# Impact of As Doping in Amorphous Ge on Solid-Phase Crystallization

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## Abstract

As doping in amorphous Ge significantly promoted the lateral growth during solid-phase crystallization, resulting in large grains (19  $\mu$ m). The electron mobility (370 cm<sup>2</sup>/Vs) was the highest among n-type polycrystalline Ge directly grown on insulators at low temperatures (< 900 °C).

## 1. Introduction

Low-temperature synthesis of polycrystalline (poly-) Ge on insulators is a key technology to integrate Ge-CMOS into existing devices. We recently fabricated a poly-Ge layer with a hole mobility of 620 cm<sup>2</sup>/Vs by using solid phase crystallization (SPC) of a densified amorphous (a-) Ge at 500 °C [1]. However, n-type poly-Ge on insulators with high electron mobility (> 200 cm<sup>2</sup>/Vs) have yet to be achieved. In present study, we aimed at the fabrication of n-type poly-Ge with high electron mobility using SPC with As doping.

## **2. Experimental Procedures**

As-doped Ge precursors (200 nm thickness) were deposited on SiO<sub>2</sub> glass substrates at RT using a Knudsen cell of a molecular beam deposition system. To modulate the As concentration of the Ge layer, the temperature of the As Knudsen cell, TAs, ranged from 200 to 270 °C. Using secondary ion mass spectrometry (SIMS), the As concentration was determined to be  $2.8 \times 10^{19}$  cm<sup>-3</sup> for  $T_{As} = 210$  °C,  $1.2 \times 10^{20}$  cm<sup>-3</sup> for  $T_{As} = 230$  °C, and  $5.9 \times 10^{20}$  cm<sup>-3</sup> for  $T_{As} =$ 250 °C, which were constant regardless of before and after annealing. The samples were then loaded into a conventional tube furnace under a  $N_2$  (99.9%) atmosphere and annealed at a growth temperature,  $T_{\rm g}$ , of 450 °C for 5 h and 375 °C for 140 h to induce crystallization. For all samples, we performed post annealing (PA) at 500 °C for 5 h. The grown layers were analyzed by the Raman measurement, electron backscattering diffraction (EBSD) measurement, and Hall effect measurement (van der Pauw method).

## 3. Results and Discussion

Fig. 1(a) shows that the samples with  $T_g = 450$  °C exhibit sharp peaks near 300 cm<sup>-1</sup>, corresponding to crystalline (c-) Ge-Ge bonding in the whole  $T_{As}$  range. These peaks are almost symmetrical, suggesting that the Ge layers are completely crystallized. As representatively shown in Fig. 1(b), annealing at 375 °C for 140 h crystallized the samples with  $T_{As} \le 240$  °C, but not those with  $T_{As} \ge 250$  °C. This is likely because segregation of excess As suppressed nucleation. The Raman shift and the full width at half maximum (FWHM) of c-Ge peaks were evaluated from the Raman spectra and are



Fig. 1. (a,b) Raman spectra of the samples with  $T_g =$  (a) 450 and (b) 375 °C. (c) Raman shift and FWHM of the Ge-Ge peaks as a function of  $T_{As}$ .

summarized in Fig. 1(c). All peaks shifted to lower wavenumbers than that of a bulk Ge substrate, originating from the tensile strain. The peak shifts are almost constant with respect to  $T_{As}$  while the peaks for  $T_g = 450$  °C shifted to the lower wavenumber than that for  $T_g = 375$  °C. This behavior suggests that the strain likely originates from the difference in the thermal expansion coefficients between Ge and the SiO<sub>2</sub> substrate. FWHM is almost constant for  $T_{As} \le 240$ °C and significantly increases with  $T_{As}$  for  $T_{As} \ge 250$ °C.

Fig. 2(a)–2(d) shows that the grain size dramatically varies with  $T_{As}$ . Fig. 2(e) shows that the average grain size increases with increasing  $T_{As}$  and then begins to decrease. The decrease in grain size at higher  $T_{As}$  ( $\geq 250$  °C) is likely attributed to the suppression of lateral growth caused by segregation of excessive As. This behavior well accounts for the results of the Raman FWHM. In contrast, when doping amount of As is sufficiently small ( $T_{As} \leq 240$  °C), the grain size increases with  $T_{As}$ , suggesting that As atoms accelerated the lateral growth of Ge. A similar behavior has also been reported in Sn and Sb doped SPC-Ge [2,3]. The lower  $T_g$  provides a larger grain size, which agrees with the non-doped SPC-Ge [1]. The sample with  $T_{As} = 230$  °C and  $T_g = 375$  °C exhibited a grain size of 19 µm, which is the largest among poly-Ge formed by SPC.

The electrical properties were evaluated and shown in Fig. 3. All samples showed n-type conduction owing to the self-organizing activation of As during SPC. We first discuss



Fig. 2. (a-d) EBSD images of the samples with  $T_g = 450$  °C and  $T_{As} =$  (a) 200, (b) 230, (c) 260, and (d) 270 °C. (e) Average grain size as a function of  $T_{As}$  for samples with  $T_g = 375$  and 450 °C.

the data before PA. Fig. 3(a) shows that electron concentration *n* for  $T_g = 375$  °C is lower than that for  $T_g = 450$  °C in the whole  $T_{As}$  range. This is attributed to the fact that lower  $T_{\rm g}$  has the lower solid solubility of As in Ge. Fig. 3(b) shows that electron mobility  $\mu_n$  tends to increase with increasing grain size. However, for  $T_{As} = 230 \text{ °C}$ ,  $\mu_n$  for  $T_g = 375 \text{ °C}$  are lower than those for  $T_g = 450$  °C, which may reflect larger carrier scattering caused by more segregation of excess As. PA improved the electrical properties of the samples. Fig. 3(a) shows that *n* for  $T_g = 450$  and 375 °C increases to the similar value by PA for each  $T_{As}$ . *n* is maximized at around  $T_{\rm As} = 230$  °C where the grain size is maximum (Fig. 2(e)). This behavior is likely because the larger grain size provides the lower defect-induced acceptors and/or the less As segre gation at grain boundaries. Fig. 3(b) shows that  $\mu_n$  increases by PA in whole  $T_{As}$  range, reflecting the decrease of carrier scattering by inactive As.



Fig. 3. (a,b) Electrical properties of the samples with  $T_g = 375$  and 450 °C before and after PA (500 °C) as a function of  $T_{As.}$  (c) Arrhenius plot of  $\mu_n T^{1/2}$  for samples with  $T_{As} = 200, 230$ , and 260 °C. (d) Trap-state density  $Q_t$  and energy barrier height  $E_B$  as a function of  $T_{As.}$ 



Fig. 4. Comparison of the electron mobility  $\mu_n$  and electron concentration *n* of poly-Ge on insulators.

According to the carrier conduction model proposed by Seto for polycrystalline semiconductors,  $\mu_n$  limited by grainboundary scattering can be determined by using the following equation:

$$\mu_{\rm n} T^{1/2} = \frac{Lq}{\sqrt{2\pi m^* k}} \exp\left(-\frac{E_{\rm B}}{kT}\right)$$

where  $E_{\rm B}$  is the energy barrier of the grain-boundary, *T* is the absolute temperature, *L* is the grain size, *q* is the elementary charge, *m*<sup>\*</sup> is the effective mass, and *k* is the Boltzmann constant. Fig. 3(c) shows that the Arrhenius plot of  $\mu_{\rm n}T^{1/2}$  makes almost-downward-sloping straight lines for whole  $T_{\rm As}$  region. The trap-state density  $Q_{\rm t}$  in the grain boundaries can be determined by using the following equation:

$$Q_{\rm t} = \frac{\sqrt{8\varepsilon nE_{\rm B}}}{q}$$

where  $\varepsilon$  is the dielectric permittivity. Fig. 3(d) shows that  $Q_t$  decreases with increasing  $T_{As}$ , suggesting that As atoms passivate the grain boundary traps. The minimum value of  $E_B$  is obtained for the highest  $\mu_n$  sample with  $T_{As} = 230$  °C.

As shown in Fig. 4, the  $\mu_n$  of 370 cm<sup>2</sup>/Vs obtained in this study is the highest value among the Ge layers formed on insulating substrates at temperatures below the melting point of Ge (937 °C). The findings in this study will provide a pathway for the monolithic integration of high-performance Ge- CMOS ont o Si-LSIs and flat-panel displays.

#### 4. Conclusions

As doping into an a-Ge precursor significantly influenced the subsequent SPC. By optimizing As amount ( $T_{As} = 230 \text{ °C}$ ) and lowering  $T_g$  (375 °C), the grain size reached 19  $\mu$ m. The subsequent PA (500 °C) provided the highest electron mobility (370 cm<sup>2</sup>/Vs) among n-type poly-Ge directly grown on a glass substrate.

#### References

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