Surface passivation of Ge(100) with $LaLuO_3$ for application in nanoelectronics

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Abstract

Lanthanum lutetium oxide ($LaLuO_3$) films, 6 and 12 nm-thick, were prepared on Ge(100) by molecular beam deposition and submitted to thermal annealing in N_2 or O_2. Electrical characterization revealed that such treatments can have beneficial effects on the characteristics of the dielectric layer. Nevertheless, $LaLuO_3$/Ge interface characteristics are modified depending on annealing parameters and mostly on the employed atmosphere. Electrical characterization was correlated with atomic transport and chemical bonding in the resulting structures, evidencing that oxygen annealing, in certain conditions, promotes substrate oxidation. A more stable interface without the formation of excessive Ge oxidized species was achieved using N_2.

Introduction

The continued downscaling of Si-based metal-oxide-semiconductor field-effect transistors (MOSFETs) using SiO_2 as a gate dielectric has reached fundamental limits. The required SiO_2 layer thicknesses (~1 nm) gives rise to unacceptable values of gate leakage current. To continue the scaling of Si-based MOSFETs, new materials of higher dielectric constant (high-*k*) replaced thermally grown SiO_2. Because new materials are being used in place of SiO_2, the dominant role played by Si as semiconductor material is being re-evaluated. Materials of higher intrinsic carrier mobility such as Ge could be used to build faster devices. However, one must find an adequate gate insulator material that forms an interface with Ge with a sufficiently low density of active interface defects. The dielectric/Ge structure must also withstand the transistor fabrication process, which involves temperatures above 400°C.

A number of Ge passivation routes have been investigated, such as surface treatments before high-*k* deposition and formation of interlayers between Ge and the gate insulator.[1] The latter strategy consists of creating a layer that efficiently passivates the Ge surface and isolates it from the deposited high-*k* dielectric. These interlayers can be (i) thermally grown GeO_2 or GeO_xN_y or (ii) rare-earth oxides (for example, La_2O_3), which interact with the substrate forming germanates.[2]

In the present work, we investigate the passivation properties of lanthanum lutetium oxide ($LaLuO_3$) deposited on Ge. This dielectric material is a promising candidate for high-*k* applications. $LaLuO_3$ thin films deposited on Si presented thermal stability up to 1000°C. Electrical characterization revealed good capacitance-voltage (C-V) behavior, low leakage current density, and *k* value of ~32.[3] This ternary rare-earth oxide may interact with Ge forming an interlayer, resulting in a dielectric/Ge structure with a low density of interface states (D_{it}). However, the formation of a germanate at the dielectric/Ge interface can also result in a film of low dielectric constant and a rather high leakage current, as observed for La_2O_3 deposited on Ge.[2] Aiming at obtaining a dielectric layer with simultaneously good bulk and interfacial properties, $LaLuO_3$/Ge structures underwent different postdeposition annealings (PDAs). The electrical characteristics of the resulting samples were correlated with physicochemical modifications.

p-Type epi-ready Ge(100) doped with Ga wafers (Umicore) with a resistivity of 0.24 - 0.47 Ω cm were first cleaned in a mixture of acetone and propanol. They were then etched in a 2% HF aqueous solution for 4 min. After rinsing the samples in deionized water for another 4 min, they were immediately loaded in the deposition chamber. The remanent oxidized Ge was sublimed by sample heating at 450°C under ultrahigh vacuum conditions for several minutes. $LaLuO_3$ films (6 and 12 nm-thick) were deposited by molecular beam deposition using a conventional chamber with a controlled admission of oxygen for oxide growth. Samples were kept at 300°C during deposition. Thermal processing was performed in a resistively heated quartz tube furnace under a static pressure of 150 mbar of either N_2 (<1 ppm of H_2O) or O_2 enriched to 97% in the isotope of mass 18 (termed $^{18}O_2$) at 300 or 400°C. For electrical characterization of the formed structures, Pt top contacts were deposited by electron-beam evaporation through a shadow mask, followed by a forming gas anneal at 300°C for 10 min. C-V and conductance–voltage curves were measured using an impedance analyzer (HP 4192A). D_{it} was extracted according to Terman's method and by considering the peak conductance.[4] The EOTs of the films were determined by fitting the experimental C-V curves with a Hauser fit,[5] taking into account quantum-mechanical corrections. The depth distribution of ^{18}O in the annealed samples was determined by nuclear reaction profiling (NRP) using the resonance at 151 keV in the cross-section curve of the $^{18}O(p,\alpha)^{15}N$ nuclear reaction.[6] X-ray photoelectron spectroscopy (XPS) was performed in an Omicron SPHERA station using Al Kα radiation.

Figure 1 shows electrical characterstics of the $LaLuO_3$/Ge structures before and after different thermal treatments. All samples were prepared by deposition of a 12 nm-thick oxide film. The as-deposited layer revealed C-V curves without humps or irregularities (Fig. 1a), relatively low D_{it} levels around 6×10^{11} eV^{-1} cm^{-2} (Fig. 1b), and a high EOT (~3.3 nm). To improve the electrical characteristics of the dielectric film, different PDAs were performed. In the present work, PDAs were performed in N_2 or $^{18}O_2$ atmospheres at 300 or 400°C for 10 or 30 min. EOT values of the resulting samples decreased in all cases. For samples treated in $^{18}O_2$, the harsher the annealing conditions (higher temperature and longer time), the lower the EOT. The best EOT value was obtained for the sample annealed in N_2. However, PDA led to stretch-out of the C-V curve at the depletion region (Fig. 1a), which is an indication of a higher D_{it}. Indeed, as shown in Fig. 1b, the treatments in $^{18}O_2$ resulted in higher D_{it} values compared with the sample treated in N_2 and even with the as-deposited one, which indicates that oxygen is triggering unwanted modifications in the dielectric film.

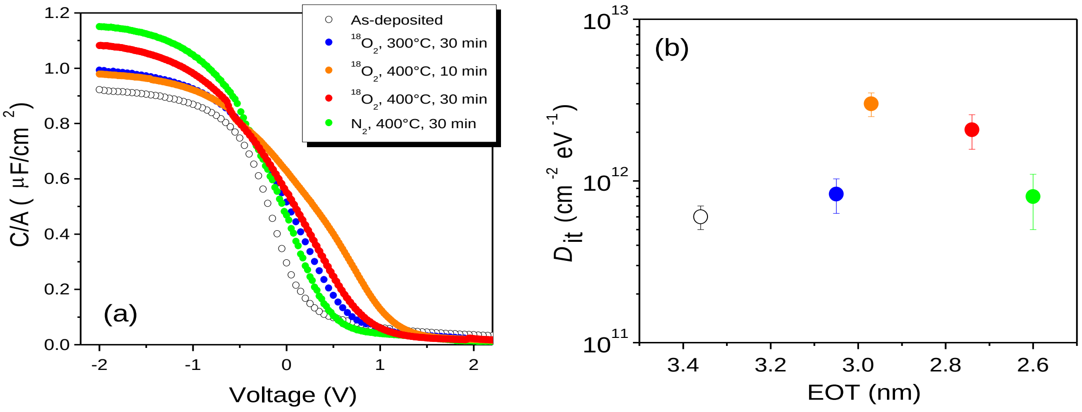

Figure 1. (a) C-V curves at 100 kHz for as-deposited and annealed $LaLuO_3$ films on Ge. Figure 1. (b) D_{it} values obtained from the peak conductance plotted as a function of the EOT of the $LaLuO_3$ films before and after different PDAs. D_{it} levels determined by Terman's method (not shown) reveal similar values.

Aiming at identifying the role played by the oxygen atmosphere on the properties of the dielectric/semiconductor structure, we performed ^{18}O depth profiling. Because we employed an isotopically enriched gas, we were able to distinguish oxygen originally present in the dielectric layer from that incorporated after PDA. Comparing the excitation curves (Fig. 2), one can observe that higher amounts of ^{18}O are incorporated as temperature and time of the annealing are raised. Harsher annealing conditions also result in deeper regions reached by ^{18}O, indicating that oxygen from the gas phase interacts with the semiconductor substrate at least for samples oxidized at 400°C for 30 min. This fact could explain the high D_{it} values obtained from these structures, which are probably a result of substrate oxidation. Counterpart samples were prepared on Si to infer about the influence of the substrate material in ^{18}O incorporation. ^{18}O profiles of these samples were similar to their Ge counterparts, evidencing that most part of ^{18}O incorporation results from its interaction with the $LaLuO_3$ matrix. ^{18}O profiles of Ge samples are slightly wider than their Si counterparts, which is probably a result of the higher reactivity of Ge with incoming oxygen.

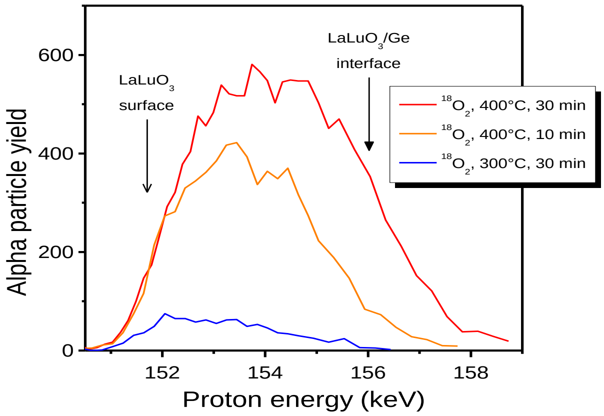

Figure 2. Excitation curves for the $^{18}O(p,\alpha)^{15}N$ nuclear reaction in $LaLuO_3$/Ge structures after different PDAs in $^{18}O_2$. The surface and $LaLuO_3$/Ge interface positions are indicated.

The formation of oxidized Ge has a strong impact on the electrical characteristics of the final structure. XPS analysis was performed to identify chemical modifications at the dielectric/semiconductor interface. To probe this interfacial region, thinner $LaLuO_3$ films (6 nm-thick) were deposited. Figure 3 shows O 1s and Ge 3p regions of the XPS spectra for the as-deposited and annealed samples. The as-deposited sample presents a Ge 3p signal with two peaks characteristic of bulk Ge. After PDA, a signal component at higher binding energy (BE = 123.1 eV) is observed, indicating that Ge is oxidized. Comparing the spectra of the sample annealed in $^{18}O_2$ with that annealed in N_2, higher amounts of oxidized Ge are observed in the former. Because higher D_{it} values were obtained for samples annealed in $^{18}O_2$, the formation of such compounds could be considered detrimental to interfacial characteristics.

The sample annealed in N_2 presented D_{it} comparable to that of the as-deposited sample despite the occurrence of a component at high BE in the Ge 3p signal. This result indicates that besides the formation of $LaGeO_x$,[8] which was shown to be beneficial to interfacial characteristics, other Ge oxidized species are formed during annealing in O_2. The formation of volatile GeO (Ref. 14) resulting from Ge oxidation is a probable explanation for this observation and for the detrimental electrical effects of PDAs performed in O_2. O 1s spectra corroborate this scenario. The signal from the as-deposited sample has two contributions: (i) at 529.1 eV related to oxygen in LaLuO3 and (ii) at 531.3 eV related to carbonate and hydroxide species.[8] The relative intensity of the $LaLuO_3$ component rises after PDAs, indicating a reduction of hydroxide-related surface contamination and of carbonate species incorporated in the film, simultaneously with a reduction in the amorphous character of the annealed films.[8] Similar results were observed for $LaLuO_3$ films deposited on Si substrates.[9] Such modifications are likely to have an effect on the electrical characteristics of the final structure, as evidenced by the EOT values in Fig. 1. Another contribution at a higher BE (~532.3 eV) is also observed for annealed samples, related to oxygen bonded to Ge. This component is most intense for the sample annealed in oxygen, evidencing that Ge oxidation is triggered by such annealing.

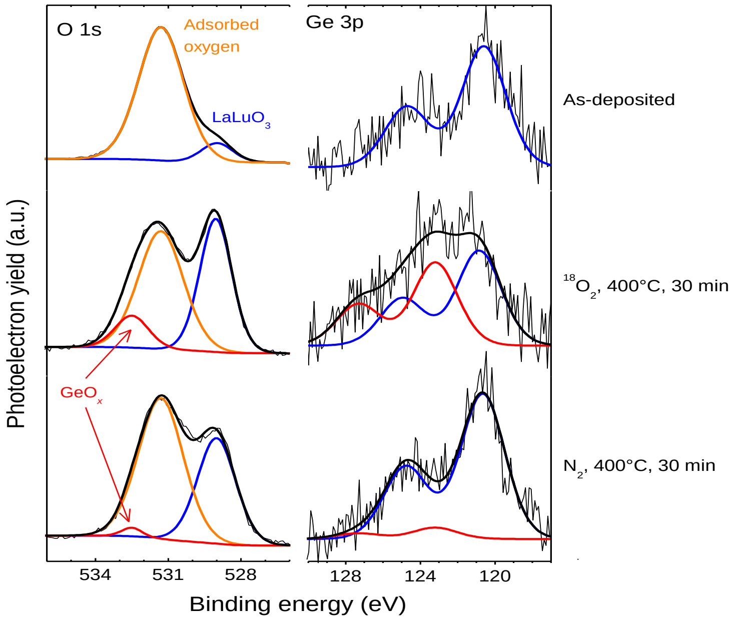

Figure 3. O 1s and Ge 3p regions of XPS spectra corresponding to $LaLuO_3$/Ge structures as deposited (top) and submitted to annealing as shown. The energy position of the components used in the fitting procedure of both regions is indicated; a.u. stands for arbitrary units.

In summary, $LaLuO_3$ films deposited on Ge substrates underwent different PDAs. Depending on the parameters (time and temperature) and mostly on the annealing atmosphere, different electrical characteristics of the resulting MOS structure are obtained. Annealing in oxygen results in Ge substrate oxidation, degrading interfacial characteristics. Annealing in N_2 was more beneficial because it promotes the formation of interfacial compounds responsible for substrate passivation ($LaGeO_x$) without the formation of oxidized Ge species responsible for electrical degradation.

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