Materials Science in Semiconductor Processing xx (xxxx) xxxx–xxxx

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

$Si_{1-x}Ge_x$ bulk single crystals for substrates of electronic devices

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ARTICLE INFO

Keywords:
Growth from solution
Traveling solvent zone growth
Germanium silicon alloys
Hole mobility
Substrate

ABSTRACT

$Si_{1-x}Ge_x$ bulk crystals ($0.2 < x < 0.85$) with various B doping levels were grown by the traveling liquidus zone (TLZ) method for fabricating substrates of high mobility electronic devices. Large single crystals with a diameter ranging from 30 to 50 mm were achieved. $Si_{1-x}Ge_x$ crystals were characterized by measuring concentration profile along and perpendicular to the growth axis, indicating good compositional homogeneity. High crystalline quality was evaluated by electron backscatter spectroscopy and X-ray diffraction. Measured hole mobility was higher than the previously reported data for the similar dopant concentration and Ge content, suggesting smaller alloy scattering effects and high crystalline nature in the TLZ-grown $Si_{1-x}Ge_x$ bulk crystals.

1. Introduction

$Si_{1-x}Ge_x$ bulk single crystals are promising substrate materials for high mobility electronic devices [1]. When Si or Ge thin films are epitaxially grown on $Si_{1-x}Ge_x$ substrates, they are strained due to lattice mismatch between Si or Ge and $Si_{1-x}Ge_x$. The strained n-channel Si and strained p-channel Ge have higher mobility than unstrained ones. The mobility of the tensile strained Si n-channel on the $Si_{0.5}Ge_{0.5}$ substrate is reported to be 3500 cm^2/Vs [2]. On the other hand, the mobility of the strained Ge p-channel on the $Si_{0.5}Ge_{0.5}$ substrate is expected to be about 5000 cm^2/Vs [3], which is one order higher than that of the untrained p-channel Si. For example, strained p-channel Ge QWFETs on the $Si_{0.7}Ge_{0.3}$ buffer layer were fabricated [4]. However, the hole mobility of the fabricated FET was about 770 cm^2/Vs, which was considerably lower than the expected value. The reason why the high mobility was not achieved is a bad crystallinity of the $Si_{1-x}Ge_x$ buffer layer. It is well known that many 60° dislocations are caused when $Si_{1-x}Ge_x$ buffer layers are grown on Si substrates [5] and mosaic structure is produced in the buffer layer [6]. This mosaic structure deteriorates the uniformity of the strain in the epitaxially grown films [7]. Therefore, mosaic free high quality $Si_{1-x}Ge_x$ bulk single crystals are strongly required as substrates. However, growth of homogeneous bulk single crystals is very difficult due to large separation between the liquidus and the solidus lines in the phase diagram [8]. For overcoming this difficulty, many crystal growth methods were investigated [9–11], but compositionally uniform $Si_{1-x}Ge_x$ bulk single crystals were not grown. We investigated the crystal growth in space by suppressing convection in a melt. In the course of the study, we have invented a new crystal growth method named the traveling liquidus-zone (TLZ) method [12,13] to grow homogeneous $Si_{1-x}Ge_x$ crystals [14]. We have increased the crystal diameter with improving the crystal quality [15,16]. It is noted that the systematic study of mobility as a function of Ge content and doping level is needed to characterize electronic properties of $Si_{1-x}Ge_x$ crystals [17]. Therefore, we grew various Ge content $Si_{1-x}Ge_x$ bulk crystals with various B doping level. Here, we report results of $Si_{1-x}Ge_x$ bulk crystal growth experiments by the TLZ method and characterization of crystal quality.

2. Experiments

The TLZ method is a kind of zone melting method but is different from the conventional one in forming a melt zone at a relatively low temperature gradient [13]. In the TLZ method, low melting temperature (T_{ml}) material is sandwiched between high melting temperature (T_{mh}) materials and a melt zone is formed by heating the constituent materials at temperatures higher than T_{ml} and lower than T_{mh} by imposing a temperature gradient (Fig. 1(a)). Whereas, in the conventional zone melting method, a steep temperature gradient is imposed and small part of the raw material where heated temperatures exceed its melting temperature (T_m) is melted for melt zone formation (Fig. 1(b)). In the $Si_{1-x}Ge_x$ crystal growth, low melting temperature Ge is sandwiched between a Si seed and a Si feed. The melting temperature of Si is 1414 °C. They are inserted in a crucible and the crucible is sealed in a quartz ampoule in vacuum at about 1×10^{-5} Pa. When the ampoule is heated to around 1100 °C in a temperature gradient furnace, Ge is melted since its melting temperature is 938 °C

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http://dx.doi.org/10.1016/j.mssp.2016.10.012
Received 28 June 2016; Received in revised form 4 October 2016; Accepted 10 October 2016
Available online xxxx
1369-8001/

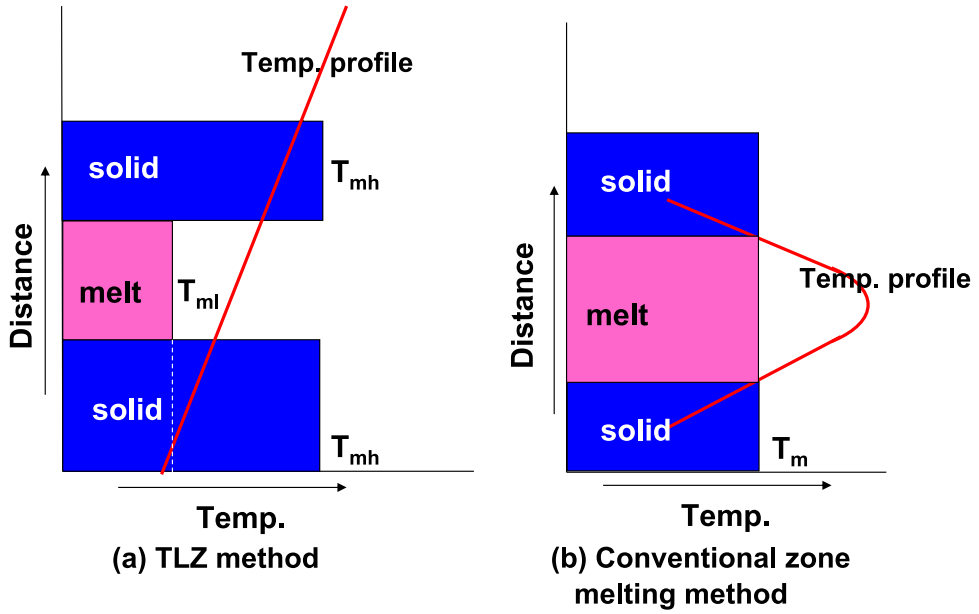

Fig. 1. Schematic diagram showing the difference of zone forming method: (a) TLZ method, (b) conventional zone melting method. A melt zone is formed by steep temperature gradient in the conventional zone melting method, while a melt zone is formed at low temperature gradient of 5–10 °C/cm in the TLZ method.

and a melt zone is formed. The melted Ge dissolves part of the adjacent solid Si on both sides. At two interfaces, the seed-melt interface (the growth interface) and the melt-feed interface (the dissolving interface), Si concentration is saturated due to coexistence of solid and liquid phases, namely the liquidus concentration is realized. When the melt zone width is narrow enough and the imposed temperature gradient is low enough, i.e. 5–10 °C/cm, the whole of the melt zone is almost saturated with Si and liquidus concentration is realized. This means that the concentration gradient corresponding to the temperature gradient is formed in the melt zone. The concentration gradient causes inter diffusion between Ge and Si in the melt zone. As noted by the phase diagram [8], Ge is richer at the lower temperature seed side. Therefore, when Ge is transported to higher temperature feed side by diffusion, the Si concentration exceeds its equilibrium concentration (supersaturated) and a $Si_{1-x}Ge_x$ crystal begins to grow on a Si seed. The composition of the grown crystal corresponds to the solidus composition at the growth interface temperature. Ge is segregated upon crystallization because the segregation coefficient is less than 1 [8], and the segregated Ge is transported away from the growth interface by diffusion to the higher temperature side and the transported Ge dissolves the feed Si at the dissolving interface. Thus, crystal growth proceeds spontaneously by diffusion and the melt zone shifts towards higher temperature feed side. When we keep the growth interface temperature constant by translating a sample device or a heater zone relatively in accordance with the growth rate, we can grow compositionally uniform crystals. Since the melt zone composition almost coincides with that of the liquidus throughout the zone and crystals were grown by traveling the zone, we named the new crystal growth method as “traveling liquidus zone method”.

$Si_{1-x}Ge_x$ crystals with 30–50 mm diameter and various Ge content ($0.2 < x < 0.85$) were grown at temperature gradients of 5–7 °C/cm. The sample translation rate was 0.1 mm/h. According to the one dimensional TLZ growth model [18], temperature gradient of 7 °C/cm gives spontaneous crystal growth rate of 0.1 mm/h for the composition $Si_{0.5}Ge_{0.5}$ [14]. The growth rate varies when the temperature gradient and/or composition of the grown crystal are changed. However, the difference is very small for the compositional variation and it is 40% for the temperature gradient change from 5 to 7 °C/cm. Therefore, the sample translation rate was fixed at 0.1 mm/h for all growth experiments. The setting accuracy of furnace temperatures was ± 1 °C and the freezing interface temperatures were controlled within ± 3 °C. For growing a $Si_{0.5}Ge_{0.5}$ crystal, the freezing interface temperature was set at 1110 °C and for a $Si_{0.4}Ge_{0.6}$ crystal it was set at 1068 °C. Since the growth rate was about 0.1 mm/h, it required more than 200 h for growing crystals longer than 20 mm. For higher temperature gradients, higher growth rates are realized. However, temperature gradients were set below 7 °C/cm because high temperature gradients degrade crystal quality [19]. Boron doping level was controlled by the doping level of the Si seed and crucible materials. When a boron nitride crucible was used higher doping level (10^{17}–10^{19} cm^{-3}) was detected and when a quartz crucible was used lower doping level (10^{14}–10^{15} cm^{-3}) was realized. Orientation of a Si seed was ⟨100⟩.

Grown crystals were cut parallel or perpendicular to the growth axis and square plates or disc samples were prepared. After mirror polishing of the surface of thus prepared samples, the composition, crystal quality, hole mobility and B concentration were evaluated. For compositional analysis, electron probe micro analyzer (EPMA) was used. Acceleration voltage of 20 kV, irradiation current of 20 nA and beam spot size of 30 nm were applied. Measurement accuracy is ± 0.1 at% for both Si and Ge concentration. Electron backscatter diffraction (EBSD) was used for crystal orientation analysis. Acceleration voltage was 25 kV and irradiation current was 0.5 nA. Orientation of a grown crystal was determined within an error of ± 2°. X-ray diffraction (XRD) was applied for crystal quality evaluation. Cu Kα X-rays from a generator operated at 40 kV, 30 mA were monochromated by a four-crystal Ge (440). In the ω-scanned rocking curve measurements, the spot size was 1×10 mm^2 and the total accuracy was ± 14″. Boron concentration was measured by secondary ion mass spectroscopy (SIMS). Beam voltage of 3 kV and bean current of 100 nA were applied. Raster size was 300×300 μm^2. Measurement accuracy was dependent on B concentration. It was described with the respective measured concentrations. Hole mobility was measured by Van der Pauw method. Square samples with a side length between 8 and 10 mm and thickness between 80 and 100 μm were used. The errors for the Hall data are ± 2%. All of the measurements were made at room temperature.

3. Results and discussion

An outer view and a cross sectional view of a grown crystal are shown in Fig. 2(a) and (b). The seed part, grown crystal part, quenched melt part, and feed part are indicated in the figure. The seed/crystal interface is clear in the cross sectional view as well as in the outer view.