

Validity of direct-gap photoluminescence analysis for non-destructive characterization of oxide/germanium interface

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Abstract

We have demonstrated the validity of direct-gap photoluminescence analysis for non-destructive method to evaluate the interface electrical properties at gate dielectric films/Ge without making actual devices nor environmental control.

1. Introduction

Germanium (Ge) recently attracts a great attention as a promising alternative of Si as the MOSFET channel material. The performance of Ge MOSFETs has been dramatically improved by achieving good oxide/Ge interfaces [1]. For further improvement, simple and non-destructive characterization techniques probing Ge interfaces are mandatory. Since photoluminescence (PL) certainly includes defect density both at the surface and in the bulk of semiconductors [2], it seems to be useful for the interface characterization. However, only a few studies oxide/Si or III-V semiconductor interface with PL measurement have been reported [3, 4]. Concerning GeO_x/Ge interface, Hashemi et al., reported PL characterization on Ge nanowires in terms of the surface passivation [5]. Then, the objective of this work is to show that PL analysis is quite useful for Ge gate stack characterization without making actual devices.

Possible recombination processes at oxide/Ge interfaces are summarized in **Fig. 1** [5]. In the low D_{it} sample, both direct and phonon-mediated indirect gap recombination processes contribute to the spontaneous photo-emission, resulting that PL intensity should be high. On the other hand, in the high- D_{it} samples, electrons in the L-valley are recombined in a non-radiative way (the Shockley-Read-Hall type recombination) through the interface gap-states. In addition, Γ electrons are also reduced due to the fast relaxation process to L-valley, which is much faster than the recombination [6]. As a result, the PL intensity becomes much lower than that in the low- D_{it} case. In this way, PL intensity is expected to be a good indicator to evaluate the oxide/Ge interface quality.

2. Experimental Method

The experimental procedure in this work is summarized in **Fig. 2**. 30-nm-thick Y_2O_3 or HfO_2 film was deposited on HF-last p-Ge (111) substrates by rf-sputtering. Then, the samples were annealed in O_2 at 550°C from 1 to 20 min. GeO_2/Ge sample was also prepared in the same condition. The PL measurement at room temperature was carried out through oxides on Ge. Continuous wave diode-pumped solid-state laser (second harmonic Nd:YVO₄ laser) with $\lambda=457$ nm and

40 μm dia. on each sample was used as the excitation laser. The photon penetration depth into Ge is around 17 nm, according to the reported absorption data [7]. The laser power dependence was checked to exclude the thermal effect, and 4 mW was used in this work. Meanwhile, to estimate electric characteristics at Ge/oxide interfaces, MIS capacitors were fabricated, in which Al were deposited for both gate electrode and back ohmic contact.

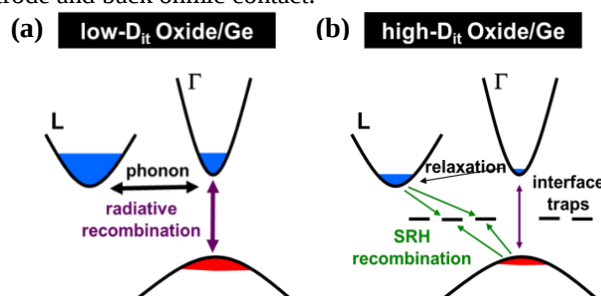


Fig. 1 Schematic images of recombination processes in the oxide/Ge interface with (a) low- D_{it} and (b) high- D_{it} cases. PL intensity is expected to be strongly related to the D_{it} . The same picture was discussed for Ge in ref. [5].

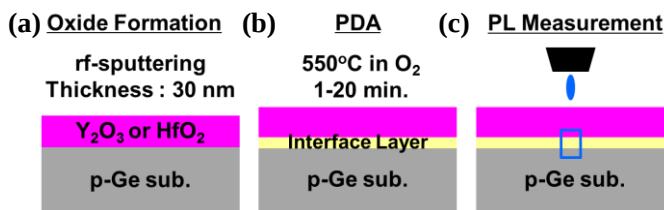


Fig. 2 Schematic images of experimental procedure in this work. (a) Y_2O_3 or HfO_2 film was deposited by rf-sputtering, followed by (b) O_2 -PDA at 550°C . Then, (c) PL measurement through the oxide was carried out.

3. Results and Discussion

Fig. 3 shows PL spectra from three kinds of oxide/Ge samples. In all samples, a peak around 0.8 eV and a kink around 0.7 eV are observed. Each of them is attributable to the direct-gap and phonon-mediated indirect-gap radiative recombination, respectively, by considering electronic structure of Ge. Here, it is noted that the direct-gap radiative recombination is clearly observable in Ge, which is significantly different from Si. It is thanks to the “quasi-direct gap nature” of Ge, which is the key point for the fact that we can use the direct-gap PL intensity for Ge gate stack analysis.

Fig. 3 shows that PL intensities of both direct- and indirect-gap emission are significantly different from each other. Since all of oxide films in this experiment are transparent for the excitation laser and the same Ge substrate were employed, PL intensity difference should provide the information of oxide/Ge interface.

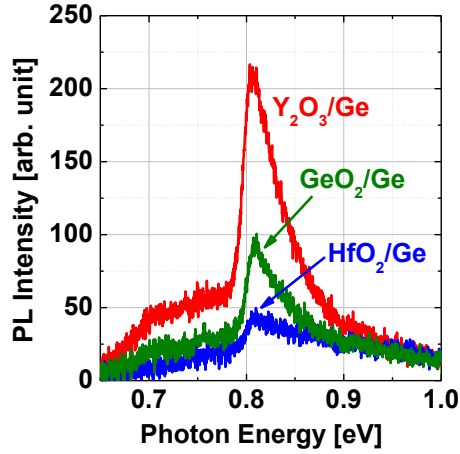


Fig. 3 PL spectra from three kinds of oxide/Ge samples. PL intensity is dependent on the oxide on Ge, while the peak position is not sensitive to the oxide.

Fig. 4 shows the O₂-PDA time dependence of the peak intensity in the direct-gap recombination for three kinds of oxide/Ge samples. Three characteristic features are pointed out.

- (1) PL peak intensity is significantly high in Y₂O₃/Ge, while it is reduced in HfO₂/Ge than in GeO₂/Ge.
- (2) PL signals from three samples saturate at a very early stage in O₂-PDA.
- (3) GeO_x can passivate Ge surface to a certain extent even in the air.

These facts clearly indicate that non-radiative recombination centers at the interfaces are well-passivated by intermixing of Y₂O₃ with GeO₂ in O₂-PDA, while they are newly generated in case of HfO₂ with GeO₂. The saturation of PL intensity suggests that the interface defects are saturated at the initial stage of O₂-PDA [8]. As a matter of fact, the results are quite reasonable from the viewpoint of electrical characteristics so far investigated in our group [1, 8, 9]. Thus, it is strongly suggested that the direct-gap PL intensity is a good indicator probing the oxide/Ge interface characteristics.

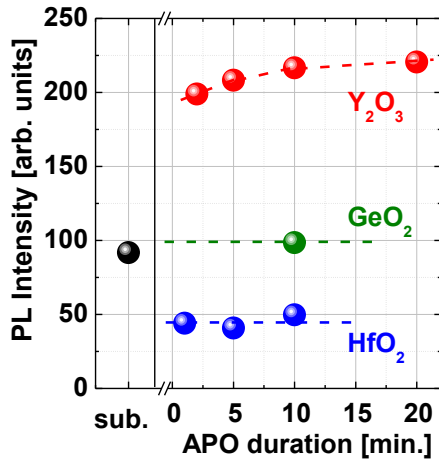


Fig. 4 PL peak intensity of the direct-gap radiative recombination as a function of O₂-PDA time. PL of as-received Ge is also shown for the reference.

Finally, C-V characteristics of Y₂O₃/ and HfO₂/Ge samples used for the present PL measurement are discussed. **Fig. 5 (a)** shows that well-controlled C-V characteristics are obtained in Al/Y₂O₃/Ge stack in O₂-PDA. Meanwhile, **Fig. 5 (b)** shows that C-V curves in Al/HfO₂/Ge stack are not controlled, which indicates a huge amount of D_{it} at the interface. HfO₂ is likely to form the Hf-Ge metallic bond at HfO₂/Ge interface, and the gap states [9]. This fact is also pointed out theoretically [10]. Thus, the PL intensity reduction in HfO₂/Ge stack is attributable to the increase of non-radiative recombination through the interface defects generated by Hf-Ge metallic bond formation.

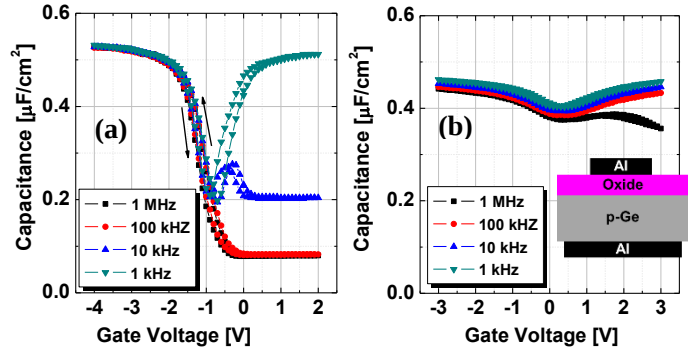


Fig. 5 Bi-directional C-V characteristics of the fabricated (a) Al/Y₂O₃/p-Ge and (b) Al/HfO₂/p-Ge MISCAPs, measured at room temperature. In both samples, O₂-PDA was performed at 550°C for 10 min. The inset in (b) shows the schematic image of the MISCAP.

4. Conclusion

The simple and non-destructive characterization method of the oxide/Ge interface by PL measurement through the oxide was proposed and its validity was confirmed experimentally. The direct-gap PL intensity is a good indicator for estimating the oxide/Ge interface quality, thanks to the “quasi-direct gap nature” of Ge. It is quite different from Si case, in which the direct gap is far from the indirect-gap.

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References

- [1] C. H. Lee et al., IEDM Tech. Dig., (2013) pp. 40-43.
- [2] T. Konishi et al., Jpn. J. Appl. Phys. **31** (1992) L1216.
- [3] J. G. Kim et al., ECS Solid State Lett. **3** (2014) N11.
- [4] M. Akazawa et al., J. Vac. Sci. Technol. B **27** (2009) 2028.
- [5] F. Hashemi et al., Appl. Phys. Lett. **102** (2013) 251122.
- [6] A. Othonos, J. Appl. Phys. **83** (1998) 1789.
- [7] D. E. Aspnes et al., Phys. Rev. B **27** (1983) 985.
- [8] C. Lu et al., Appl. Phys. Lett. **104**, (2014) 092909.
- [9] C. Lu et al., MRS spring Meeting 2014, BB 8.01.
- [10] M. Houssa et al., Appl. Phys. Lett. **92** (2008) 242101.