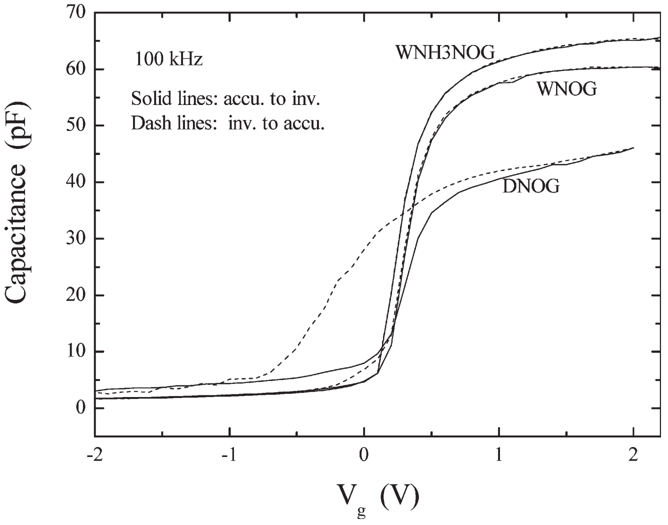

Fig. 2. High-frequency *C–V* curves of the samples under dark condition at room temperature, swept in both directions at 100 kHz. Area of capacitor is 7.85×10^{-5} cm^2.

density were extracted from the 100-kHz *C–V* curve. The interface-state density near midgap was extracted also from the 100-kHz *C–V* curve by the Terman method [12] for the purpose of a relative comparison between different samples. The gate-leakage current was measured by HP 4156A precision semiconductor parameter analyzer. All measurements were carried out under a light tight and electrically shielded condition.

III. RESULTS AND DISCUSSION

Fig. 1 shows the typical HF *C–V* curves of the samples under dark condition, swept in both directions and measured at frequencies of 1 MHz and 100 kHz, respectively. As expected, a large hysteresis is observed for the DNOG sample due to the growth of the GeO_x interlayer during dry-NO oxidation, leading to high-interface and near-interface trap densities. However, the growth of the GeO_x interlayer gets effectively suppressed when the oxidation is carried out in wet-NO ambient, as shown by the very small hysteresis in the *C–V* curves of the WNOG and WNH3NOG samples, and their identical C_{ox} values measured at 1 MHz and 100 kHz, which implies less interface and near-interface traps. For comparing the qualities of these oxynitrides and their interface properties with Ge substrate more clearly, their *C–V* curves measured at 100 kHz are replotted in Fig. 2. The values of electrical thickness (t_{ox}) of the gate oxynitride and flatband voltage (V_{fb}) extracted from the 100-kHz *C–V* curves are listed in Table I, where the flatband voltage V_{fb} is determined from the flatband capacitance (C_{fb}) formula [13] modified by replacing the dielectric constant of Si with that of Ge

$$\frac{C_{\mathrm{fb}}}{C_{\mathrm{ox}}} = \left(1 + \frac{75.7\sqrt{T/300}}{t_{\mathrm{ox}}\sqrt{N}}\right)^{-1}$$

where T is the temperature in Kelvin, and N is the carrier concentration equal to donor doping as an approximation. The equivalent oxide-charge density (Q_{ox}) is calculated as $-C_{\mathrm{ox}}(V_{\mathrm{fb}} - \varphi_{\mathrm{ms}})/\mathrm{q}$, where the work-function difference φ_{ms} between Al and Ge is calculated to be 0.053 V. Obviously, the DNOG sample has the smallest C_{ox}, and thus the largest thickness, mainly due to the growth of GeO_x interlayer during dry-NO oxidation. However, the growth of the GeO_x and GeON with low N content is considerably suppressed due to their hydrolyzation in the water-vapor atmosphere (i.e., once the GeO_x or GeON with low N content is grown, it is hydrolyzed in the wet ambient), thus giving an almost perfect GeON gate dielectric with smaller thickness and higher N content for the two samples oxidized in wet-NO ambient. For the WNH3NOG sample, the wet NH_3 surface pretreatment prior to the wet-NO oxidation forms a thin nitrogen-terminated passivation layer, which can further prevent the growth of the GeO_x interlayer during the subsequent wet-NO oxidation due to its O_2-blocking role, giving a smaller GeON thickness than that of the WNOG sample. The suppressed growth of GeO_x interlayer in the wet-NO ambient is highly desirable for fabricating advanced small-scaled Ge MOSFET with the GeON as gate dielectric or as ultrathin interlayer of high-κ stack gate dielectrics. The two wet-NO-oxidized samples exhibit almost identical oxynitride bulk and interface properties with reduced Q_{ox} and D_{it} as compared to the DNOG sample, further supporting the negligible growth of the GeO_x interlayer and thus better interface quality. It should be noted that the WNH3NOG sample seems to have the lowest interface-state density, as shown in Table I, extracted from 100-kHz *C–V* curves. But its large frequency dispersion in the depletion region and near accumulation indicates a high density of interface states near the bottom of the conduction band. This is probably attributed to the higher nitrogen content in the near-interface GeON induced by the NH_3 pretreatment plus NO oxidation. Therefore, the wet-NO oxidation without NH_3 pretreatment should be more beneficial for preparing high-quality thin GeON as the gate dielectric or interlayer of high-κ stack gate dielectric in Ge MOSFET. In addition, the still higher interface-state density of 6×10^{11} cm^{-2} eV^{-1} for

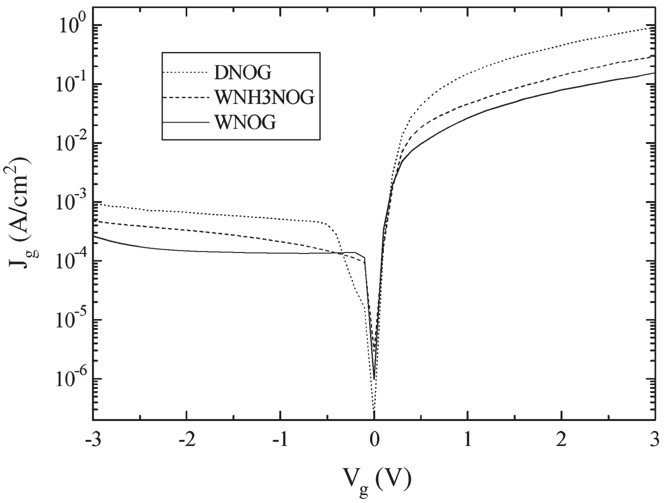

Fig. 3. Gate-leakage properties of the samples.

the WNOG sample (even though it is lower than that of DNOG sample) is speculated to result from the Ge diffusion into GeON to generate some defects near the interface [14] and possible roughness of the oxynitride/Ge interface. A further study is needed to improve the interface quality.

Fig. 3 shows the gate-leakage properties of the samples. The DNOG sample shows the largest gate-leakage current due to the existence of the GeO_x interlayer. For the two wet-NO-oxidized samples, lower gate-leakage current is observed, despite their smaller t_{ox}s, than that of the DNOG sample. This should be due to the greatly suppressed GeO_x growth and, thus, low oxide-charge and interface-state densities when the oxidation is performed in the wet-NO ambient, as mentioned above. Slightly larger gate-leakage current of the WNH3NOG sample than that of the WNOG sample is probably associated with the existence of electron traps in the film induced by the NH_3 pretreatment [15] as well as its smaller t_{ox}. The negative equivalent oxide charge should be related to the forming-gas anneal and wet oxidation/anneal ambient. The former tends to decrease the positive fixed oxide charge generated by nitridation [16] while the latter could induce negative charges near/at the interface [17]. The origin of the negative charges might be OH^-, which cannot diffuse out from the interface at a low temperature of 550 °C [17]. For the DNOG sample, the negative Q_{ox} should be mainly due to the high fixed interface-charge and/or near-interface oxide-trap densities of the GeO_x interlayer because the flatband voltage (thus the equivalent oxide charge) results from the combined effects of fixed oxide charge, mobile ions, and/or near-interface oxide-trap charges near the Fermi level, which respond to the C–V sweeping at room temperature.

IV. SUMMARY

A new wet-NO oxidation with or without wet NH_3 surface pretreatment is employed to fabricate GeON gate dielectric on the Ge substrate. Compared with dry-NO oxidation, the wet-NO oxidation followed by a wet N_2 anneal gives an almost perfect GeON gate dielectric with a negligible GeO_x interlayer, greatly reduced interface-state and oxide-charge densities an gate-leakage current. The mechanisms involved probably lie in the hydrolyzable property of GeO_x in water-containing atmosphere. In a word, this technique is highly promising for preparing high-quality GeON gate dielectric in Ge MOS devices. Moreover, it can easily make excellent ultrathin GeON interlayer when HfO_2 or other high-κ dielectrics is used as the gate dielectric of Ge MOSFET.

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