Extended Abstracts of the 2016 International Conference on Solid State Devices and Materials, Tsukuba, 2016, pp647-648

PS-1-02

Growth of Heavily Doped *n*-Ge Epitaxial Layer by *In situ* Phosphorus-doping with Low-temperature Metal-Organic Chemical Vapor Deposition

Shinichi Ike[1,2], Wakana Takeuchi[1], Osamu Nakatsuka[1], and Shigeaki Zaima[1,3]

[1]*Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan*
[2]*Research Fellow of the Japan Society for the Promotion Science, Japan*
[3]*IMaSS, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan*
Phone: +81-52-789-3819, E-mail: sike@alice.xtal.nagoya-u.ac.jp

Abstract

We report the epitaxy of n^+-Ge layer by *in situ* P-doping MOCVD with tertiary-butyl-germane and tri-ethyl-phosphine precursors for the first time. The crystalline and electrical properties were investigated in detail. The electron concentration of P-doped Ge epitaxial layer is measured by Hall effect and the Hall electron concentration is achieved as high as 1.8×10^{19} cm^{-3} at a growth temperature of 350 °C.

1. Introduction

Ge has attracted much attention as a channel material for low-power CMOS transistors because of its higher bulk carrier mobility than those of Si and compatibility with the conventional Si CMOS process. In contrast to Ge *p*-MOSFET, however, it is well known that the high diffusivity and the low equilibrium solid solubility of *n*-type dopants (P, As, Sb) make it difficult to form high quality n^+-Ge S/D junction in Ge *n*-MOSFET and several groups reported various doping methods for *n*-Ge to overcome the above issues [1-5].

We focus on *in situ* P-doping in Ge layers to exceed the equilibrium solid solubility and to grow damage-free epitaxial layers. Moreover, as reported in the literature [5], lowering the growth temperature possibly leads to an increase of electrically active P concentration owing to the growth condition far from a thermal-equilibrium one. Recently, we reported that the metal-organic chemical vapor deposition (MOCVD) growth of undoped Ge and $Ge_{1-x}Sn_x$ epitaxial layers at low growth temperatures of 280–350 °C [6], and selective epitaxial growth of Ge on SiO_2/Si substrates at growth temperatures of 300–400 °C [7]. MO materials have generally advantages of riskless explosive, pyrophoric, and toxic compared to conventional hydride and chloride precursors. It is expected that formation of heavily *in situ* doping in Ge can be realized by low-temperature MOCVD as well as the conventional *in situ* doped Ge CVD.

In this study, we examined *in situ* P-doping in Ge on Si substrate for the formation of n^+-Ge epitaxial layers with a P concentration as high as 10^{20} cm^{-3} by low-temperature MOCVD. We revealed structural and electrical properties of MOCVD-grown P-doped Ge epitaxial layers.

2. Experimental

A high-resistivity Si(001) substrate (ρ≥1000 Ω·cm) was chemically cleaned by dipping first into an alkaline solution (NH_4OH:H_2O_2:H_2O=1:6:20) and second into a 1% HF solution, followed by thermal cleaning at 1000 °C for 15 min in a quartz chamber with a pressure of 2.4×10^3 Pa in H_2 ambient. A 200–300 nm thick P-doped Ge layer was grown on the Si substrate using a MOCVD system. Tertiary-butyl-germane (TBGe) and tri-ethyl-phosphine (TEP) were used as MO precursors of Ge and P, respectively. The substrate temperatures during the growth were 350 and 400 °C. The total pressure and the TBGe flow rate were 3.0×10^3 Pa and 1.0 sccm, respectively. The TEP flow rate was ranged from 1.7×10^{-3} to 1.1 sccm. The carrier type, the carrier concentration, and the sheet resistance of P-doped Ge layers were estimated by Hall effect measurement. In addition, X-ray diffraction (XRD) and atomic force microscopy (AFM) were performed to study the crystallinity and the surface morphology of P-doped Ge layers.

3. Results and discussion

Figure 1 shows the secondary ion mass spectroscopy (SIMS) depth profiles of P in the Ge:P/Si samples grown at 400 °C with various TEP flow rates. This result exhibits that the P concentration in the Ge:P layer increases with the TEP flow rate. The average P concentration as high as 1.0×10^{20} atoms/cm^3 is achieved for the TEP flow rate of 1.1×10^{-1} sccm, which exceeds the P equilibrium solid solubility of 2×10^{19} atoms/cm^3 in Ge at 400 °C [8]. For all samples, note that SIMS depth profiles of P near the Ge/Si interface is possibly inaccurate owing to existing some interfering ion clusters such as GeSi, GeSiH, and so on.

The XRD two dimensional reciprocal space mapping (XRD-2DRSM) result for the Ge:P/Si sample grown at 400 °C with a TEP flow rate of 1.1×10^{-1} sccm indicates that the fully strain-relaxed Ge:P layer is grown on Si substrate (**Fig. 2(a)**). XRD ω-rocking curves of Ge004 were obtained to study the influence of the P incorporation on crystallinity of Ge:P layers. Increasing the TEP flow rate hardly affects the full width of half maximum (FWHM) values of Ge004 peaks for both growth temperatures of 350 and 400 °C (**Fig. 2(b)**).

Figure 3(a) shows AFM images of Ge layers without P and with a TEP flow rate of 1.1×10^{-1} sccm for growth temperatures of 350 and 400 °C, respectively. Increasing the TEP flow rate little degrade the surface morphology, and we can see no agglomeration of P atoms on the surface for all samples in this study. Moreover, the RMS roughness of Ge:P layers grown at 350 °C is smaller than that of 400 °C as shown in **Fig. 3(b)**, which means lowering the growth temperature suppresses the three-dimensional island growth of Ge layers.

Figures 4(a) and (b) show results of the carrier concentration and the sheet resistance of Ge:P layers as a function of the TEP flow rate. For all Ge:P layers, *n*-type conduction was observed with Hall effect measurement. **Fig. 4(a)** demonstrates the increase in the P concentration in the layer with the TEP flow rate. The Hall electron concentration which corresponds to the electrically active P concentration are achieved as high as 1.7×10^{19} and 1.8×10^{19} cm^{-3} for the growth temperatures of 400 and 350 °C, respectively. The sheet resistance of Ge:P layers decreases with the TEP flow rate as shown in **Fig. 4(b)**. Here, we can see a plateau of electrically active P concentration of $1–2\times10^{19}$ cm^{-3} in **Fig. 4(a)**. It is considered that this plateau concentration is related to the equilibrium

solid solubility of P in Ge at the growth temperature. From these results, *in situ* P-doping by low-temperature MOCVD enables us to form the heavily doped n^+-Ge epitaxial layers with a concentration at least as high as the P equilibrium solid solubility limit in Ge.

Finally, we show the comparison of our achieved carrier concentration and reduced process temperature in this work with previous reports of various *n*-type doping techniques in **Table I**. *In situ* P-doping with MOCVD enables the reduced thermal budget as low as 350 °C although the carrier concentration in the Ge:P layer is not still beyond the P equilibrium solid solubility. For achieving a higher electrically active P concentration, further investigations of the relationship between the growth condition and the substitutional incorporation of P beyond the equilibrium solid solubility limit will be needed.

4. Conclusions

We investigated the crystalline and electrical characteristics of *in situ* P-doped Ge epitaxial layers. *In situ* P-doping by low-temperature MOCVD demonstrated the incorporation of P in Ge as high as 1.0×10^{20} atoms/cm^3 which exceeds P solid solubility. Heavily n^+-Ge epitaxial layers with the electrically active P concentration of 1.7×10^{19} and 1.8×10^{19} cm^{-3} at growth temperatures of 400 and 350 °C, respectively, were achieved.

Acknowledgements

This work was partly supported by a Grant-in-Aid for Scientific Research (S) (Grant No. 26220605) from the JSPS in Japan.

References

[1] J. Vanhellemont *et al.*, J. Electrochem. Soc. **154** (2007) H572.
[2] M. Takenaka *et al.*, Opt. Express **20** (2012) 8718.
[3] W. M. Klesse *et al.*, Appl. Phys. Lett. **102** (2013) 151103.
[4] Y. Moriyama *et al.*, Appl. Phys. Express **7** (2014) 106501.
[5] Y. Shimura *et al.*, Thin Solid Films **602** (2015) 56.
[6] Y. Inuzuka *et al.*, Thin Solid Films **602** (2014) 7.
[7] T. Washizu *et al.*, ICCGE-18, Nagoya, Aug. 2016, *accepted*.
[8] J. Vanhellemont *et al.*, Mater. Sci. Semicond. Process. **15** (2012) 642.

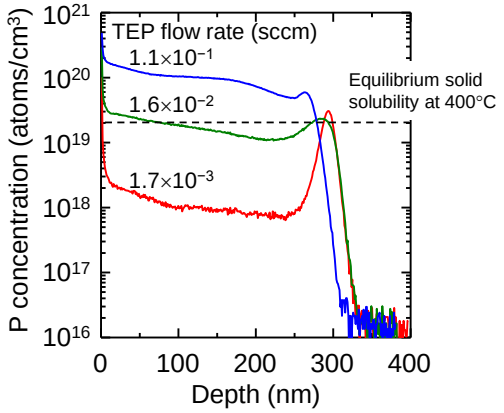

Fig. 1 SIMS depth profiles of P for the Ge:P/Si samples grown at 400 °C with various TEP flow rates.

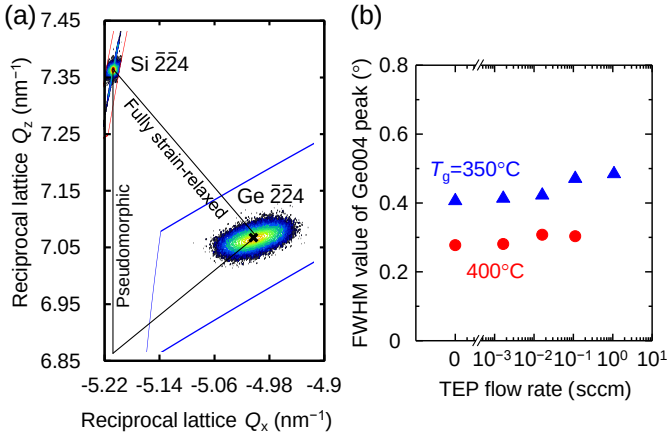

Fig. 2 (a) XRD-2DRSM result of Ge:P(TEP=1.1×10^{-1} sccm)/Si sample grown at 400 °C. **(b)** FWHM values of the Ge004 peaks of undoped- and P-doped Ge/Si samples as a function of the TEP flow rate.

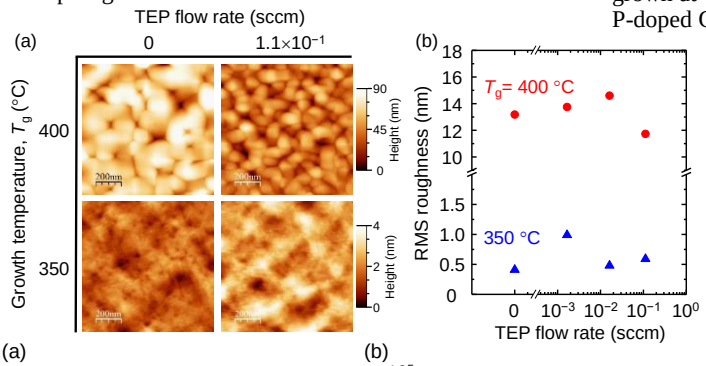

Fig. 3 (a) 1×1 μm^2 AFM images of Ge and Ge:P(TEP=1.1×10^{-1} sccm) layers grown at 400 and 350 °C. **(b)** RMS roughness as a function of the TEP flow rate.

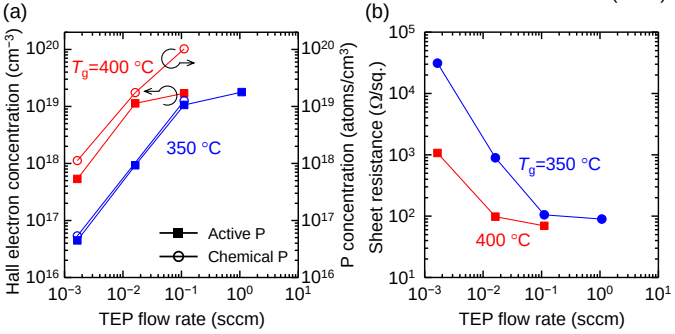

Fig. 4 (a) The TEP flow rate dependence of the Hall electron concentration, the P concentration (from SIMS), and **(b)** the sheet resistance in Ge:P/Si samples.

Table I Summary of achieved carrier concentration and the process temperature for various *n*-doping techniques for n^+-Ge.

Doping method	Carrier conc. (cm^{-3})	Process temp. (°C)	Precursors
Ion implantation	5–6×10^{19}	600	P [1]
Gas-phase doping	4×10^{19}	600	Tertiary-butyl-arsine [2]
δ-doping	1×10^{20}	530	GeH_4, PH_3 [3]
In situ doping	7×10^{19}	400	GeH_4, PH_3 [4]
	6.2×10^{19}	320	Ge_2H_6, PH_3 [5]
	1.8×10^{19}	**350**	**TBGe, TEP [This work]**
	1.7×10^{19}	**400**	