VNU Journal of Science: Mathematics – Physics, Vol. 34, No. 3 (2018) 48-54

VNU Journal of Science: Mathematics - Physics

Journal homepage: https://js.vnu.edu.vn/MaP

Optical Properties of Sb Doped Ge Films Deposited on Silicon Substrate by Molecular Beam Epitaxy

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Received 08 March 2018
Revised 06 September 2018; Accepted 08 September 2018

Abstract: To enhance the photoluminescence efficiency of the Ge films, we can apply a tensile strain or introduce an electron doping in the Ge epi-layers for engineering the energy band gap of the Ge bulk. In this work, we combined both the electron doping method from a Sb source and a tensile strain via two-step growth in the Ge films. Sb-doped Ge films were grown on Si(001) substrate by molecular beam epitaxy technique. The dependence of the photoluminescence intensity on the substrate temperature in the range of 130-240^{o}C and on the Sb source temperature from 240 to 300^{o}C were investigated. The active electron concentration was obtained as large as 2.5x10^{19}cm^{-3}. The tensile strain level in the Sb-doped Ge epilayers was twice larger than that of the P-doped Ge films using GaP solid source or PH_3 gas precursor. The results have a significant suggestion in the realization of Si-based photoelectronic devices that could be compatible to the main stream CMOS technology.

Keywords: n-doped Ge; Sb source; photoluminescence; tensile strain; optoelectronic.

1. Introduction

Photonics and optoelectronics play an important role in many fields of communication and information technology. In recent years, research on tensile strain Ge/Si with high electron doping has been developed [1-5]. Although Ge exhibits an indirect band gap material, it is demonstrated that the radiative recombination of Ge film could be greatly enhanced by inducing a tensile strain as well as

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https//doi.org/ 10.25073/2588-1124/vnumap.4261

using n-doping method in Ge epilayers [3, 5]. In addition, Ge is a semiconductor having a high mobility of charge carriers. Compared to Si the electron mobility of Ge is by a factorof 2.5 higher while the hole mobility of Ge is by a factor of 4 [6]. Thus Ge/Si-based optoelectronic integrated circuit with microelectronics will open new opportunities of on-chip optical interconnect for high clock frequencies or cost effective solution for fiber to the home.

To this end, a prerequisite is getting a high activated dopant concentration in Ge films. With doping process, we can use dopant atoms of elements from the group V such as P, As or Sb. Recent studies showed that P-doped Ge from specific GaP solid source could enhance the doping level up to $2\times10^{19}cm^{-3}$ [7-8] thanks to the GaP cell which enables to produce P_2 molecules with a sticking coefficient of 10 times higher than that of P_4 from PH_3 precursor gas [9-10]. Nevertheless, with this approach, tensile strain induced in Ge can be negligible because the growth temperature is set up at low temperature and a rapid thermal annealing is applied after the deposition process. However, the thermal parameter is a key factor to induce tensile strain in the case of Ge on Si. Because the difference of thermal expansion coefficient between Ge and Si was employed to accumulate a tensile strainin Ge film when growing the Ge epilayers on Si substrate at high temperature before cooling down to room temperature [11-14].

In this work, we investigated the Sb doping process in the Ge thin films which are grown by molecular beam epitaxy, allowing for an efficient incorporation of the dopants above the solubility limit of the binary Ge-Sb and at low temperature to restrict the diffusion effect. Additionally, the atomic radius of Sb is 16 % larger than that of Ge and when Sb atom substitutes Ge atom in the matrix, it might induce a local tensile strain in Ge layers. Therefore, we also studied the accumulation of the tensile strain in the Ge epilayers due to the incorporation of Sb atoms.

2. Experimental set-up

Ge epilayer growth was performed in a standard MBE system (at CINaM, Aix-Marseille University, France) with a base pressure lower than 2.10^{-8} Pa. The growth chamber was equipped with a reflection high-energy electron diffraction (RHEED) operated at 30 kV, 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 ÷5nm/min.

The flat n-type Si (001) substrates were chosen for the growth. Cleaning of the substrate surface was followed by chemical and thermal treatments described elsewhere [15]. After the treatments, the Si surface exhibits a well-developed (2x1) reconstruction.The substrate temperature was maintained with accuracy of about $\pm20^{o}$C and estimated using a thermal-couple in contact with the backside of the Si substrate. After the growth, all samples were annealed to activate the dopant atoms for occupying the substitution sites in Ge latticeas well ameliorating the crystalline quality of the Ge films.

The epitaxial growth of Ge on Si substrate is technically challenging because of the lattice mismatch of 4% between Si and Ge. Two-steps growth method consists of an 50-nm-thick Ge buffer layer grown at 270^{o}C followed by a thick Sb-doped Ge layer at the growth temperature in the range of $130\text{-}240^{o}$C [11].

The strain in the Ge epilayers was deduced from X-ray diffraction (XRD) measurements using a diffractometer (PhilipsX'pert MPD) equipped with a copper target for Cu-Ka_1 radiation (λ=1.54059A°). The angular resolution is $\sim0.01^{o}$.

The PL was measured (FLS 1000 spectrometer) with a 532nm laser focused on the sample surface. The PL signal is detected with an InGaAs detector. PL spectra were recorded at room temperature. The active Sb concentration was estimated by mean of both Hall effect measurements and band gap narrowing phenomenon.

3. Results and discussion

We first investigate the surface morphology ofthe sample which was grown at the temperature of about 160^{o}C while the Sbsource temperature varies from 240 to 320^{o}C. Figure 1 shows typical RHEED pattern of the as-grown Ge layers when the Sb cell temperature was set up between 240 and 280°C. The RHEED pattern becomes slightly spotty but half-ordered ½ streaks characteristic of the 2x1 reconstruction of the Ge surface are stillvisible or pronounced. This means that the growth of the corresponding Sb doped Ge film is still layer by layer and the sample surface is smooth and uniform. The presence of the 3D spots presumably results or stems from the Sb incorporation into the Ge lattice.

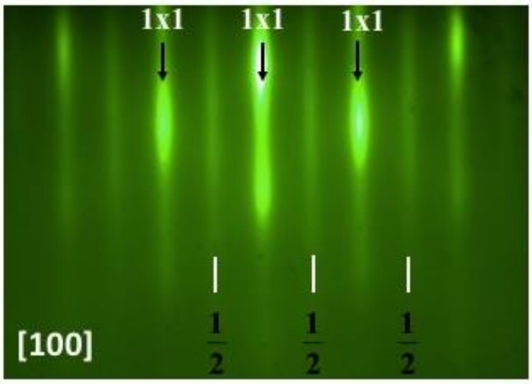

Figure 1. Typical RHEED patterns taken along the [100] azimuth of the Sb-doped Ge film grown on the Si (100) substrate. The Sb source temperature varies in the range of 240-280^{o}C.

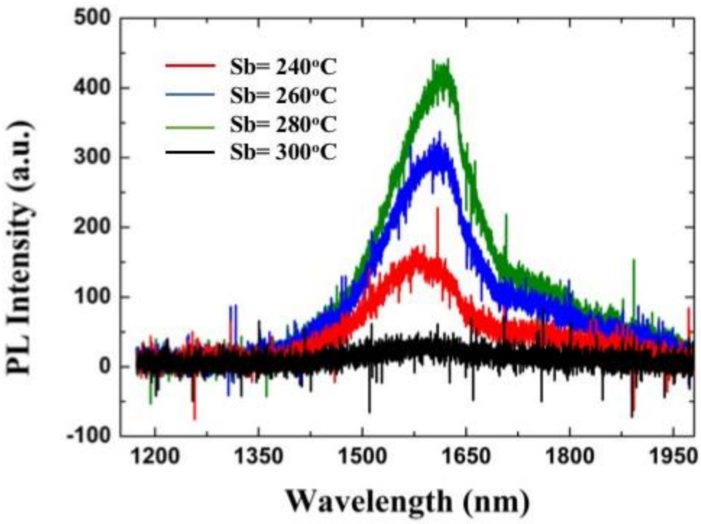

Figure 2. Evolution of the photoluminescence spectrum versus the Sb source temperature measured at room-temperature.

We now study the influence of the Sb source temperature on the photoluminescence properties. Figure 2 displays the evolution of the room-temperature photoluminescence spectra versus the temperature of the Sb cell. For all samples, the substrate temperature was kept at 160°C and the film thickness was controlled at 600 nm. The temperature of the Sb source was ranged from 240 to 300 °C. After the growth, all samples were annealed in the growth chamber at 600°C during 30s to activate the dopants and to reduce the dislocation density. As can be seen from Fig. 2, the photoluminescence intensity increases with increase of the Sb-source temperature in the range of 240 ÷ 280°C; the highest PL intensity was reached at 280°C. For the Sb source temperature of 300°C, the PL was decreased dramatically. To explainthe above mentioned phenomena, we suggest that when the Sb-source temperature increasesto a critical value, the amount of Sb atom incorporating into Ge lattice increases. Thus, the increasing number of the activated electrons leads to the increase of the PL intensity. However, if the doping Sb atoms in the Ge film exceed the critical value, the crystal structure of Ge lattice will be deteriorated, resulting in Sb-rich clusters. This result correlates with the RHEED observation of the Sb doped Ge sample when Sb source temperature is above 300^{o}C. The streaky patterns disappear and crystal structure turns into amorphous state with the presentative rings (not shown here).

One of the most important growth parameter is the substrate temperature. In order to investigate the effect of the doping level versus the substrate temperature and the role of the sticking coefficient of Sb on Si substrate, we keep the Sb source at a constant temperature of 280 °C. Figure 3 displays the evolution of the PL intensity versus the substrate temperature. As can be seen, the PL intensity is found to increase with decreasing the substrate temperature from 240 to 130 °C and the highest intensity is found at the temperature of 160 °C. At the growth temperatures higher than 190^{o}C, the PL intensity decreases dramatically because of the large precipitation of Sb in Ge film [16].

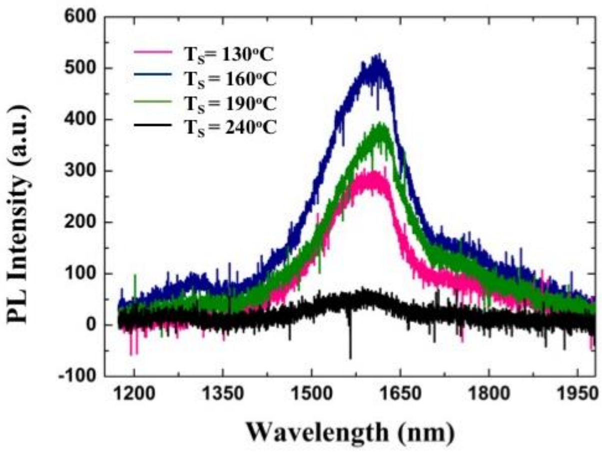

Figure 3. Evolution of the room-temperature photoluminescence spectrum versus the growth temperature. All the samples have the same a film thickness of 600nm.

The previous studies showed that, when Ge is under degenerate doping, i.e. when the n-type doping concentration is higher than $1x10^{19}$ atoms.cm^{-3}, a clear red shift in emission wavelength is observed. The phenomenon is called 'band gap narrowing' [17-19]. Thus, one can evaluate the activated electron concentration from the shift of the emitted wavelength. Figure 4a shows the evolution of Ge peak wavelength (corresponding to the maximum photoluminescence intensity) versus the Sb source temperature. As can be seen, when the Sb source temperature increases from 240 to 280^{o}C, the Ge peak increases from 1620 to 1624nm.

Continuing to increase the temperature to 300^{o}C, the peak wavelength decreases due to the crystal quality of Ge film. Figure 4b depicts the dependence of Ge peak wavelength on the substrate temperature. From the figure we can observe that the peak varies from 1617 to 1631nm with the increase of the substrate temperature from 130 to 160°C. For further increase of the growth temperature, the Ge peak decrease because of the large segregation of Sb atoms in Ge film at high temperature. At the substrate temperature of 160°C and the Sb cell temperature of 280°C, the PL spectrum peak is located at around 1631 nm, i.e. corresponding energy of 0.761 eV, arising from the direct band gap emission narrowing at high n-doping levels. This transition can be attributed to a radiative recombination of the electron-hole pairs at the direct band gap energy of the n-doped Ge layer. Compared to the energy maximum around 0.810 eV found for relaxed and un-doped Gelayers, we observe here a redshift of 49 meV, which can be attributed to band gap narrowing at high n-doping levels. Taken into account a tensile strain of about 0.20 % in our samples (deduced from XRD measurements that will be discuss in the next part) and with a maximum of the PL spectrum located at 1631 nm, we can deduce an activated electron concentration of about $2.5 \times 10^{19}.cm^{-3}$. The value of the electron concentration is in good agreement with the one obtained from Hall measurements shown in figure 5. We note that for Hall measurements, we have grown thick samples (1150 nm) on a SOI substrate (Silicon On Insulator) to avoid any transport contribution coming from the substrate.

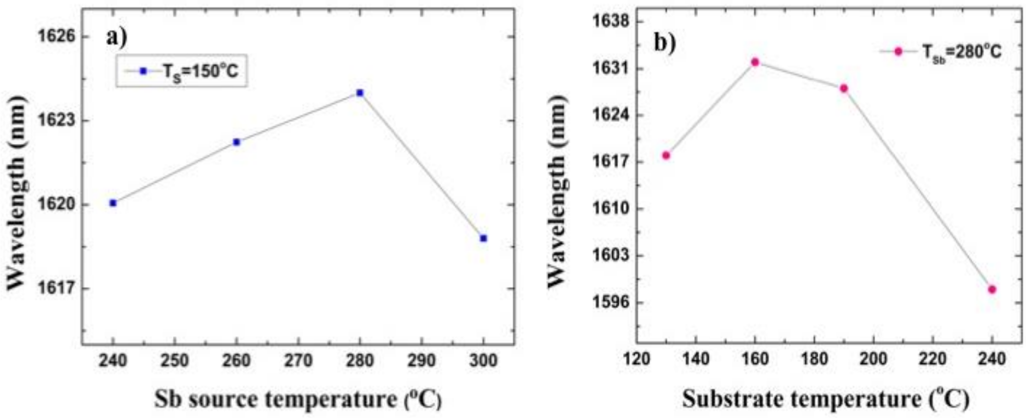

Figure 4. Evolution of Ge peak corresponds to the maximum wavelength of the direct transition emission versus the growth condition a) on the Sb source temperature; b) on the substrate temperature.

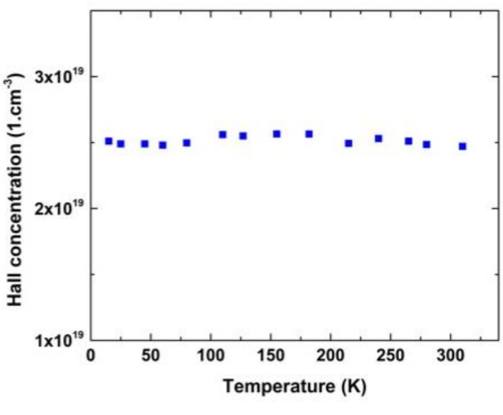

Figure 5. Dependence of electron concentration on the measurementtemperature of Sb doped Ge epilayers on the SOI substrate.

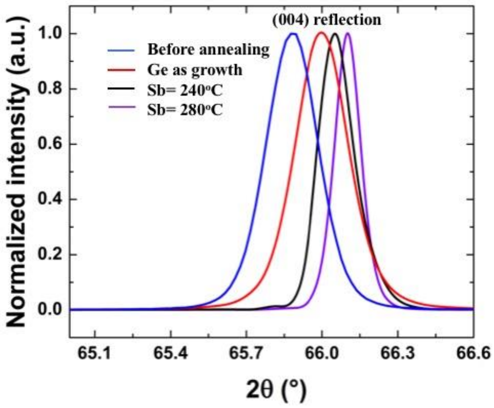

Figure 6. Theta-2theta scans of theSb-doped Ge epilayers grown on the Si (001) substrate shows the shift of the (004) reflections corresponding to different strain states. The film thickness is 600nm.

As we mentioned above, one of the reason to choose Sb as a dopant element in Ge is its atomic radius. Due to the atomic radius of Sb is 16 % larger than that of Ge, a compensation of the local strain fields is expected and when the Sb concentration is high enough, the Ge layer can be compressively strained. Figure 6 shows the evolution of the strain state in the Ge layer prior to annealing and after annealing at 600°C for 30s. It's worth noting that before annealing (the blue curve) the Ge layer is compressively strained by a value of about -0.20 %. After annealing, the strain in the Ge layer becomes tensile of about 0.20 % (the pink curve). The XRD measurement also reveals that the film quality has greatly improved after thermal annealing since the intensity of the (004) reflection increases and its half-width decreases. Regarding the effect of the Sb concentration on the tensile strain we found that the tensile strain value increases from 0.10% to 0.20% when the Sb source temperature varies from 240 to 280^{o}C (the red curve and the pink curve, respectively). Finally, in addition to the increase of the total electron concentration, Sb also allows to enhance the final value of the tensile strain in the Ge film.

4. Conclusion

We have successfully shown Sb doping in the Ge films by using molecular beam epitaxy method. The growth conditions were investigated by varying the substrate temperature between 130 and 240°C and the Sb-source temperature between 240 and 330°C. The optimal substrate temperature and Sb temperature for the highest PL intensity were determinedat 160^{o}C and 280^{o}C, respectively. Owning to the MBE technique, one can elaborate the Sb-doped Ge films at low temperatures, eliminating the phenomenon of the large Sb-segregation in the Ge layers. A highly activated dopant concentration was achieved (up to 2.5×10^{19}cm^{-3}) after a rapid thermal annealing at 600^{o}C in 30 s. The effect of the Sb incorporation in Ge epilayers on the tensile strain was also investigated. Due to the atomic radius of Sb being16 % larger than that of Ge, Sb induced a tensile strain of about 0.20% in Ge film.

Acknowledgments

This research is funded by Vietnam National Foundation for Science and Technology Development (NAFOSTED) under grant number 103.02-2015.106.

References

[1] M. Oehme, J. Werner, E. Kasper, M. Jutzi and M. Berroth, "High bandwidth Ge pi-n photodetector integrated on Si", Appl. Phys. Lett. 89 (2006)071117.

[2] J. Michel, J. Liu, L.C. Kimerling, "High-performance Ge-on-Si photodetectors", Nature Photonics 4 (2010)527.

[3] J. Liu, X. Sun, D. Pan, X. Wang, L.C. Kimerling, T.L. Koch, and J. Michel, "Tensile strained n- type Ge as a gain medium for monolithic laser intergration on Si", Opt. Exp. 15 (2007) 11272.

[4] M. El Kurdi, G. Fishman, S. Sauvage, and P. Boucaud, "Band structure and optical gain of tensile-strained germanium based on a 30 band k-p formalism", J. Appl. Phys. 107 (2010)013710.

[5] X. Sun, J.F. Liu, L.C. Kimerling, and J. Michel, "Direct gap photoluminescence of n-type tensile strained Ge-on-Si", Appl. Phys. Lett. 95 (2009)011911.

[6] M. Oehme, J.Werner, E.Kasper, "Molecular beam epitaxy of highly antimony doped germanium on silicon", Journal of Crystal Growth 310 (2008) 4531.

[7] Luong T K P et al, "Molecular-beam epitaxial growth of tensile-strained and n-doped Ge/Si(001) films using a GaP decomposition source", Thin Solid Films, 557 (2014) 70.

[8] Thi Kim Phuong Luong et al, "Making germanium, an indirect band gap semiconductor, suitable for light-emitting devices", Advances in Natural Science: Nano-science and Nanotechnology 6 (2015) 015013.

[9] Shitara T and Ebert K, "Electronic Properties of InGaP Grown by Solid‐source Molecular Beam Epitaxy with a GaP Decomposition Source",Appl. Phys. Lett. 65 (1994) 356.

[10] Lippert G, Osten H J, Krüger D, Gaworzewski P and Eberl K, "Heavy Phosphorus Doping in Molecular Beam Epitaxial Grown Silicon with a GaP Decomposition Source", Appl. Phys. Lett. 66 (1995) 3197.

[11] Luong T K P et al,"Control of Tensile Strain and Interdiffusion in Ge/Si(001) Epilayers Grown By Molecular-Beam Epitaxy",J. Appl. Phys. 114 (2013) 083504.

[12] J. Liu, X. Sun, D. Pan, X. Wang, L.C. Kimerling, T.L. Koch, and J. Michel, "Tensile strained n- type Ge as a gain medium for monolithic laser intergration on Si", Opt. Exp. 15 (2007)11272.

[13] X. Sun, J.F. Liu, L.C. Kimerling, and J. Michel, "Direct gap photoluminescence of n-type tensile strained Ge-on-Si", Appl. Phys. Lett. 95 (2009)011911.

[14] X. Sun, J.F. Liu, L.C. Kimerling and J. Michel, "Toward a germanium laser forintegrated silicon photonics", IEEE J. Sel. Top. Quantum Electron. 16 (2010)124.

[15] Luong Thi Kim Phuong, "A New Approach For Heavy N-doping Process In Ge Epilayers Using Specific Solid Source", Optic and Photonic Journal, 8 (2018)No.2

[16] K.Nakagawa, N.Sugii, S.Yamaguchi, M.Miyao, "Ge concentration dependence of Sb surface segregation during SiGe MBE", J.CrystalGrowth 201/202 (1999)560.

[17] R. Camacho-Aguilera, Z. Han, Y. Cai, L.C. Kimerling and J. Michel,"Direct Band Gap Narrowing in Highly Doped Ge". Appl. Phys. Lett. 102 (2013)152106

[18] S. C. Jain and D. J. Roulston,"A Simple Expression for Band Gap Narrowing (BGN) In Heavily Doped Si, Ge, GaAs and Ge_xSi_{1-x} Strained Layers", Solid State Electron, 34 (1991)453.

[19] M. Oehme, M. Gollhofer, D. Widmann, M. Schmid, M. Kaschel, E. Kasper, and J. Schulze, "Direct Bandgap Narrowing in Ge LED's On Si Substrates", Opt. Exp. 21 (2013) 2206.