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Electrical properties of epitaxial Lu- or Y-doped La_2O_3/La_2O_3/Ge high-k gate-stacks

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ABSTRACT

Electrical properties of epitaxial La_2O_3/germanium (Ge) structures can be significantly improved by using epitaxially grown Lutetium(Lu)- or Yttrium(Y)-doped La_2O_3 passivation layers. For the metal-insulator-semiconductor (MIS) devices, hysteretic nature of capacitance-voltage (C-V) characteristics becomes negligibly small and the interface trap density (D_{it}) is estimated to be less than 10^{12} cm^{-2} eV^{-1} at around the midgap. We discuss a possible mechanism of the improvement of the electrical properties.

1. Introduction

Because of an intrinsic limit of the technologies for complementary metal-oxide-semiconductor (CMOS) transistors, the use of new channel materials has been explored. Germanium (Ge) is promising for a next generation channel material in future CMOS technologies because of relatively high electron and hole mobility compared to Si [1]. From a viewpoint of high-k gate insulators for high-performance Ge metal-insulator-semiconductor field-effect-transistors (MISFETs), a direct contact between a high-k gate insulator and Ge is desirable for reducing the equivalent oxide thickness (EOT). However, since lots of traps generally occur at the interfaces between high-k and Ge, many groups have mainly inserted some interfacial layers such as GeO_2 to reduce the interfacial traps [2–8].

Among the candidate materials as a high-k gate insulator, lanthanum oxide (La_2O_3) is focused from the viewpoint of its high dielectric constant (k~30) and large band gap (~6 eV) [9]. To utilize La_2O_3 as the high-k gate insulator, there are some issues including its hygroscopic nature [10,11] and a large interface state density at the La_2O_3/Ge interface. To overcome hygroscopic nature, stacked structures or capping layers have been reported [12–21]. To reduce an interface state density, La_xGe_yO interfacial layers that were formed by La_2O_3/Ge intermixing have been explored [18–21]. However, the permittivity (k) of the La_xGe_yO interfacial layers is 8–9 and these values are close to that of GeO_2 (k~6–7) [22,23]. That is, one needs to improve the permittivity as a high-k insulator.

Recently, we have demonstrated the epitaxial growth of a high-quality La_2O_3 layer on Ge(111) as a high-k gate insulator, where there is an atomic-arrangement matching condition between La_2O_3(100) and Ge(111) [24]. Even without inserting an interfacial layer, reasonable capacitance-voltage (C-V) characteristics were obtained in Au/La_2O_3/Ge MIS structures after post-metallization annealing (PMA). Also, relatively low interface state density of ~10^{12} cm^{-2} eV^{-1} was estimated from the conductance method [25]. However, there was counter-clockwise hysteresis in the C-V curves of the Au/La_2O_3/Ge MIS structures [24]. In general, the imperfections and/or boarder traps near the interface between La_2O_3 and Ge should be taken into account. Since it seems that the C-V hysteresis is hardly related to the interface state density [18,20,21], the origin of the C-V hysteresis in the Au/La_2O_3/Ge MIS structures remains to be clarified. In general, it is important to control a moisture absorption in La_2O_3 [11,26]. Here we focused on Lu- or Y-doped La_2O_3 layers, because it is reported that the moisture absorption of La_2O_3 can be suppressed by Lu- and Y-doping [12,27].

In this paper, we demonstrate significant improvements of electrical properties of epitaxial La_2O_3/Ge structures by using the epitaxial Lu- or Y-doped La_2O_3 passivation layer. This structure has advantages that crystalline materials are expected to show a high-k value. Hysteretic nature of C-V characteristics in the MIS structures becomes negligibly small and relatively low interface trap density (D_{it}) less than 10^{12} cm^{-2} eV^{-1} can be achieved at around the midgap. The origin of the improvement can be interpreted by the fact that suppresses moisture absorption from air.

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2. Experimental details

La_2O_3 and Lu- or Y-doped La_2O_3 layers were successively grown by pulsed laser deposition (PLD) on p-Ge(111) substrates at 350 °C, where an energy density is about 1 J/cm^2 and repetition rate is 1 Hz. The targets used were stoichiometric La_2O_3, stoichiometric $LaLuO_3$ and $La_{1.8}Y_{0.2}O_3$ ceramics. A typical film thickness of La_2O_3 is ~10 nm, and that of Lu- or Y-doped La_2O_3 is ~10 nm. Prior to the growth, Ge native oxides were removed from the Ge surface by dipping in an HF (1%) solution and an HCl (10%) solution, followed by rinsing the surface in deionized water. The Ge substrates were also dipped in an $(NH_4)_2S$ solution to passivate the Ge surfaces. After the deposition, some samples were annealed in N_2 for 30 min. For electrical measurements, Au top and Al bottom electrodes were formed by thermal evaporation. Crystallinity of the grown layers was characterized by X-ray diffractometer (XRD) (Rigaku, RINT-2000) and scanning transmission electron microscopy (STEM). *C-V* and current density-voltage (*J-V*) characteristics were measured by 1 MHz C-V plotter (HP4280A), impedance analyzer (Agilent 4294A), and semiconductor parameter analyzer (HP4155C). Interface state density (D_{it}) was evaluated by the constant-temperature deep level transient spectroscopy (DLTS) using a SEMILAB DLS83D system with a lock-in integrator, where the slow trap influence was eliminated at all temperature for p-Ge-MIS structures [6,28]. The interface between La_2O_3 and Ge was characterized from the measurement of Ge *3d* photoelectron spectra excited by monochromatic Al Kα radiation by using a high-resolution X-ray photoelectron spectroscopy (XPS) equipment (Scienta Instruments AB, ESCA-300) and Ge *2p* photoelectron spectra excited by synchrotron radiation in SPring-8.

Chemical bonding states of lanthanum (La) were examined from oxygen (O) *1s* photoelectron spectra excited by monochromatic Al Kα radiation by using a XPS equipment (SURFACE SCIENCE INSTRUMENTS, SSX-100). Before these XPS measurements, the Lu- or Y-doped La_2O_3 and La_2O_3 surfaces were thinned by Ar^+ sputtering.

3. Results and discussions

3.1. Crystal growth of La_2O_3 and doped La_2O_3

We preliminarily investigated the growth temperature dependence of the crystallinity of Lu-doped La_2O_3 and Y-doped La_2O_3 layers on Ge(111). The XRD patterns (θ-2θ scan) of the Lu-doped La_2O_3 layer grown at around 350 °C showed the same peaks as La_2O_3(002) and (004) [24]. For Y-doped La_2O_3, the same features were also seen for the growth at 290–350 °C. Thus, (001)-oriented Lu- or Y-doped La_2O_3 layers were grown directly on Ge(111) at ~350 °C. However, in comparison with the La_2O_3 layer grown on Ge(111), process margin for the doped La_2O_3 layers was small. Also, the peak intensities were relatively small and an unknown peak at around 21.8° was seen in the case of Y-doped La_2O_3. Therefore, La_2O_3 is suitable for the formation of the heterointerface on Ge(111). In previous report [29,30], heteroepitaxy of single-crystal $LaYO_3$ and $LaLuO_3$ on GaAs(111)A by atomic layer deposition has been reported, showing relatively low interface state density. However, their capacitors were subjected to high-temperature rapid thermal annealing (RTA) such as 700 and 800 °C for electrical characterizations. In the case of La_2O_3/Ge MIS structures, such high temperature annealing causes an interfacial reaction at the interface and/or degradation of interface structure. From these considerations, Lu- or Y-doped La_2O_3/La_2O_3/Ge(111) structures grown at 350 °C in vacuum were also examined. As a result, only La_2O_3(00*l*) (*l*=2, 3, and 4) peaks in XRD θ-2θ scan were observed in both cases, as shown in Fig. 1. This indicates that the doped La_2O_3 layers are not polycrystalline. Based on the results that the doped La_2O_3 on Ge(111) was crystallized at 350 °C, these stacked layers should also be crystallized on the La_2O_3 layer. Because we can infer that the Lu- or Y-doped La_2O_3 layers are epitaxially grown on La_2O_3/Ge(111), we hereafter

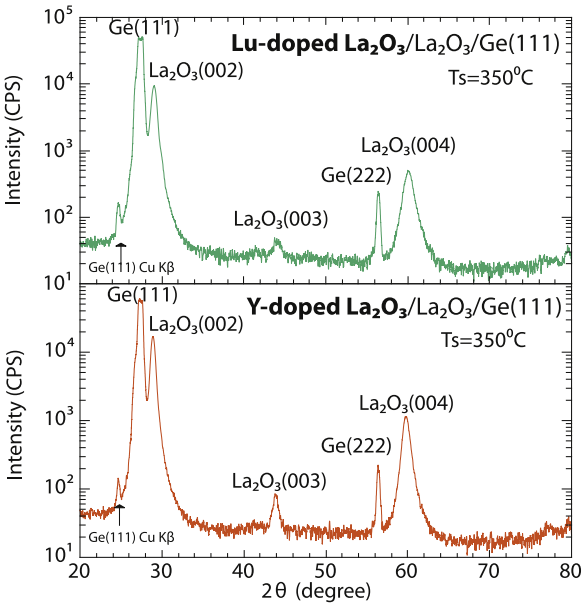

Fig. 1. XRD patterns of Lu-doped La_2O_3/La_2O_3/Ge(111) and Y-doped La_2O_3/La_2O_3/Ge(111) grown at 350 °C.

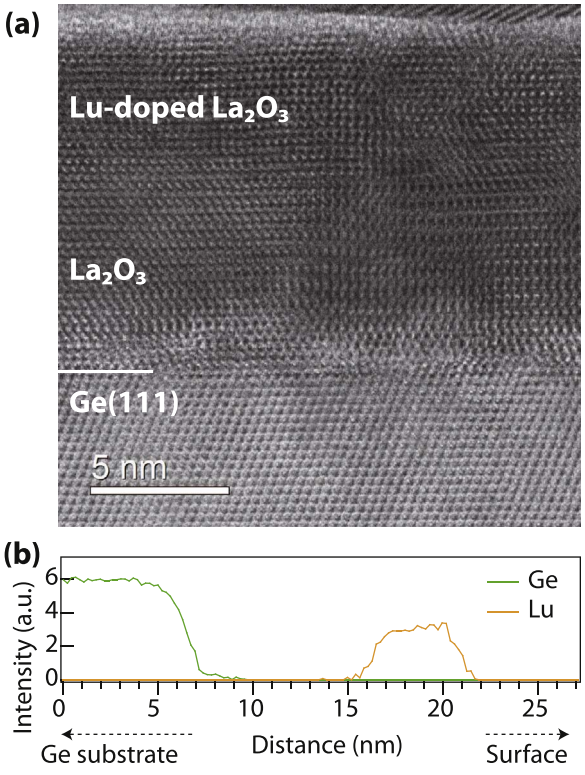

Fig. 2. (a) Cross-sectional STEM image of Lu-doped La_2O_3/La_2O_3/Ge(111), and (b) STEM-EELS line profiles of Ge and Lu atoms.

focus on the Lu- or Y-doped La_2O_3/La_2O_3/Ge layers for crystalline gate-stack structures in Ge-MISFETs.

Fig. 2 shows a cross-sectional STEM image of the Lu-doped La_2O_3/La_2O_3/Ge(111) grown at 350 °C in vacuum and (b)STEM-electron energy loss spectroscopy (EELS) line profiles of Ge and Lu atoms. As shown in our previous work [24], the single-domain crystalline layer and the high-quality heterointerface between La_2O_3 and Ge(111) are observed. As expected, the interface between Lu-doped La_2O_3 and La_2O_3 is not clear and is a continuous structure, meaning that the crystal structure of the Lu-doped La_2O_3 layer is the same as that of