High-quality molecular-beam-epitaxy-grown \( \text{Ga}_2\text{O}_3(\text{Gd}_2\text{O}_3) \) on Ge (100): Electrical and chemical characterizations

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High-\( \kappa \) dielectric \( \text{Ga}_2\text{O}_3(\text{Gd}_2\text{O}_3) \) (GGO) has been deposited on Ge (100) at room temperature using molecular beam epitaxy. \textit{In situ} angular-resolved x-ray photoelectron spectroscopy on the GGO/Ge after gate dielectric deposition and 500 °C postdeposition annealing has exhibited negligible Ge interdiffusion, thus revealing high thermal stability of the heterostructure. The CF\(_4\)-plasma treatment on the passivated GGO/Ge has greatly improved the capacitance-voltage characteristics of the metal-oxide-semiconductor capacitors, besides the very low gate leakage current density of \( 3.2 \times 10^{-9} \text{A/cm}^2 \) at a flat-band voltage +1 V. These excellent interfacial characteristics have been achieved without employing any intentional passivation layers. © 2010 American Vacuum Society. [DOI: 10.1116/1.3271143]

I. INTRODUCTION

Recently, Ge metal-oxide-semiconductor (MOS) devices have attracted much attention as Ge is a very promising candidate to replace Si channel for complementary MOS applications beyond the 16 nm node. Compared to Si, Ge exhibits a higher carrier mobility, \( -2.7 \) times in electron and \( -4.2 \) times in hole, and further provides scaling in power supply voltage owing to the smaller band gap. However, the germanium native oxide, GeO\(_x\), is thermally unstable and water soluble and is undesirable for device fabrication.\(^1\)

Therefore, extensive research activities have been taken using interfacial passivation layers such as thin Si and GeO\(_2\) films to modify the gate dielectric/Ge interfaces.\(^{2,3}\) However, the \( \kappa \) values of Si and GeO\(_2\) are considered to be relatively low, compared to other generally used dielectrics and our \( \text{Ga}_2\text{O}_3(\text{Gd}_2\text{O}_3) \) (GGO) (\( \kappa \approx 14–16 \)).\(^{4,5}\) The existence of these interfacial passivation layers with a relatively low \( \kappa \) limits the downsizing of the device dimension due to their unavoidable and unfavorable contribution to equivalent oxide thickness.\(^6\)

One ultimate solution is to directly deposit high-\( \kappa \) dielectrics on Ge, while maintaining high-quality dielectric/Ge interface without employing any interfacial low-\( \kappa \) passivation layer. Molecular beam epitaxy (MBE) GGO, deposited at high substrate temperature (\( >500 \) °C), has effectively passivated Ge and InGaAs compound semiconductor surfaces and gave excellent MOS device performances;\(^{1,5,7-9}\) many advantages include the absence of interfacial layers between GGO and the semiconductors, high-\( \kappa \) value of GGO in the range of 15, and good thermal stability at high temperatures.

In this work, GGO film has been deposited directly on Ge (100) at room temperature (RT-GGO) to achieve a GGO/Ge interface with less Ge interdiffusion compared to the counterpart with high-temperature (\( \sim 500 \) °C) deposited GGO (HT-GGO), as probed using angular-resolved x-ray photoelectron spectroscopy (AR-XPS). In addition, a CF\(_4\)-plasma treatment\(^{10}\) has been employed to improve the RT-GGO/Ge interface and to reduce both the bulk oxide traps and the interfacial states, leading to significant improvements in the electrical properties on the high-\( \kappa \)/Ge gate stacks.

II. EXPERIMENT

2 in. Sb-doped n-type Ge (100) wafers with resistivity of \( 0.07–0.2 \Omega \cdot \text{cm} \) were dipped in 2% diluted HF solution and rinsed with de-ionized water. The wafers were then immediately loaded into a multichamber MBE/analysis system, which includes GGO deposition chamber, \textit{in situ} AR-XPS analysis chamber, and ultrahigh vacuum connecting modules.\(^{11,12}\) Prior to the oxide deposition, annealing at 450 °C for 10 min for the Ge wafers was implemented to get rid of the residual Ge native oxide and to achieve oxide-free and atomically ordered Ge surfaces, as evidenced by sharp and streaky (\( 2 \times 2 \)) reconstructed reflection high energy electron diffraction (RHEED) patterns [Fig. 1(a)] and also by \textit{in situ} AR-XPS analysis. The featureless RHEED patterns after the oxide deposition revealed that the RT-GGO was amorphous, as shown in Fig. 1(b).

For probing the chemistry of the RT-GGO/Ge interface and bulk Ge by \textit{in situ} AR-XPS without thinning GGO using sputtering, 2 nm thick RT-GGO was directly deposited on Ge with e-beam evaporation; the as-deposited sample and the same sample after \textit{in situ} 500 °C annealing for 30 min were studied. Furthermore, for comparison, \textit{in situ} AR-XPS was also performed on HT-GGO (0.6 nm)/Ge.

Part of the samples with a thicker RT-GGO (13.8 nm) received a CF\(_4\)-plasma treatment for 3 min plus a 500 °C annealing for 5 min in N\(_2\) ambient. The CF\(_4\)-plasma treatment was carried out in an inductively coupled plasma cham-
ber with flow rates of CF₄ and O₂ of 50 and 5 SCCM, respectively, where SCCM stands for cubic centimeters per minute at standard pressure. The total pressure was kept at ~10 Pa and the rf power was 20 W. RT-GGO/Ge MOS capacitors (MOSCAPs) were fabricated for electrical and microstructural measurements.

In situ high resolution XPS system was set up using a SPECS-PHOIBOS-150 hemispherical electron analyzer. Mg Kα (hv=1253.64 eV) and Al Kα (hv=1486.65 eV) were used as the dual anode x-ray source. The photoelectron take-off angle of AR-XPS varied from 0° to 90° (0° is the normal vector to the specimen surface) to provide nondestructive depth profile information about films with thickness in the range of nanometers. The structural characterization was studied with high-resolution transmission electron microscopy (HR-TEM) micrograph. The TEM sample preparation includes mechanical polishing, dapping, and ion milling processes. The analytical work was performed using JEOL 2100F type TEM.

For the MOSCAPs, Ti/Au were deposited as the gate electrodes through a shadow mask with a dot size of 6.4 × 10⁻⁵ cm² in area. Capacitance-voltage (C-V) and current density–electrical field (J-E) characteristic measurements were carried out utilizing Agilent 4284 and 4156C, respectively.

### III. RESULTS AND DISCUSSION

Figure 1(c) shows the HR-TEM image of the as-deposited RT-GGO/Ge stack, indicating that GGO is amorphous and the GGO/Ge interface exhibits an atomically sharp interface without the presence of an interfacial layer that is usually observed and/or needed for direct deposition of oxide on Ge. Note that a similar micrograph was also observed for HT-GGO on Ge.

For probing more detailed chemical bonding at the oxide/Ge interfaces for RT- and HT-GGO, the in situ AR-XPS was employed: Figs. 2(a) and 2(b) display the Ge 3d spectra at take-off angle of 0° from HT-GGO and RT-GGO, respectively. After deconvoluting the Ge 3d spectra in Fig. 2(a) for HT-GGO/Ge, a peak with a binding energy of ~32 eV, besides the one at a binding energy of ~30 eV for Ge, indicates the formation of Ge–O–Ga and Ge–O–Ga bonding, resulted from the Ge interdiffusion during the GGO deposition. This was observed and discussed previously. In comparison, Ge interdiffusion was very much minimized, if not completely suppressed (below the detection limit of XPS), for RT-GGO as no bump in addition to the Ge peak appeared, as shown in Fig. 2(b). Very importantly, however, there is no further Ge interdiffusion for the HT-GGO/Ge after postdeposition high-temperature annealing.

Figure 3 shows the XPS spectra of Ge 3d, Gd 3d, and Ga 2p for the RT-GGO on Ge with and without an in situ annealing at 500 °C for 30 min. Apparently, there is no change in and shift of all the peaks in the Ge 3d, Gd 3d, and Ga 2p spectra. The Ge 3d spectra were taken under different take-off angles, i.e., 0°, 45°, and 75°, to thoroughly study the possible Ge interdiffusion. The unchanged spectra indicated that the chemical characteristics of the RT-GGO/Ge interface remain the same. In other words, there is no Ge interdiffusion and the RT-GGO/Ge heterostructure is thermally stable, withstanding the 500 °C annealing. This interfacial behavior with respect to the thermal stability is similar to that of HT-GGO on Ge (Ref. 4) and is different from that of HfO₂ (Ref. 13) and Y₂O₃ (Ref. 14) on Ge, where Ge diffused into the gate dielectrics slightly after the high-temperature annealing.

Figure 4(a) shows the C-V characteristics from AuTi/RT-GGO/Ge MOSCAPs with a CF₄-plasma treatment for 3 min and a 500 °C annealing in N₂ for 5 min. Small frequency dispersion in accumulation region (~4.3%), sharp transition from inversion to depletion, and clear inversion behavior
corresponding to various measurement frequencies (10 kHz–1 MHz) have been achieved, suggesting the high-quality RT-GGO and RT-GGO/Ge interface. The dielectric constant of the GGO was calculated to be \(14.5\) from the maximum oxide capacitance, which is consistent with that in our previous work.\(^4,5\)

The gate \(J\)-\(E\) characteristics of the MOSCAPs with and without the CF\(_4\)-plasma treatment are shown in Fig. 4\(b\). The gate leakage current density of \(3.2 \times 10^{-9}\) A/cm\(^2\) at a flat-band voltage +1 V has been attained for the CF\(_4\)-treated sample. The improvement, as compared to the sample with only 500 °C N\(_2\) annealing, is probably due to the reduction in traps both in bulk dielectric and interface.

Interfacial density of states \(D_{it}\) is one important index to evaluate the quality of the oxide/semiconductor interface. To obtain the \(D_{it}\) value, a commonly used frequency-dependent conductance method was performed. The corresponding energy level (within the band gap) of each extracted \(D_{it}\) is correlated with an applied characteristic frequency according to the Fermi–Dirac statistic.\(^15\) In this work, the midgap energy for hole in \(n\)-Ge corresponds to a characteristic frequency of \(4 \times 10^4\) Hz.\(^15\) As shown in Fig. 5, the equivalent parallel conductance loss \((Gp/w)\) is plotted as a function of measurement frequencies. A \(D_{it}\) value of \(3.6 \times 10^{12}\) cm\(^{-2}\) eV\(^{-1}\) at midgap was then extracted by the equation,

\[
D_{it} = 2.5 \frac{(Gp/w)_{max}}{q},
\]

where \((Gp/w)_{max}\) and \(q\) are the peak conductance loss and electron charge, respectively.

To further study the influence of the Ge interdiffusion on the electrical characteristics, one HT-GGO sample received identical postdeposition treatments that were used for the aforementioned RT-GGO/Ge sample. Consequently, the HT-GGO/Ge sample showed a much higher \(D_{it}\) value of \(9 \times 10^{12}\) cm\(^{-2}\) eV\(^{-1}\) at midgap by conductance method. The determinant frequency \((4 \times 10^4\) Hz\) corresponds to an applied gate bias that indicates the weak inversion region in the \(C\)-\(V\) characteristics. Therefore, a more reasonable \(D_{it}\) value may be about one order of magnitude lower due to the weak

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**Fig. 3.** In situ XPS spectra of Ge 3\(d\), Gd 3\(d\), and Ga 2\(p\) for the as-deposited and postdeposition annealed RT-GGO.
inversion contribution. The overestimation has also been discussed in the previous work on high-$\kappa$/In$_{0.53}$Ga$_{0.47}$As, where the In$_{0.53}$Ga$_{0.47}$As has a small band gap as well.

More characterizations, including charge pumping measurement and quasi-static $C$-$V$ measurement, have been carried out on the RT-GGO/Ge samples for further understanding the heterointerface electrically, leading to better device performances.

IV. CONCLUSION

Without employing any interfacial layers, high-quality MBE-GGO directly deposited on Ge at room temperature along with the CF$_4$-plasma treatment exhibits excellent $C$-$V$ characteristics and very low gate leakage, comparing favorably to the state-of-the-art results. The GGO/Ge interface for the as-deposited and 500 °C annealed samples is atomically smooth and chemically sharp without Ge interdiffusion according to the XPS and HR-TEM studies, strongly indicating a robust heterostructure of high thermal stability.

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