Structure and Transport Properties of Microcrystalline SiGe Films

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Abstract

Amorphous $Si_{1-x}Ge_x$ films (x=0, 0.25, 0.5, 0.75 and 1, having Boron concentrations of $5\cdot10^{18}$, $5\cdot10^{19}$ and $5\cdot10^{20}cm^{-3}$), were deposited at low temperature by a molecular beam processing on SiO_2/Si(001) substrates. Samples were studied by *in-situ* TEM and *in-situ* XRD to follow the crystallization process. In addition, transport properties were studied in samples which were annealed in vacuum by a hot-wall furnace at temperatures between 500 to 900°C for 1 hour. The microstructure of B-doped SiGe films is characterized by a relatively large grain size (about 1µm). The $Si_{0.5}Ge_{0.5}$ films have a rather high and temperature independent Hall mobility (25 to 60 cm²/Vsec), Seebeck coefficient (~150 to 250 µV/K at room temperature) and conductivity ($(200$ to 2000 (Ohm·cm)$^{-1}$ at room temperature). Therefore, the highly-doped µc-SiGe films that we produce in the present research project show transport characteristics comparable to the sintered SiGe materials for thermoelectric applications.

I. Introduction

Bulk $Si_{1-x}Ge_x$ is used for thermoelectric applications in the form of sintered powder having a composition varying between x=0.2 and x=0.7 and a grain size ranging from 1 to 100µm. The advantages of $Si_{1-x}Ge_x$ as a thermoelectric material are: 1) low thermoconductivity (λ) having a minimum value at x≈0.5; and 2) high charge carriers mobility. Increase of the figure of merit $Z=S^2\sigma/\lambda$ of SiGe by decreasing the grain size from 100 to 1µm was predicted, but was found to be not effective since while the thermal conductivity is decreased with grain size, the electrical conductivity is also slightly decreased, so that no sufficient change in the figure of merit is observed [1]. Some thermoelectric properties of Ga-doped nanocrystalline SiGe films were recently reported by us [2].

SiGe Peltier elements can be incorporated in a Si chip because SiGe material is compatible with VLSI processing. However, up to now, only one article was published concerning SiGe film application as a thermoelectric integrated element [3].

The main advantages of microcrystalline $Si_{1-x}Ge_x$ films on insulating SiO_2 substrate are: a) clean molecular beam deposition processing, b) wide range of Ge content (x) and doping type/concentrations. Here we present the first results of structure and thermoelectric properties studies of p-type microcrystalline $Si_{1-x}Ge_x$ films.

II. Experimental

B-doped $Si_{1-x}Ge_x$ films, 0.2µm thick, having the composition x=0, 0.25, 0.5, 0.75 and 1, and dopant (B) concentration of $5\cdot10^{18}$, $5\cdot10^{19}$ and $5\cdot10^{20}$ cm^{-3}, were deposited by molecular beam processing on SiO_2/Si(001) substrates at a temperature of 200°C.

In-situ X-Ray Diffraction (XRD) experiments were carried out at ESRF, Grenoble-France. A special high-temperature chamber with vacuum of 10^{-6}Torr was used to detect (220) SiGe reflection during the crystallization process in the temperature range of 300 to 1000°C and exposures from 15 min to 12 h.

The crystallization of the $Si_{1-x}Ge_x$ films was studied also by means of *in-situ* TEM, equipped with a hot stage, at the temperature range between 500 to 800°C, in Max-Planck-Institute of Microstructure Physics, Halle/Saale.

Annealing of the films for measurement of transport properties was done in a hot-wall furnace, having a vacuum near 10^{-7}Torr at temperatures between 600 and 900°C and times between 15 min and 16 hours.

The electrical conductivity σ, the Hall coefficient R_H and the Seebeck coefficient S were measured in the temperature range between 85 and 375K. All measurements were carried out at the Laboratory of Thin Films at Physical Faculty of the Martin-Luther University Halle-Wittenberg.

III. Results and Discussion

III.1. Structure of B-doped $Si_{1-x}Ge_x$ films

After thermal annealing during 1h at T≥450°C (Ge), T≥750°C (Si) and at the intermediate temperatures (SiGe), amorphous films crystallized to the microcrystalline state. Fig.1a shows crystallization kinetics of a-$Si_{0.5}Ge_{0.5}$ films, undoped and B-doped, at 550 and 600°C.

The TEM plan-view in Fig.2 demonstrates a typical microcrystalline morphology of the B-doped ($[B]=5\cdot10^{20}cm^{-3}$) $Si_{0.5}Ge_{0.5}$ film. An average grain size was about 1µm and the film was totally crystallized at 600°C for 1h. Precipitation of SiB_6 in highly B-doped films was observed in course of the *in-situ* TEM experiments at 650-800°C for 15 to 30 min. Selected area diffraction (SAD) in Fig.2 shows SiB_6 (precipitates) reflections (arrows). The morphology of the plate-like precipitates produced striations along <110> directions of SiGe in the large grains, when {001} face oriented perpendicular to the electron beam. Solubility limit of Boron in SiGe is not known, however, upper limit of Boron solubility in Si at T=700°C is only $2\cdot10^{19}cm^{-3}$ and B-phase precipitation in SiGe with $[B]=5\cdot10^{20}cm^{-3}$ [4] is expected.

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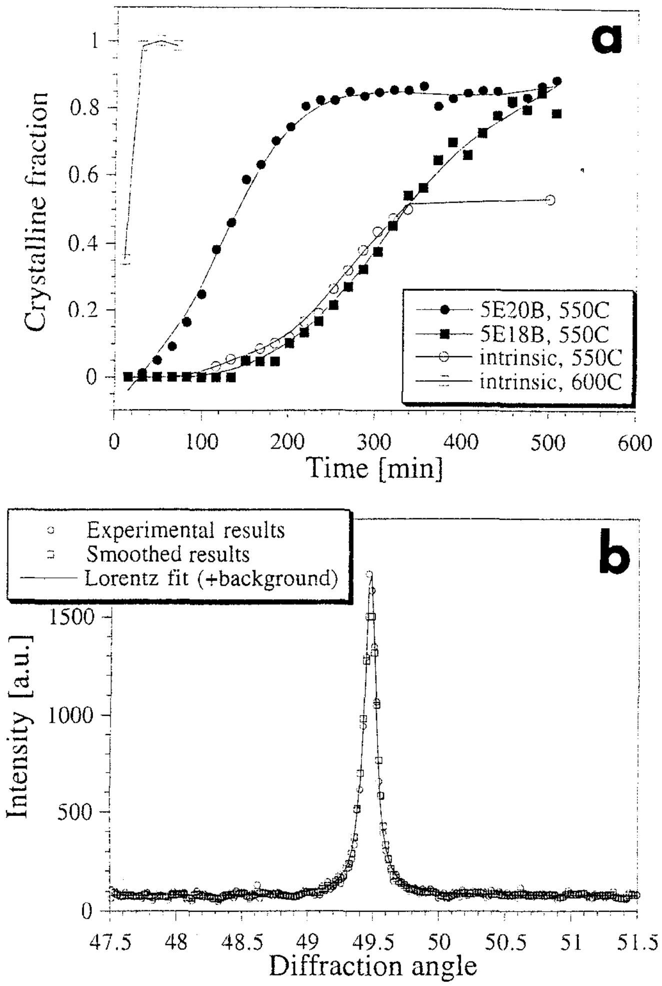

Figure 1. Structure of microcrystalline SiGe films.
(a) Crystallization kinetics of a-Si$_{0.5}$Ge$_{0.5}$ intrinsic and doped films at 550°C and 600°C via *in-situ* XRD and (b) (220) crystalline Si$_{0.5}$Ge$_{0.5}$ peak.

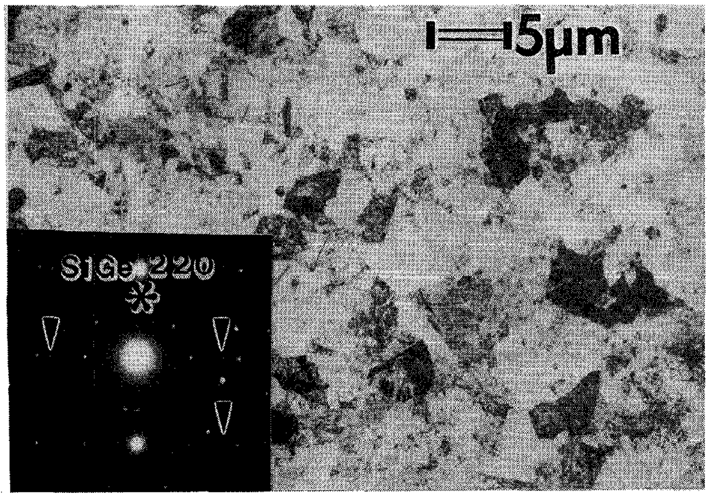

Figure 2. Plan-view TEM micrograph and SAD of Si$_{0.5}$Ge$_{0.5}$ Boron-doped film ([B]=5·10^{22}cm^{-3}) annealed at 600°C for 1h.

III.2. Transport properties of B-doped microcrystalline Si$_{1-x}$Ge$_x$ Films

Data of Hall mobility, Seebeck coefficient, and power efficiency factor which were measured by us in the temperature range of -188 to 107°C for Si$_{1-x}$Ge$_x$:B film crystallized at 600°C for 1h are presented as a function of the doping level, Ge content (x) and crystallization temperature in Figs.3-5.

A weak temperature dependence of the carrier concentration (not shown in Figs) , the mobility and, consequently, of the conductivity was found, as expected from degenerated crystalline SiGe material [5,6]. The increase of S (Fig.4) with temperature results in the gain of the power efficiency parameter, $S^2\sigma$.

It is important to notice that after 600 to 800°C annealings for 1 hour, all the Si$_{1-x}$Ge$_x$ films have a rather high and temperature independent Hall mobility values (Fig.3) in the range of 25 to 60 cm^2/Vsec. All the typical transport characteristics observed for microcrystalline Si$_{0.5}$Ge$_{0.5}$:B films were also typical for Si$_{0.25}$Ge$_{0.75}$:B films with [B]=5·10^{20}cm^{-3}. The power factor $S^2\sigma$ was found to be practically indifferent to the Ge concentration (x) and the film annealing temperature .

The carrier transport, like in MOS devices, developes via drift process, with a drift mobility (μ_D or μ) typical to this transport. Detailed analysis of the Hall factor $r_H= \mu_H/\ \mu_D<1$ of epitaxial p-Si$_{1-x}$Ge$_x$ films with 0<x<0.36 is given for doping level of [B]=10^{14} to 10^{20}cm^{-3} in Ref.7. The main result obtained in Ref.8 is that the value of μ is about 5 to 7 times greater than μ_H, with r_H=0.15 to 0.2 for x=0.36 to 0.17, respectively. Therefore, a hole drift mobility of 200 to 350 cm^2/Vsec is expected in SiGe thermoelectrical transport devices.

Presently, thermoelectric Peltier elements are produced by using SiGe powder sintered or zone-levelled in a bulk form. The first Si$_{1-x}$Ge$_x$ alloys were studied by RCA group [8] , which reported S value of about 80 to 240 µV/K (depending on x) and a room temperature the Hall hole mobility of the order of 35 to 90 cm^2/Vsec, decreasing with the doping level and Si-content. Later an improved thermoelectric conversion efficiency at T=1000K was reported [9] for a small-grained (3 to 5µm) compacts, compared to a large-grained (>10µm) SiGe samples. A detailed analysis of the mobility and the carrier concentration in sintered p-Si$_{0.7}$Ge$_{0.3}$ bulk samples [10] showed that the composition and temperature dependence of the mobility, μ, in Si$_{1-x}$Ge$_x$ alloy can be given by a semi-empiric formula:

$$\mu=[\mu_a/4x(1-x)]\cdot(300/T)^{0.5}, \qquad (1)$$

where the parameter μ_a=160cm^2/Vsec. Using this relationship and the data of B solubility in Si, the calculated hole Hall mobility in Si$_{0.7}$Ge$_{0.3}$ for large grain-size sintered samples, or for single crystal, was found to be in the range from 65 cm^2/Vsec for [B]=10^{19}cm^{-3} to 55 cm^2/Vsec for [B]=5·10^{21}cm^{-3}. These values fit with our data, as measured for microcrystalline Si$_{1-x}$Ge$_x$ films with x=0.25 to 0.75 (Fig.3).

As it was shown in Ref.1, the thermal conductivity of sintered $Si_{0.8}Ge_{0.2}$ samples decreased with decreasing of the particle size (from 134 to 3μm). However, the figure of merit was not significantly increased due to a reduction in the electrical conductivity with grain size decrease. Experimental values measured for hole Hall mobilities varied within the range of 25 to 35 cm²/Vsec at room temperature. Thermal conductivity data on our microcrystalline films would allow a calculation of Z values for comparison purposes.

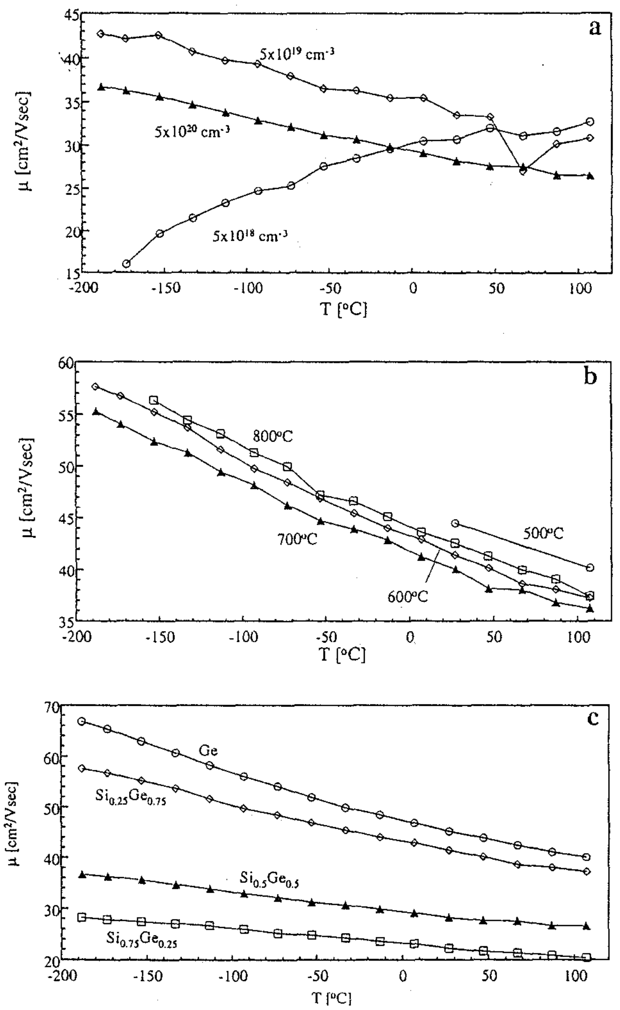

Figure 3. The hole Hall mobility of $Si_{1-x}Ge_x$ films having different Boron concentration, after 600°C/1h annealing (a), films with $[B]=5\cdot10^{20}cm^{-3}$ crystallized at different temperatures (b) and having different Ge content, after annealing at 600°C/1h and containing $[B]=5\cdot10^{20}cm^{-3}$ (c).

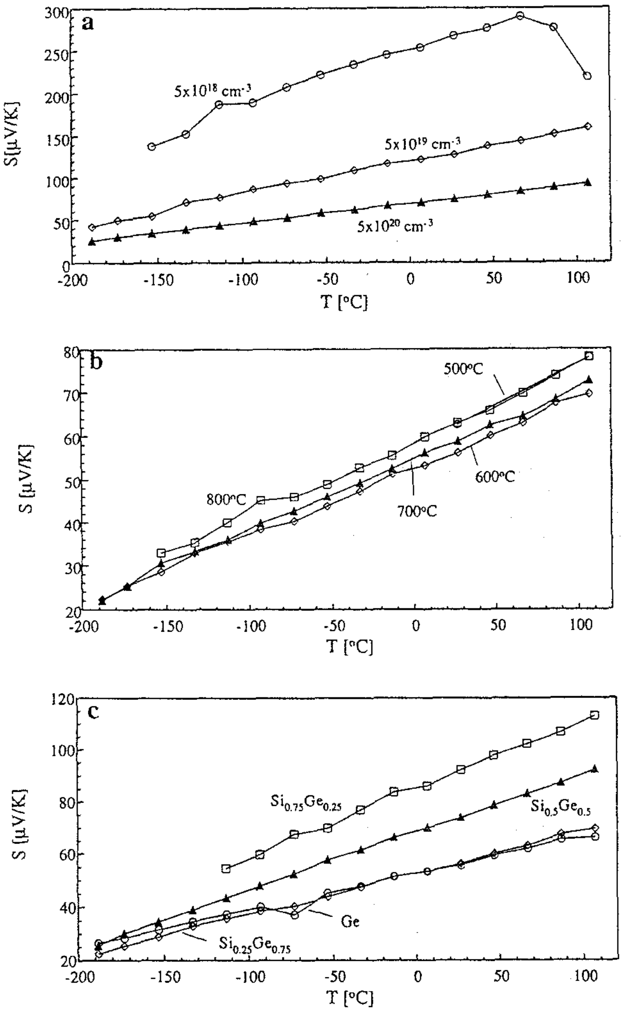

Figure 4. The Seebeck coefficient of $Si_{1-x}Ge_x$ films having different Boron concentration, after 600°C/1h annealing (a), films with $[B]=5\cdot10^{20}cm^{-3}$ crystallized at different temperatures (b) and having different Ge content, annealed at 600°C/1h and containing $[B]=5\cdot10^{20}cm^{-3}$ (c).

IV. Conclusions

(i) Amorphous $Si_{1-x}Ge_x$ films (x=0, 0.25, 0.5, 0.75 and 1, having Boron concentrations of $5\cdot10^{18}$, $5\cdot10^{19}$ and $5\cdot10^{20}cm^{-3}$, were deposited at low temperature by a molecular beam processing on SiO_2/Si(001) substrates and then the films were annealed in vacuum at temperatures between 500 to 900°C for 1 hour. Annealed SiGe films were polycrystalline having an average grain size of ~ 1μm.

(ii) The SiGe films demonstrated Hall mobility of 25 to 60 cm²/Vsec, Seebeck coefficient of 150 to 250 μV/K) and conductivity 200 to 2000 $(Ohm\cdot cm)^{-1}$ at room temperature.

(iii) Therefore, the μc-SiGe films that we produce in the present research show transport characteristics comparable to the sintered SiGe materials for thermoelectric application.

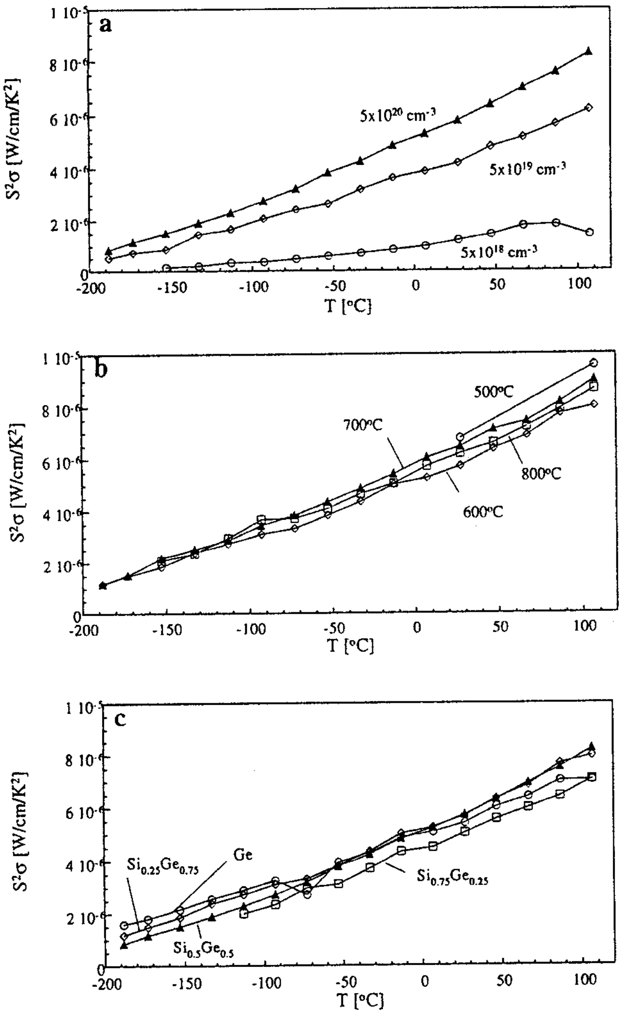

Figure 5. Power efficiency factor of Si$_{1-x}$Ge$_x$ films having different Boron concentration, after 600°C/1h annealing (a), films with [B]=5·10^{20}cm^{-3} crystallized at different temperatures (b) and having different Ge content, annealed at 600°C/1h and containing [B]=5·10^{20}cm^{-3} (c).

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