# Improvement of Interface Properties of Ge-MISFET with Crystalline La<sub>2</sub>O<sub>3</sub> high-k/Ge(111) Gate Stacks by Wet Treatments

Takeshi Kanashima, Hitohisa Furusho, Kyoichi Takayama, Hiroshi Nohira\*, Keisuke Yamamoto\*\*, Hiroshi Nakashima\*\*\*

Graduate school of Engineering Science, Osaka University, 1-3 Machkaneyama, Toyonaka, Osaka 560-8531, Japan \*Tokyo City University, 1-28-1 Tamazutumi, Setagaya-ku, Tokyo 158-8557, Japan

\*\*Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, Kasuga-koen, kasuga 816-8580, Japan

\*\*\*Global Innovation Center (GIC), Kyushu University, 6-1 Kasuga-koen, kasuga 816-8580, Japan

E-mail: kanashima@ee.es.osaka-u.ac.jp

## Abstract

We have demonstrated that the interface state density between epitaxially grown high-k La<sub>2</sub>O<sub>3</sub> gate insulator and germanium (Ge) without any passivation layers can be reduced by dipping Ge substrates into the I<sub>2</sub> solution of low concentration before the growth. This treatment shows enough stability for the preparation of Ge-MISFETs by using Lu-doped La<sub>2</sub>O<sub>3</sub>/La<sub>2</sub>O<sub>3</sub>/Ge stacked structure, and their electrical properties such as the sub-threshold swing which relates to the interface state density are improved in comparison with the conventional sulfur treatment.

# 1. Introduction

Germanium (Ge) has been considered as the promising candidate channel material because of its high electron and highest hole mobility, and the gate stack between high-*k* and Ge without any low permittivity interfacial layer is desirable for future miniaturization. We have demonstrated low interface defects between the crystalline La<sub>2</sub>O<sub>3</sub> high-*k* gate insulator and Ge(111) by using the atomic-arrangement matching condition at a low growth temperature [Figs. 1(a) and (b)] [1]. Moreover, we have achieved a significant reduction of *C-V* hysteresis width by using crystalline Lu-doped La<sub>2</sub>O<sub>3</sub> capping layers [Fig. 1(c)], and the sufficient stability have been achieved for the preparation of Ge-MISFETs [2]. However, a surface state and roughness much affect their interface properties [Figs. 1(d) and (e)], and the interface state density (*D*<sub>it</sub>) is ~10<sup>12</sup> cm<sup>-2</sup>eV<sup>-1</sup>.

Fluorine or sulfur treatment methods are reported to improve the interface property [3, 4]. Moreover, the passivation of Ge substrates with hydrogen halide solutions is also reported and the passivation robustness for growth of native oxide increases from HF, HCl, HBr to HI [5]. However, passivation effects on the interface of the epitaxially grown high-k on Ge are rarely reported unlike gate stacks with the interfacial layer such as GeO<sub>2</sub>.

In this report, passivation effects on Ge surfaces before the growth of crystalline  $La_2O_3$  are characterized by using several wet treatments from a viewpoint of reduction of the  $D_{it}$ .

## 2. Experimental

 $La_2O_3$  and Lu-doped  $La_2O_3$  capping layers were grown by pulsed laser deposition (PLD) successively on a p-Ge(111) substrate at 350°C in a vacuum chamber where an energy density is about 1 J/cm<sup>2</sup> at 1 Hz. Typical film thickness is about 8 nm in each layer. Native oxides were removed from the Ge surface by dipping in a HF (1%) solution and a HCl (12%) solution, followed by rinsing the surface in deionized water (DIW). The surface wet treatments were done by dipping the Ge substrates in (NH<sub>4</sub>)<sub>2</sub>S<sub>x</sub> (5–8 % S), I<sub>2</sub> (0.5 or 0.005 mol/L) and H<sub>2</sub>O:H<sub>2</sub>O<sub>2</sub>:NH<sub>4</sub>OH (dilute SC-1) solutions for 3 to 20 min. The interface state densities were evaluated by the conductance method measured at room temperature [6,7]. Many top electrodes were formed on a substrate (about 5 x 10 mm rectangular) and several randomly selected points were measured in the case of MIS samples.

The Ge-MISFETs with the crystalline  $La_2O_3$  gate stacks were prepared. The source and drain (S/D) regions were formed by thermal diffusion of phosphorus (P) from a solid diffusion source [8,9]. After the S/D formation, the crystalline  $La_2O_3$  and Lu-doped  $La_2O_3$  layers were grown at 350°C. Au and AuSb thin films as the gate and S/D contact electrodes were formed by thermal evaporation and were patterned.

#### 3. Results and Discussion

Figure 2 shows the  $D_{it}$  under the flat band condition of the Au/Lu-doped La<sub>2</sub>O<sub>3</sub>/La<sub>2</sub>O<sub>3</sub>/Ge MIS structure treated in the various solutions. The  $D_{it}$  of the samples dipped in I<sub>2</sub> solution is ~5x10<sup>11</sup> cm<sup>-2</sup>eV<sup>-1</sup> and is almost half of the conventional sulfur treatment. Moreover, the treatment by 0.005 mol/L I<sub>2</sub> solution (low iodine concentration) is better than that by 0.5 mol/L (high iodine concentration), since scattering is seen in the latter. A similar tendency is observed in the *J*-*V* characteristics, and the leakage current at  $V_g = -1.0$  V of the sample treated by the solution of low iodine concentration is less than  $10^{-6}$  A/cm<sup>2</sup>.

It is well known that Ge can be etched by dipping into oxidant solutions, and we observed the surface roughness of the Ge substrate before and after treatments by AFM. These results show that the RMS roughness of the sample treated in the low iodine concentration is smaller than that in the high iodine concentration or the conventional sulfur treatment. Moreover, Fig. 3 shows the I *3d* XPS spectra of the Ge substrate treated by the I<sub>2</sub> solution. Iodine peaks are clearly observed and this indicates that iodine remains on the surface. From these results, the reduction of  $D_{it}$  is induced by a small surface roughness and iodine termination.



Fig.1 Atomic arrangements of (a)  $La_2O_3(001)$ , (111) and (110), and (b) Ge(111). Red, blue and green circles indicate O, La and Ge atoms, respectively. (c) HR-TEM image of Lu-doped  $La_2O_3/La_2O_3/Ge$ , and the models of (d) its interface and (e) interface imperfection [1,2].



Fig.2  $D_{it}$  of the Au/Lu-doped La<sub>2</sub>O<sub>3</sub>/La<sub>2</sub>O<sub>3</sub>/Ge MIS structure treated by the various solutions.

Figures 4(a) and (b) show the  $I_s$ - $V_d$  and  $I_d$ ,  $I_{sub}$ ,  $I_s$ - $V_g$  characteristics of the Ge-MISFET treated by the I<sub>2</sub> solution of low concentration. Reasonable electrical properties are obtained, and the value of sub-threshold swing (SS) of 128 mV/dec is smaller than that of the conventional sulfur treatment of 156 mV/dec. This indicates that the I<sub>2</sub> treatment is effective for the improvement of interface properties.

#### 4. Summary

Low  $D_{it}$  of ~5x10<sup>11</sup> cm<sup>-2</sup>eV<sup>-1</sup> was obtained when Ge substrates were dipped into the I<sub>2</sub> solution of 0.005 mol/L before crystalline La<sub>2</sub>O<sub>3</sub> growth in comparison with the conventional sulfur treatment. The AFM and XPS measurements revealed that their improvements were caused by the reduction of surface roughness and iodine termination on the Ge surfaces. Moreover, enough stability was shown and improved Ge-MISFET properties were obtained by using this method.

#### Acknowledgments

The authors would like to thank Prof. K. Hamaya and S. Yamada of Osaka University for useful discussions and comments, and Prof. F. Wakaya of Osaka University for AFM measurements. Part of this research was supported by the Tokyo City University Nanotechnology Research Center. This work was partly supported by JSPS KAKENHI Grant Number 18K04235.

#### References

- [1] T. Kanashima et al., J. Appl. Phys. 118, 225302 (2015).
- [2] T. Kanashima et al., Mater. Sci. Semicond. Process 70, 260



Fig.3 I 3d XPS spectra of the Ge substrate treated by the I<sub>2</sub> solution (0.005 mol/L).



Fig.4 (a)  $I_{\rm s}$ - $V_{\rm d}$  and (b)  $I_{\rm d}$ ,  $I_{\rm sub}$ ,  $I_{\rm s}$ - $V_{\rm g}$  characteristics of the Ge-MISFET treated by the I<sub>2</sub> solution (0.005 mol/L).

(2017).

- [3] K. Kasahara et al., Appl. Phys. Lett. 104, 172109 (2014).
- [4] D.-H. Lee et al., Jpn. J. Appl. Phys. 51, 04DA06 (2012).
- [5] J. Kim, Germanium Surface Preparation Methods, VDM Verlag Dr. Muller, 2008.
- [6] Y. Fukuda et al., IEEE Trans. Electron. Dev. 54, 2878 (2007).
- [7] Y. Fukuda et al., Jpn. J. Appl. Phys. 44, 7928 (2005).
- [8] K. Yamamoto et al., Thin Solid Films 520, 3382 (2012).
- [9] K. Yamamoto et al., Appl. Phys. Express 4, 051301 (2011).