

# Epitaxial Thickening of a Large-grained Ge Layer on Glass for Solar Cell Applications

T. Nishida, T. Suemasu, and K. Toko

Institute of Applied Physics, University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan

Phone: +81-29-853-5472, Fax: +81-29-853-5205, E-mail: take.nishida24@gmail.com

## Abstract

We investigated the formation of a light absorbing thick Ge layer on glass using a large-grained Ge, formed by Al-induced layer exchange, as a seed layer. A 500-nm-thick Ge layer formed by solid-phase epitaxy exhibited a minority carrier lifetime of 1.1  $\mu$ s, approximately 20 times larger than that of the seed layer.

## 1. Introduction

The multi-junction solar cell has continued to update the highest conversion efficiency of solar cells. Ge has been used as a bottom cell material for multi-junction solar cells because it has a narrow bandgap ( $\sim 0.67$  eV) and a lattice constant (0.566 nm) matching III-V compound semiconductors used for top and middle cells. However, the bulk Ge substrate is too expensive for consumer application. This motivates researchers to substitute bulk Ge substrates with Ge films on inexpensive substrate including glass.

We formed a large-grained ( $> 50 \mu\text{m}$ ) Ge layer on glass using Al-induced layer exchange (ALILE) at a low temperature of 325  $^{\circ}\text{C}$  [1]. The Ge layer is thin (50 nm) and highly p-doped because it contains Al atoms ( $\sim 10^{20} \text{ cm}^{-3}$ ) [2]. These properties are not preferable for a light absorbing layer. Here we investigate the formation of a thick Ge layer without Al atoms by molecular beam epitaxy (MBE) and solid-phase epitaxy (SPE) using the ALILE-Ge as a seed layer.

## 2. Experimental Procedures

The 50-nm-thick Ge seed layer on the glass substrate was prepared using ALILE (Fig. 1 (a)). In the ALILE process, Al and amorphous Ge (a-Ge) thin films (50-nm thickness each) were sequentially prepared onto a quartz glass ( $\text{SiO}_2$ ) substrate at room temperature, using a radio-frequency magnetron sputtering (base pressure:  $3.0 \times 10^{-4}$  Pa) with Ar plasma.  $\text{AlO}_x$  layer between Al and a-Ge layers was fabricated by air exposure (5 min). The sample was annealed at 350  $^{\circ}\text{C}$  for 50 h in a  $\text{N}_2$  ambient. After annealing, the upper Al layer was removed by HF (1.5%) treatment for 2 min. Then, the 500-nm-thick Ge layer was formed by MBE or SPE. For MBE, Ge layers were grown with heating the substrate at 200–650  $^{\circ}\text{C}$ . Ge was supplied by Knudsen cell where the growth rate was 1.0 nm/min. For SPE, a-Ge layers were deposited at room temperature and then annealed at 300  $^{\circ}\text{C}$ , 350  $^{\circ}\text{C}$ , and 500  $^{\circ}\text{C}$  for 50 h in a  $\text{N}_2$  ambient. The samples were evaluated by using scanning electron microscopy (SEM), electron backscatter diffraction (EBSD), Raman spectroscopy, secondary ion mass spectroscopy (SIMS), and microwave photoconductivity decay ( $\mu$ -PCD; excitation wavelength 349 nm).

## 3. Results and Discussion

Figs. 1 (b) and (c) show that the ALILE-Ge seed layer is highly (111)-oriented and large-grained. Fig. 2 (a) shows that the MBE-Ge layer is highly (111) oriented, suggesting the epitaxial growth of Ge from an ALILE-Ge seed layer. The same behavior was observed for all of the MBE samples. However, Fig. 2 (b) shows that Ge is discontinuous and island shaped. This is the typical feature of MBE growth from the (111) oriented seed layer. As a result, the minority carrier lifetime of the MBE-Ge layer (8 ns) was smaller than that of the ALILE-Ge layer (67 ns). Fig. 3 (a) indicates that

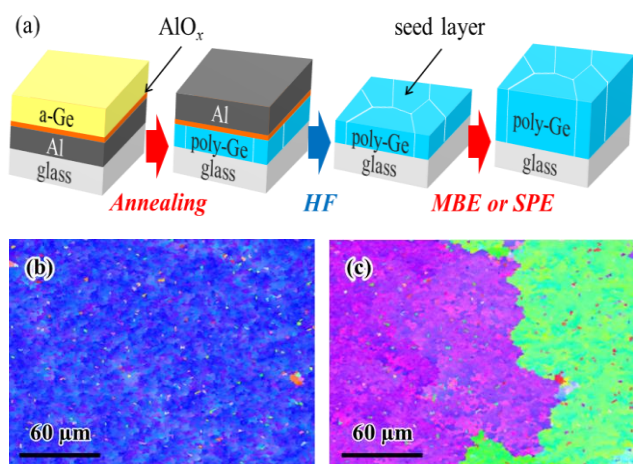


Fig. 1. (a) Schematic of the sample preparation. EBSD images of the ALILE-Ge seed layer in (b) normal and (c) transverse direction.

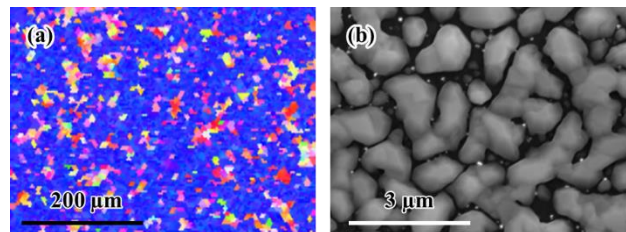


Fig. 2. (a) EBSD and (b) SEM images obtained from the MBE-Ge layer grown at 650  $^{\circ}\text{C}$ .

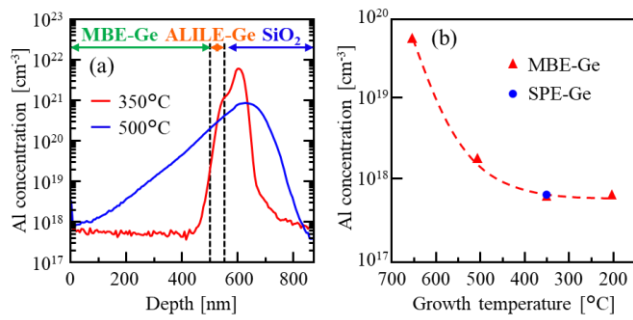


Fig. 3. (a) SIMS profiles of the MBE-Ge layers. (b) Growth temperature dependence of the Al concentration in the MBE-Ge and SPE-Ge layers.

Al in the ALILE-Ge layers diffused into the MBE-Ge layers. Fig. 3 (b) shows that the amount of Al decreased as the growth temperature decreased and saturated at 10<sup>17</sup> cm<sup>-3</sup> order. Thus, the MBE-Ge layers grown at low temperatures ( $\leq 350$  °C) had three orders lower Al concentration than that of the ALILE-Ge layer, however, had a problem of islandization degrading the minority carrier lifetime.

To solve this problem, we investigated the SPE of Ge from the ALILE-Ge seed layer. Fig. 4 (a) indicates that the Ge layer crystallizes at  $>300$  °C. Considering that at least 375 °C is necessary for nucleation in a-Ge [3], the 350 °C annealed sample likely grows epitaxially from the seed layer. Figs. 4 (b)-(d) show that only the 350 °C annealed sample inherited the (111)-orientation and large grains of the ALILE-Ge layer. From the correspondence with Raman's result, we can conclude that the 300 °C annealed sample is amorphous and the 500 °C annealed sample is micro-crystalline due to the bulk nucleation. Fig. 4 (e) shows that the Ge layer is a continuous layer reflecting the surface flatness of the as-deposited a-Ge layer. Fig. 3 (b) shows that

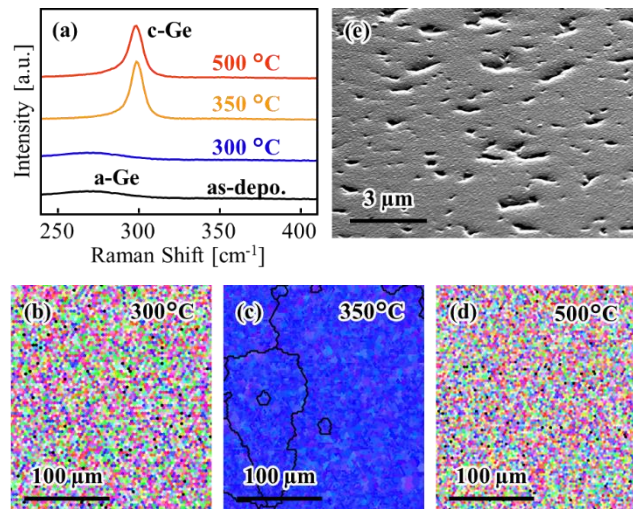


Fig. 4. (a) Raman Spectra and (b)-(d) EBSD images of the 100-nm-thick Ge layers on ALILE-Ge annealed at 300 °C, 350°C, and 500 °C for SPE. (e) SEM images of the SPE-Ge layer grown at 350 °C.

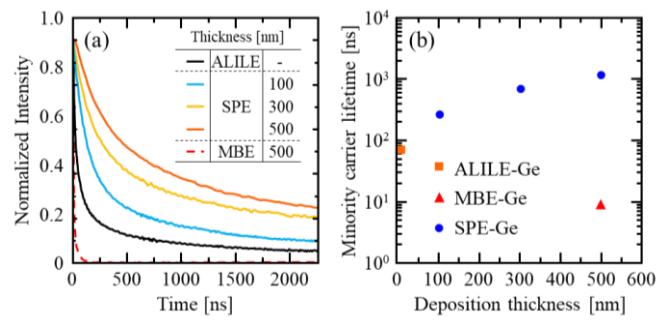


Fig. 5. (a) Photoconductivity decay curves of the samples. (b) Minority carrier lifetime of the samples as a function of the Ge thickness deposited on the ALILE-Ge layer.

the amount of Al in the SPE-Ge layer is on the order of 10<sup>17</sup> cm<sup>-3</sup> and the same as that of MBE-Ge layer grown at the same temperature (350 °C).

Fig. 5 (a) shows that the decay curve of  $\mu$ -PCD strongly depends on the sample properties. Fig. 5 (b) shows that the minority carrier lifetime of the ALILE-Ge layer is 67 ns, which is equivalent to that of a single crystal Ge substrate with the hole carrier concentration close to that of the ALILE-Ge layer. This suggests that the minority carrier lifetime of the ALILE-Ge layer is almost determined by impurity scattering. The minority carrier lifetime of the MBE-Ge layer is 8 ns even though the Al concentration is shorter than that of the ALILE-Ge layer. This is attributed to the islandization of the MBE-Ge layer. In contrast, in the SPE-Ge layers, the minority carrier lifetime is longer than that of the ALILE-Ge layer. The minority carrier lifetime increases with increasing film thickness. This behavior is considered to reflect the Al concentration near the Ge surface. For the 500-nm-thick sample, we achieved the minority carrier lifetime of 1.1  $\mu$ s, greatly exceeding that of the ALILE-Ge layer.

#### 4. Conclusion

The formation of a thick Ge layer with the low Al concentration was investigated by MBE and SPE using an ALILE-Ge as a seed layer. The Al concentration was reduced to 10<sup>17</sup> cm<sup>-3</sup> order for both MBE and SPE. However, the islandization of the MBE-Ge layer resulted in a short minority carrier lifetime (8 ns). In contrast, the SPE layer achieved a continuous Ge layer, resulting in a long minority carrier lifetime (1.1  $\mu$ s). These achievements will lead to the cost reduction of multi-junction solar cells.

#### Acknowledgement

The authors are grateful to Professor N. Usami at the Nagoya University and Dr. K. Hara at the University of Yamanashi for assistance with the  $\mu$ -PCD measurement.

#### References

- [1] K. Toko *et al.*, Appl. Phys. Lett. 101, 72106 (2012).
- [2] K. Toko *et al.*, J. Appl. Phys. 122, 155305 (2017).
- [3] K. Toko *et al.*, Sci. Rep. 7, 16981 (2017).