# Order-of-magnitude enhancement of direct-gap photoluminescence from patterned Ge epitaxial layers on Si induced by a wet chemical treatment

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## Abstract

Order-of-magnitude enhancement of direct-gap photoluminescence (PL) is reported for Ge epitaxial layers on Si. Employing a simple wet chemical treatment of selectively grown Ge mesa structures in a mixture of CH<sub>3</sub>COOH/HNO<sub>3</sub>/HF/I<sub>2</sub>, the PL intensity becomes 83 times larger than that for blanket Ge layers, being superior to other methods reported previously. The surface/interface recombination should be significantly suppressed by removing defective Ge during the wet chemical treatment.

## 1. Introduction

Near-infrared light emission from Ge is fundamentally inferior to III-V semiconductors such as InGaAsP because of the indirect band structure. The intensity of direct-gap photoluminescence (PL) around 1.55 µm from Ge is typically 4 orders of magnitude smaller than that for InGaAs [1]. Nevertheless, Ge epitaxial layer on Si has been intensively studied as a light emitting material for laser diodes (LDs) in Si photonics because of its compatibility with Si CMOS processing. The threshold current density Ith of Ge LDs is theoretically as small as 6 kA/cm<sup>2</sup> by applying a heavily n-type doping in the active layer [2], while the reported LDs showed two orders of magnitude larger Ith [3,4] in spite of the heavily n-type doping. In this regard, we have recently reported that the non-radiative recombination (NRR) of carriers at the surface/interface is responsible for the large experimental Ith [5].

In the present work, a simple wet chemical treatment is employed for selective removal of defects at the surfaces of Ge and the interfaces with Si, and the impact on the PL intensity is studied. As a result, order-of-magnitude enhancement in direct-gap PL is obtained, i.e., selectively grown Ge mesa structures treated in CH<sub>3</sub>COOH/HNO<sub>3</sub>/HF/I<sub>2</sub> mixture reveal 83 times larger PL than those for blanket Ge layers.

# 2. Sample preparation and PL characterizations

Sample preparation: epitaxial growth of Ge on Si

As the starting substrate, a B-doped p-Si(001) wafer (1– 100  $\Omega$ cm) was used. The wafer was oxidized in a tube furnace at 900°C for 2 h to form thermal SiO<sub>2</sub> as a selective epitaxial growth (SEG) mask layer. The SiO<sub>2</sub> layer was patterned into line-and-space shape using electron beam lithography followed by wet etching in buffered HF. The line direction of the SiO<sub>2</sub> mask was aligned to the [110] direction. Large growth windows (1 cm x 1 cm), regarded as blanket areas, were also prepared on the same wafer as a reference. A 1.3-µm-thick Ge layer was epitaxially grown on the window areas of patterned Si substrate using ultra-high vacuum chemical vapor deposition, followed by a growth of 50-nm-thick Si capping layer.

## Wet chemical treatment

After the selective removal of Si capping layer in 2.38% tetramethylammonium hydroxide (TMAH) at 80°C, the samples were dipped into a mixture of CH<sub>3</sub>COOH, HNO<sub>3</sub>, HF and I<sub>2</sub> for a wet chemical treatment. The mixture is known to act as an etchant to form etch pits on the Ge (001) surface, being useful to determine the threading dislocation density in the Ge epitaxial layers [6]. The etch pit formation suggests that Ge is preferentially etched around the defects by this mixture. Figures 1(a) and 1(b) show typical cross-sectional scanning electron microscope (SEM) images before and after the wet chemical treatment. In addition to the etching of Ge at the top and sidewall surfaces, Ge was preferentially etched at the Ge/Si interface laterally from the corners. There should be threading dislocations with a high density around the interface due to the 4% lattice mismatch, leading to a preferential etching of Ge near the Si substrate.



Fig. 1 Cross-sectional SEM images of SEG Ge layers (a) before and (b) after the wet chemical treatment.

#### PL characterizations

Micro-PL measurements were carried out at room temperature with a 785-nm excitation laser. The nominal  $1/e^2$  spot diameter was 2  $\mu$ m. The penetration depths of 785-nm laser in Ge and Si are 100 nm and 10  $\mu$ m, respectively, i.e., the light absorption in 50-nm-thick Si capping layer is negligible even when the Si capping layer remained.

#### 3. PL enhancement and Discussion

Typical PL spectra are shown in Fig. 2, where a linear scale was used in the vertical axis of Fig. 2(a), while a loga-

rithmic scale was used in the vertical axis of Fig. 2(b). A strong PL emission at ~1.6  $\mu$ m due to the direct transition was obtained for the SEG Ge layer after the wet chemical treatment ("SEG + wet"). Quantitatively, the peak intensity for "SEG + wet" was 27 times larger than that for the SEG Ge layer without the treatment ("as-grown SEG"), and 83 times larger than that for the blanket Ge layer without the treatment ("as-grown blanket"), as seen in Fig. 2(b). This order-of-magnitude enhancement in PL would be explained when the surface/interface recombination is significantly suppressed due to the removal of defects in Ge by the wet chemical treatment, although the efficiency of light extraction from the surface might be also enhanced by the structural change after the treatment, as seen in Fig. 1.



Fig. 2 (a) Linear plot and (b) semi-log plot of  $\mu$ -PL measurement results.

The factors of luminescence enhancement in the previous and current studies are summarized in Table I. To our knowledge, the highest enhancement factor was obtained for the present wet chemical treatment (83x) among the processes including the n-type doping (30x), rapid thermal annealing (RTA) (6x), and the surface oxidation (4x) as well as the formation of micro-cavities ( $\sim$ 2x). The obtained order-of-magnitude PL enhancement would give a useful information to realize Ge LDs on Si with small I<sub>th</sub>.

Table I Comparison of luminescence enhancement factors for Ge-on-Si.

Method	Enhancement factor from as-grown blanket Ge
RTA [5]	6x
Micro-cavity [7]	~2x (from background)
Micro-bridge & DBR [8]	9x
n-type doping [9]	30x
Surface oxidation [10]	4x
Wet chemical treatment (this work)	83x

DBR: distributed Bragg reflector

RTA: rapid thermal annealing

## 4. Conclusions

Order-of-magnitude enhancement of direct-gap PL was reported for Ge epitaxial layers on Si. Employing a simple wet chemical treatment of selectively grown Ge mesa structures in a mixture of CH<sub>3</sub>COOH/HNO<sub>3</sub>/HF/I<sub>2</sub>, the PL intensity became 83 times larger than those for blanket Ge layers, being superior to other methods previously reported. The surface/interface recombination should be significantly suppressed by removing defective Ge during the wet chemical treatment.

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