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A New Approach for Heavy *N*-Doping Process in Ge Epilayers Using Specific Solid Source

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Abstract

As an indirect band gap material, Germanium (Ge) has low efficiency of radiative recombination in the wavelength area of about 1550 nm. However, the difference between the direct and indirect band gap is very small (~140 meV) and photoluminescence emission ability of Ge could be greatly enhanced by heavy n-doping process. In this work, Ge growth directly on Si (001) substrate by molecular beam epitaxial (MBE) technique and a high n-doping level in Ge was obtained owning to using GaP decomposition source. The GaP solid source produces P_2 molecules instead of P_4 molecules, which have higher sticking coefficient than that of P_4 comparing to the traditional doping method from PH_3 gas precursor molecules. The dependence of optical property on Ge film thickness is also studied. The out-diffusion phenomenon of phosphorus dopant has been observed through SIMS profile analysis. An activated phosphorus concentration can be achieved up to more than 2×10^{19} atoms·cm^{-3} confirmed by Hall effect measurement. This result contributes to realization of Ge-on-Si devices for optoelectronic applications.

Keywords

Germanium, Heavy *N*-Doping, GaP Source, Photoluminescence, Optoelectronic Applications

1. Introduction

In the last few years, research on the tensile strained and n-doped Ge thin film on Si substrate has been the subject of many investigations with the hope to realize an Ge active layer in optoelectronic devices totally compatible with CMOS technology [1] [2] [3] [4] [5]. It has been shown that Ge could become direct band gap material when applying a tensile strained value of 1.9% on Ge layer [6]. However, Ge will emit a photon with wavelength of about 2500 nm,

which is out of the wavelength of telecommunication band. Addition, It's a big challenge to get such high tensile strained value while conserving a good quality crystalline of Ge.

Another approach to enhance the efficient radiative recombination of Ge film is fulfilling the energy level of the indirect band gap by doping electron from group V elements such as P, As or Sb. With a high n-doping level of about 7×10^{19} atoms·cm^{-3} [7], the energy state of the indirect band gap, which is equivalent to the lowest energy level at the bottom of the direct band gap is fulfilled. Thus, injected electrons will have a higher probability to occupy the direct Γ valley and a high efficiency of radiative recombination would be obtained. Nevertheless, remaining a big challenge is to achieve a high n-doping level due to low solubility of group V-element in Ge [8].

In this study, P is used for n-doping process because the solubility of phosphorus molecular in Ge is highest among V-group elements with intermediate temperature range of about 500˚C - 600˚C [8]. However, normally method for n-doped Ge film from phosphorus is by mean of using PH_3 gas, which produces tetrahedral phosphorus molecule with low sticking coefficient and the highest doping concentration only obtained in the range of 10^{18} - 1×10^{19} atoms·cm^{-3}. In this work we implement n-doped process by using GaP specific decomposition solid source, which produce P_2 molecule with sticking coefficient 10 times higher than that of P_4 [9] [10]. It is shown that activated electron concentration up to 2×10^{19} atoms·cm^{-3} can be obtained confirming by both Hall effect measurement and band gap narrowing phenomenon.

2. Experimental Details

Ge epilayer growth was implemented in a standard MBE system with a base pressure lower than 2×10^{-10} torr. The growth chamber is equipped with a 30 keV reflection high-energy electron diffraction (RHEED) apparatus allowing to observe in-situ and in real-time the Ge growth mode. Ge was evaporated from a two zone heated Knudsen effusion cell with deposited rate in range of about 2 - 5 nm·min^{-1}.

The substrates were flat, n-type Si (001) wafers. Cleaning of the substrate surface follows chemical method at the first step with a cycle of oxidation in a hot HNO_3 acid and oxide removal in a dilute HF solution to etch residual carbon contaminants on the surface. After eliminating a rough oxide layer, a very thin and smooth oxide layer is formed in an $HCl:H_2O_2:H_2O$ solution to protect the Si surface from hydrocarbon adsorption during the sample loading process.

The second step is heating process in ultra high vacuum in MBE chamber to evaporate SiO_2 thin layer at a temperature of about 650˚C before flash annealing at 900˚C in 5 seconds. After this step, the Si surface exposes a well-developed (2×1) reconstruction. The substrate temperature was estimated using a thermal-couple in contact with the backside of the Si wafer with accuracy of about ±20˚C.

The film resistivity was measured at room temperature using a standard four-

point probe technique. Gold (Au) contacts with a surface of about 3 mm^2 were prepared on the top of the Ge surface using conventional optical lithography to insure the reproducibility of the resistivity measurement.

The phosphorus concentration profiles in doped samples were measured by secondary ion mass spectrometry (SIMS), using Cs+ primary ion beams at 1 kV impact energy and with an incidence angle of about 68.4˚ from the normal of the sample surface. The phosphorus profiles were calibrated using P ion implanted Ge samples with various P concentrations; the depth calibration was performed using crater Alpha step depth measurement. The detection limit of our SIMS measurements is below 10^{14} atoms·cm^{-3}.

The PL is measured with a 532 nm laser focused on the sample surface. The PL signal is measured with an InGaAs detector. PL spectra were recorded at room temperature. Active phosphorus concentration is calculated by mean of using Hall effect measurement and reconfirming by band gap narrowing phenomenon.

3. Results and Discussion

In order to evaluate the efficiency of n-doping process from the decomposition of GaP, one of the first parameters needing to be controlled is the temperature range of the GaP cell in which only phosphorus can evaporate. Indeed, GaP is decomposed into Ga and P_2 molecules and at an intermediate temperature range it is expected that only P_2 can escape from the cell while Ga be trapped by a cap placed on top of the cell [10].

Figure 1 displays the evolution of the room-temperature photoluminescence spectrum versus the temperature of the GaP cell. For all samples, the substrate temperature is chosen to be 300˚C and the film thickness is 100 nm. The temperature of the GaP source increases from 600˚C to 750˚C. After growth, all samples were annealed in the growth chamber at 650˚C during 60 seconds to activate dopants. As can be seen from the figure, the photoluminescence intensity increases with increasing the temperature of the GaP source from 600˚C to 725˚C and the highest PL intensity is obtained at 725˚C. For the GaP source temperature at 750˚C, the PL is found to decrease. The decrease of the PL intensity at a temperature higher than 725˚C can be explained due to the presence of a tiny amount of Ga, escaped from the cell and incorporated in Ge films. The Ga concentration is probably below the detection limit of SIMS apparatus. As Ga acts as a p-type doping in Ge, Ga atoms can recombine with electrons induced by n-doping, and thus reduce the total electron concentration in Ge films. Thus, the PL result indicates that above 725˚C the Ga trap from the GaP cell becomes less efficient.

To investigate the effect of the doping level versus the substrate temperature as well the role of sticking coefficient of P_2 on Si substrate, we have therefore kept the GaP source at a constant temperature of 725˚C. Figure 2 displays the evolution of the film resistivity versus the substrate temperature. We note that

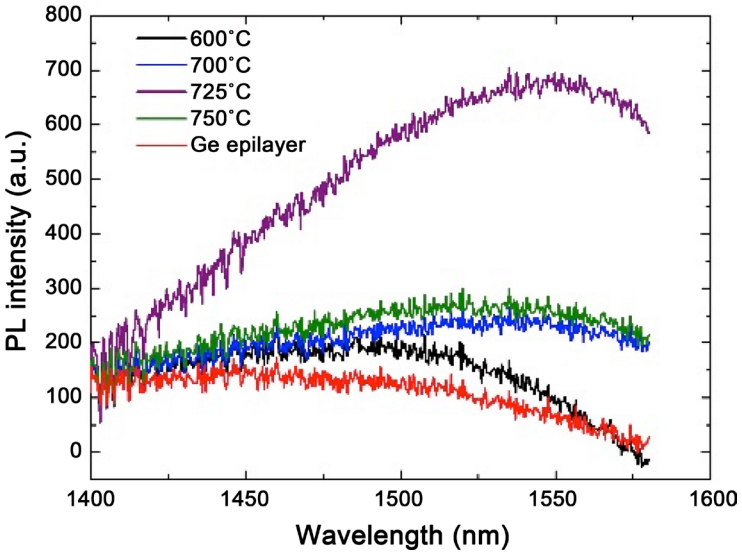

Figure 1. Evolution of the room-temperature photoluminescence spectrum versus the temperature of the GaP cell.

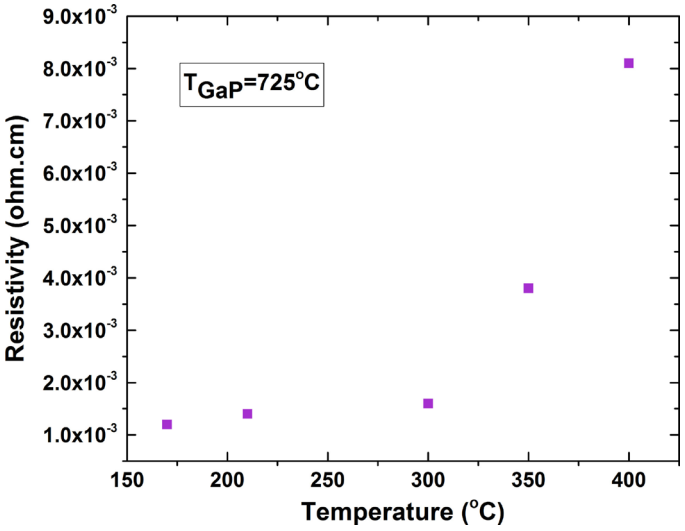

Figure 2. Evolution of the Ge layer resistivity versus the substrate temperature.

I-V measurements were carried out at room temperature and all samples have a total thickness of 100 nm (30 nm thick un-doped Ge layer deposited at 300˚C to form a smooth and strain relaxed buffer layer, followed by a 70 nm P-doped Ge film deposited at various substrate temperatures). It can be clearly seen that the resistivity decreases when increasing the substrate temperature from 170˚C to 450˚C and the lowest resistivity is obtained at a substrate temperature of 170˚C. This result is somewhat in contrast to the reference [11] which indicates that the highest solubility of P in Ge is at 580˚C. It is worth noting that based on these data, we have preformed, at the beginning, numerous doping experiences around 580˚C, the highest solubility temperature of phosphorus. However, the optical and electrical results of the corresponding samples were not as good as expected, we thus decided to investigate the P doping as function of the substrate

temperature. We believe the above data of the doping solubility in Ge is only valid for a low concentration range of dopants.

To explain our above results, we suppose that the efficiency of phosphorus doping may depend on two main parameters: the dopant solubility in a matrix and the sticking coefficient of dopants on the film surface. These two parameters are probably competing. The sticking coefficient of an atom or molecule on a substrate surface increases with decreasing the substrate temperature. Since our results reveal that P doping is more favorable at low substrate temperatures, it appears that the sticking coefficient of the P_2 molecules is the dominant parameter determining the phosphorus doping level in Ge film.

We also investigate the effect of film thickness on the optical properties of P doped Ge layers. Figure 3 shows the evolution of the PL spectrum versus the film thickness. Interestingly, the figure reveals that the PL intensity quickly increases more than 5 times when the film thickness increases from 100 to 530 nm and then slowly increases for further increase of the film thickness from 530 to 1150 nm (about 1.2 times). Taking into account the deposition time of about 3.5 - 4 hours that needs to grow a micrometer thick film by MBE, a film thickness of about 500 nm appears to be a good compromise for Ge applications in optoelectronics. The rapid increase of the PL intensity when increasing the film thickness from 100 to 530 nm can be explained by an increase of the tensile strain and in particular by a better crystalline quality of the layer. Indeed, as the Ge/Si interface region contains a high density of misfit dislocations, when the film becomes thick enough, the optically probed material is far from these defected regions giving a better optical response. We note that for an excitation laser wavelength of 532 nm used in this work, the penetration length of photons in Ge is in the order of about 10 nm. Thus, mainly a very thin region of the film surface is sensitive to the PL measurements. Therefore, when the film thickness reaches a

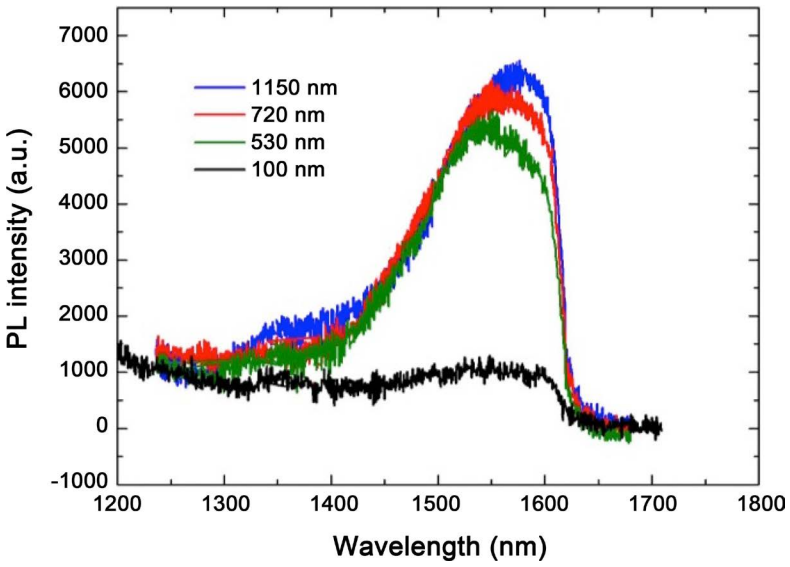

Figure 3. Evolution of the room-temperature photoluminescence spectrum versus the film thickness of P-doped Ge samples.

value of about 500 nm, the film surface becomes far enough from the interface region and as a consequent, the PL signal will slightly increase with a small increase of the average tensile strain in the film [12].

The above results have allowed us to set up key parameters of the growth condition to obtain efficient emission of the Ge direct band gap, such as the temperature of the doping GaP source (725˚C), the substrate temperature (around 170˚C) and the film thickness (around 500 nm). More importantly, the above results imply that the key parameter to get a high electron concentration is the sticking coefficient of the P_2 molecule, which is more important than its solubility (which is highest at 580˚C).

According to previous studies, when Ge is under degenerate doping, *i.e.* when the n-type doping concentration is higher than 1×10^{19} atoms·cm^{-3}, a clear red shift in emission wavelength is observed. The phenomenon is called 'band gap narrowing' [13] [14] [15]. Thus, from the shift of the emitted wavelength, one can evaluate the activated electron concentration. In **Figure 4**, at 170˚C of substrate temperature and 725˚C of GaP cell, the PL spectrum peak is located at around 1624 nm (*i.e.* the corresponding energy is 0.765 eV). This transition can be attributed to arise from the direct band gap radiative recombination of the n-doped Ge layers. As compared to the energy maximum around 0.810 eV arising from the direct band gap emission of unstrained and un-doped Ge film, we observe here a redshift of 45 meV, which can be attributed to band gap narrowing at high n-doping levels. Taken into account a tensile strain of about 0.10% in our samples (deduced from XR, measurements) and with a maximum of the PL spectrum located at 1624 nm, we can deduce an activated electron concentration of about 2×10^{19} cm^{-3}. The value of the electron concentration is in good agreement with that obtained from Hall measurements shown in **Figure 5**. We note that for Hall measurements, we have grown thick samples (1150 nm) on a SOI

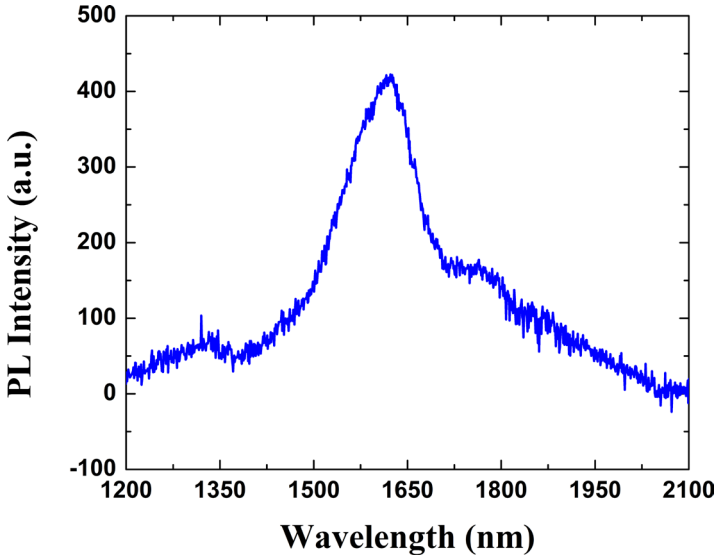

Figure 4. Room-temperature PL spectrum of a Ge layer doped with P. The film thickness is 600 nm, the substrate temperature is 170˚C and the temperatures of GaP cell is 725˚C.

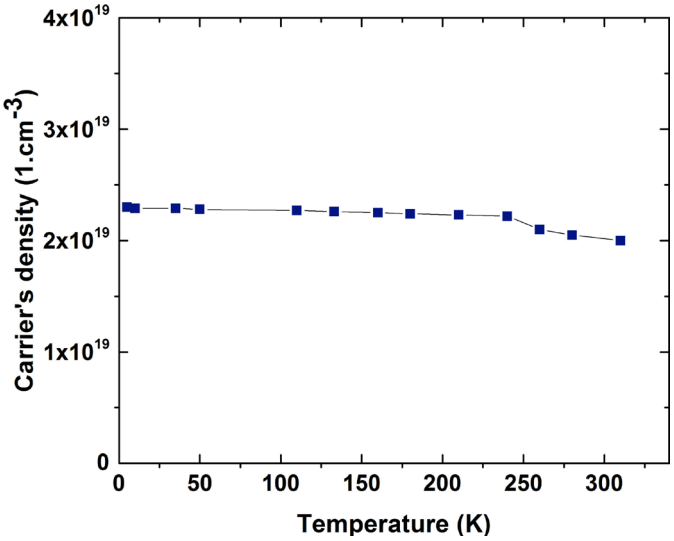

Figure 5. Dependence of carrier's density on measurement temperature.

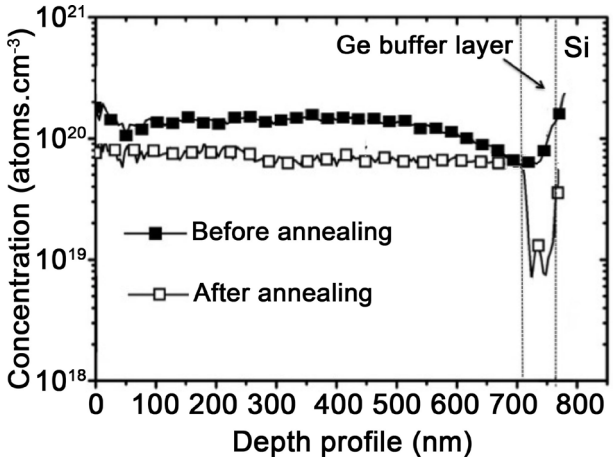

Figure 6. Concentration profiles of P in Ge epilayers before and after thermal annealing along the film thickness.

substrate (Silicon On Insulator) to avoid any transport contribution coming from the substrate.

For an active diffusion occurring, the temperature should be high enough to overcome energy barrier related to atomic motion. We use rapid thermal annealing at 700˚C for 60 s that is proposed in reference [8]. **Figure 6** displays SIMS measurements of the P concentration in Ge film before and after thermal treatment, we can recognize the drop by one order of magnitude of P concentration compared to the sample before annealing due to the out-diffusion effect. The average concentration of P is about 7.95×10^{19} atoms·cm^3 (before annealing, the P concentration is 1.37×10^{20} atoms·cm^{-3}) with a little variation along the deposition depth. It is worth noting that according to the Hall measurements, which reveal an activated dopant concentration of about 2×10^{19} atoms·cm^{-3}, it means that about 5.95×10^{19} atoms·cm^3 are still in the interstitial sites that have not been activated yet.

4. Conclusion

A new approach to increase phosphorus doping concentration in Ge has been implemented by using specific GaP solid source. The highest activated electron concentration obtained up to 2×10^{19} atoms·cm^3 by the Hall effect measurement. This result can be achieved with the following growth condition: the substrate temperature is 170˚C and the GaP source temperature is 725˚C. A film thickness of about 500 nm appears to be a good compromise for Ge applications in optoelectronics. The drop by one order of magnitude of P concentration occurs before rapid thermal annealing at 700˚C for 60 s due to out-diffusion effect.

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