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N-type doping of germanium epilayer on silicon by ex-situ phosphorus diffusion based on $POCl_3$ phosphosilicate glass

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ABSTRACT

We report an ex-situ phosphorus diffusion doping for germanium integrated photonic devices on silicon chip. Here, phosphorus oxychloride ($POCl_3$)-based phosphosilicate glass is chosen for n-type diffusion. As an alternative process to the in-situ P doping during Ge epitaxy so far reported for Ge laser prototyping, the presented external P-diffusion method demonstrates photoluminescence (PL) emission enhancement of Ge-on-Si. The PL enhancement, along with the P secondary ion mass spectroscopy profile in Ge, clearly indicates that our ex-situ diffusion method to form n-type Ge has a significant potential for Ge active device fabrication as an enabling technology. It should be also noted that PL quenching is observed at high temperature diffusion processes which is induced by intermixing at the Ge and Si interface. The presented ex-situ P-diffusion process can serve as a template to monolithically integrate Ge devices such as not only light sources but modulators and photodetectors on Si complementary metal-oxde-semiconductor platform, as it may tailor device-specific pn junctions.

1. Introduction

As the degree of integration of semiconductor chips increases, there is a growing emphasis on the limitations of the metal interconnect wires that they have difficulty in bolstering the continual increase of the microprocessor processing speed due to the bandwidth limit and power consumption [1]. Replacing metal wires with optical interconnect by using Si photonics technologies should be a breakthrough to resolve such interconnect bottlenecks [2]. As one of the most important active devices that compose the optical interconnects, many studies to develop light sources on silicon platform have been actively conducted in the recent years [3–5]. In particular, Ge is a promising group IV element material that has the advantage of being fully compatible with Si complementary metal oxide semiconductor (CMOS) processing and of lasing at the wavelength range of fiber optical communication. The recent demonstrations of electrically-pumped Ge-on-Si laser [6, 7] are opening up the possibilities of full monolithic integration of active and passive photonic devices with microelectronic integrated circuits on Si CMOS platform.

Tensile-strained, heavily n-type doped Ge is an enabler of a positive optical gain in indirect semiconductor Ge [8, 9]. In other words, it increases direct gap transition of Ge due to the increase in electron density in Γ valley as a result of reduced Γ - L energy separation. Therefore, achieving a high-concentration n-type doping in Ge is critical for Ge lasers and has been a vibrant research topic in the community [10–12]. So far, the P doping method adopted in Ge light-emitting device researches [6, 7, 12–15] has been predominantly an in-situ doping method, in which P source gas or vapor are flowed during Ge epitaxy.

However, in photonic integrated circuits there should be multiple types of Ge photonic devices with different junction profiles co-integrated on the Ge layer. For example, the Ge laser diodes need most of its gain region to be highly n-typed doped, requiring n^+-p junction structure, while Ge photodetector and modulator diodes require substantial depletion region of p-i-n structures. It is quite challenging to achieve these various profiles via a single epitaxy and the in-situ doping. Therefore, an ex-situ P-diffusion doping process need to be developed in the process line such that we could tailor p-n junction profiles for each Ge device by using a single intrinsic Ge epitaxy accompanied by selective area doping. The ex-situ diffusion doping method also allows lateral p-n junction structures which is not possible by in-situ doping.

As an ex-situ doping method, ion implantation process to Ge MOS has been widely used in the current Si CMOS processing [16–18].

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Implantation, however, introduces damages into devices that would play as carrier generation and recombination centers to deteriorate the device characteristics. Although thermal annealings to recover the crystalline qualities have extensively been studied [11, 19, 20], the complete removal of damages, especially non-radiative recombination centers, is still an issue for Ge. Therefore, the ion implantation process may not be ready yet for enhancing optical gain characteristics of Ge. On the other hand, it has been reported that "in-situ" P diffusion doping from P delta-doped layers during Ge epitaxy was successfully utilized for heavily-doped n^+ layer formation of the current-injection Ge laser [6, 12]. This clearly indicates that no damages would be introduced by in-situ P-diffusion doping, which is in clear contrast with ion implantation. The present paper has first applied an "ex-situ" P-diffusion doping with $POCl_3$-based phosphosilicate glass (PSG) widely used in the Si solar cell community [21, 22] to Ge-on-Si photonic devices as a process line. We report a clear potential of the method to successfully diffuses P to Ge and enhance its light emission. We will discuss the remaining issues to establish the presented diffusion method as the fabrication technology.

2. Experimental procedures

2.1. Necessity of a Si capping layer on Ge for PSG-based P diffusion

Among various PSG deposition methods such as chemical vapor deposition (CVD) [23, 24], spin-on dielectric method [25–28], and $POCl_3$ gas [21, 22], we chose $POCl_3$ deposition method: It is a semiconductor-compatible gas phase process, i.e., a clean process unlike spin-on-glass (SOG), and a well-known method as a low-cost and reliable n-type diffusion doping process especially popular in the Si solar cell community. The reaction formulas are as follows.

$$4POCl_3 + 3O_2 \rightarrow 2P_2O_5 + 6Cl_2 \quad (1)$$

$$2P_2O_5 + 5Si \rightarrow 5SiO_2 + 4P \quad (2)$$

$$SiO_2 + P_2O_5 \rightarrow P_2O_5 \cdot SiO_2 \text{ (PSG)} \quad (3)$$

$POCl_3$ gas oxidizes Si and forms PSG that includes a high concentration of P dopant, indicating that a sacrificial Si layer on top of Ge epitaxial layer is required for forming the PSG layer. Also, the Si capping film on top of Ge has been popularly adopted in many Ge photonic devices [14] (including the recently-developed current-injection Ge laser that typically adopted 180-200 nm Si capping layer [6, 7]), due to the benefits such as protecting Ge against forming native germanium dioxide (GeO_2), its capabilities of forming a well-known, stable metal silicide leading to excellent electrical contacts, and forming a Si cladding layer to help confine optical modes in active Ge medium (e.g. in waveguide-integrated photodetectors and double-heterostructure laser structure [6, 7]) and to maintain some distance between Ge layer and light-absorbing metal contacts. On the other hand, a too thick Si capping layer may impede P diffusion from the PSG layer into Ge due to the P diffusivity in Si being four orders of magnitude lower compared to that in Ge [29]. This diffusion-barrier concern of Si capping layer may lead us to prefer relatively thinner layer. However, the present Si capping layer on Ge film is a lattice-mismatch system and should have high concentration of dislocations in the film. Therefore, we can still expect that the actual P diffusivity in the Si capping layer must be enhanced much beyond what has been reported for Si wafer, as shown to be the case in the later section of this paper. Based on such considerations, we chose 100 nm of Si capping layer thickness.

2.2. Sample preparation

The Ge samples to develop ex-situ $POCl_3$ diffusion doping process were grown on Si via ultrahigh vacuum chemical vapor deposition (UHVCVD) at 600 °C. A typical sample layer was 100 nm thick Si capping layer on 400 nm thick Ge epi-layer on a Si-on-Insulator (SOI) substrate. The top Si layer and the buried oxide layer of the SOI substrate were 220 nm and 3 μm thick, respectively. The structure was observed by scanning electron microscopy to confirm these layer thicknesses of Si capping layer and Ge layer.

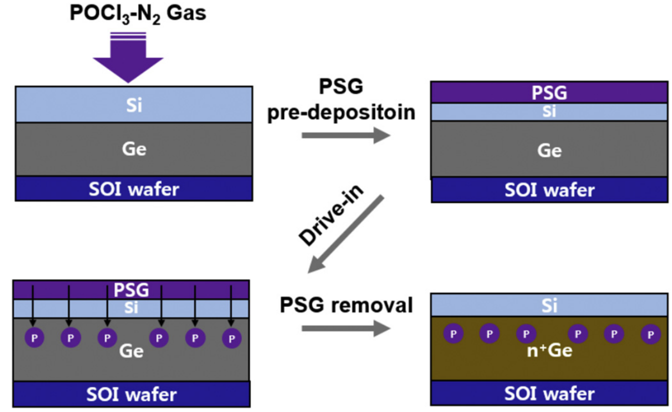

Fig. 1. Schematic diagram of n-type doping of Ge-on-Si using $POCl_3$ diffusion doping at three different temperatures.

Setting the flux of $POCl_3$-N_2 gas at 500 sccm, the PSG deposition was carried out for 30 min at the temperatures of 750, 800 and 850 °C, followed by the drive-in diffusion process for 60 min at the same temperatures as for PSG deposition process. Fig. 1 indicates the processes carried out for the ex-situ $POCl_3$ P-diffusion doping experiments. After removing PSG from the sample using diluted HF, we analyzed the phosphorus doping concentration profiles using secondary ion mass spectrometry (SIMS). The depth profiles of Si and Ge compositions were obtained by X-ray photoemission spectroscopy (XPS). We investigated the optical characteristics of P-doped Ge by measuring the PL spectra, using the 457 nm laser (power: 4.4 mW) as an excitation source, which has the penetration depth of ~20 nm in Ge. The Ge epilayer on Si without P-diffusion was used as a reference to compare with PL spectra of P-diffused samples.

3. Results and analyses

Fig. 2 shows a typical cross-sectional SEM image of the epilayer grown by UHVCVD. The structure is identical to our design. Fig. 3 shows the PL spectra of P diffused Si capped Ge samples processed at

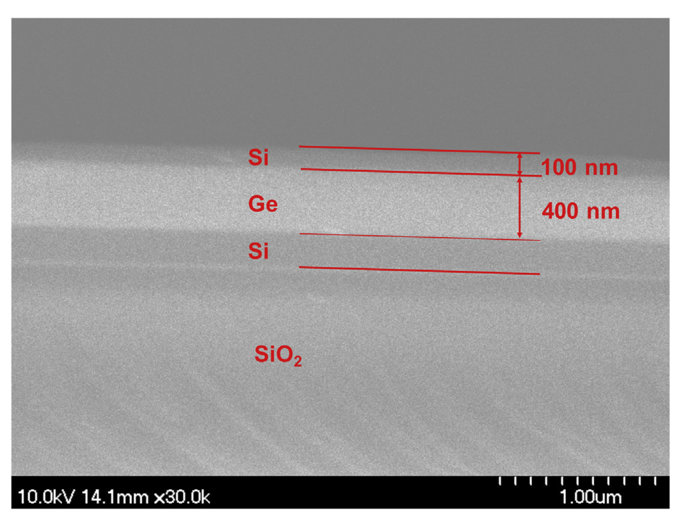

Fig. 2. Cross sectional SEM image of the Ge sample for the presented P-diffusion doping: 100 nm-thick Si capping layer and 400 nm-thick Ge epilyaer on SOI.