Crystallization of $Si_{1-x}Ge_x$ alloy semiconductor during rapid cooling for thermoelectric applications

$Si_{0.7}Ge_{0.3}$ was prepared by rapid (~330 °C/min) and slow cooling (1 °C/min) for thermoelectric applications. Despite of various cooling rates, the EBSD pattern revealed almost same grain structure of both samples. To understand the reason, crystal growth of $Si_{0.7}Ge_{0.3}$ sample was in-situ observed under rapid and slow cooling. The initially grown fine dendrites were re-melted and recrystallized under rapid cooling. The re-melting was not observed under slow cooling. The re-melting and recrystallization are responsible for same grain structures in the alloy.

Rapid cooling of alloys will result polycrystalline material with fine grain structures since large number of nucleation instantaneously forms under rapid cooling as observed in various alloy materials [1]. Therefore, the rapidly cooled $Si_{1-x}Ge_x$ is expected to have fine grain structures with relatively low variations of Ge composition and thereby the thermoelectric performance can be further improved. However, such kind of rapid crystallization experiments of $Si_{1-x}Ge_x$ alloy is not reported in detail except few molecular dynamics simulations of quenching of Si-Ge alloy [2].
Therefore, in the present work we have investigated the growth process of Si-rich $Si_{1-x}Ge_x$ (x=0.1, 0.2 and 0.3) under rapid cooling to realize the fine grain structures for high thermoelectric performance. The crystallized $Si_{0.7}Ge_{0.3}$ samples were analyzed by EDX and EBSD to study the compositional variation and grain structures.

Figure 1 shows the EBSD patterns of $Si_{0.7}Ge_{0.3}$ samples grown under rapid (a) and slow cooling (b) process. In contrast to the expectation, the grain size and structures are almost the same for both crystals even though the cooling rate in the rapid cooling experiment is more than 300 times faster than that in the slow cooling experiment.

To know the reason for the similar grain structures, crystal growth of $Si_{0.7}Ge_{0.3}$ was performed under rapid cooling and the growth process was in-situ observed using high speed microscopic camera with recorder. Further, the experiments were repeated by varying the Ge composition as 0.2, and 0.1. Moreover, the crystal growth of $Si_{1-x}Ge_x$ (x=0.1, 0.2 and 0.3) was performed under slow cooling with the cooling rate of 1°C/min and the growth process was in-situ observed for comparative analysis.

Figure 2 shows the snapshots recorded during the in-situ observation of crystal growth process of $Si_{0.7}Ge_{0.3}$ and Si under rapid cooling. The first and second rows of

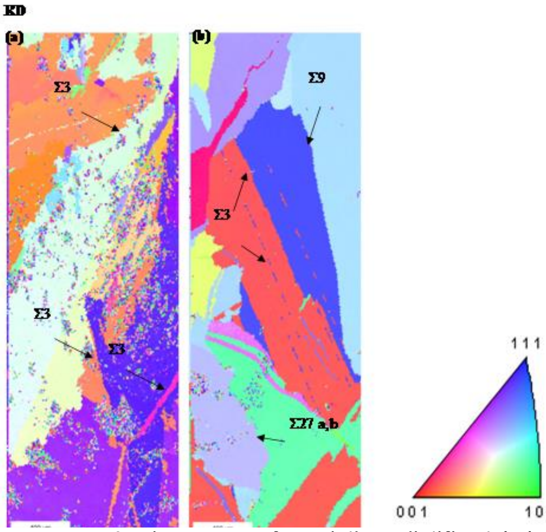

Figure 1: EBSD images of rapidly solidified (a) and slowly solidified (b) $Si_{0.7}Ge_{0.3}$ sample with colored standard triangle of orientations.

the images show the crystal growth process of $Si_{0.7}Ge_{0.3}$ at different time periods. Fine dendrites are started to grow nearly 26 seconds after shut downing the power of the heaters. The dendrites are rapidly grown for a short period of 3 seconds and started to re-melt as observed in the snapshot at 30 seconds. The re-melting is continued up to 45 seconds and completely re-melted at 50 seconds. Finally, the recrystallization is observed nearly after 70 seconds as shown in second row of Fig.2. The third row of Fig.2 show the snapshots of growth process of Si at different time periods. Two dendrites are grown under the observed area and the size of the dendrites increased with time without re-melting. From the in-situ observation experiments, it is obvious that the initially gown fine dendrites of Si0.7Ge0.3 completely re-melted under rapid cooling.

The dendrites are easily formed under rapid cooling as well as slow cooling in $Si_{1-x}Ge_x$ samples. Whereas the dendrites

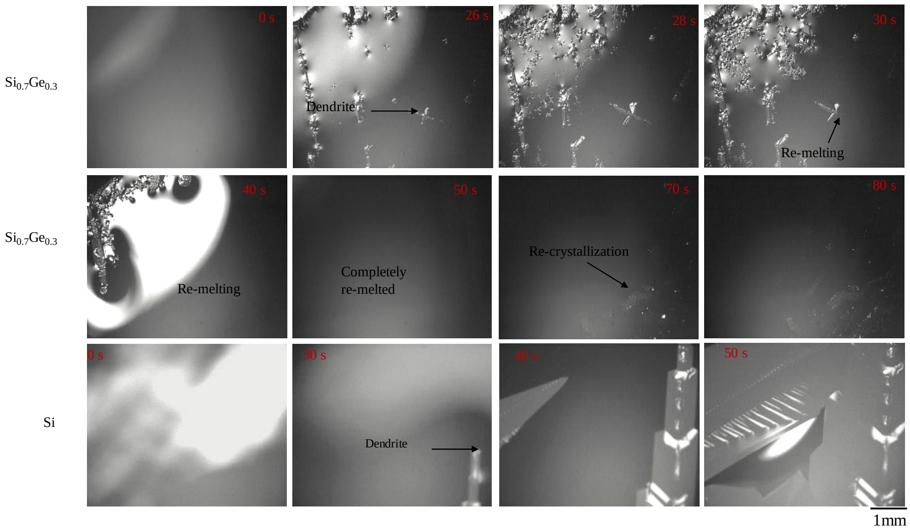

Figure 2: Snapshot images of Crystal/melt interface of $Si_{0.7}Ge_{0.3}$ and Si at different time. Re-melting is clearly indicated in the images.

are formed in Si during the rapid cooling alone and flat interface with no dendrites are observed under slow cooling. From our previous reports it is cleared that the dendrites are formed through twin boundaries [3]. The present results suggest that the formation energy of twin boundaries may be relatively low in $Si_{1-x}Ge_x$ compared to Si and thereby the dendrites are easily formed in $Si_{1-x}Ge_x$ even under slow cooling process. However, further experimental results are needed to confirm the same. Moreover, the similar grain structures of $Si_{1-x}Ge_x$ under rapid cooling as well as slow cooling is mainly attributed due to re-melting of initially grown fine dendrites and recrystallization at relatively low temperature.

<u>References</u>

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List of Publications:

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