Growth of $CaSi_2$ layers on Si substrates induced by Kirkendall void formation

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Introduction: The $CaSi_2$ is one of template materials to form Si nanosheets for the application to Li ion batteries [1]. Even though the Ca atoms extracted from $CaSi_2$, the 2D silicon backbone is maintained [2]. Therefore, to extract the Ca atoms from $CaSi_2$, electrochemical methods in solutions or CVD methods using chloride vapor have been investigated [3−5]. It has been also reported that $CaSi_2$ layers were epitaxially grown on Si substrates. It is expected that Si nanosheets rooted to the substrates can be gown using $CaSi_2$ layers prepared on Si substrates. To obtain high quality Si nanosheets, it is important to grow structurally controlled $CaSi_2$ layers on the Si substrates. On the other hand, the Kirkendall-effect related processes have been recognized as one of the useful methods to fabricate nano- and micro-sized structures [6]. In this study, the formation of $CaSi_2$ layers on Si substrates by Kirkendall effect was examined, and the structural property of the resulted $CaSi_2$ was clarified.

Experiment: $CaSi_2$ layers are grown by exposure of Si substrate to Ca flux. Chemical treatment of the Si substrates before the growth was shown elsewhere [7]. Ca source and Si substrate were located at the bottom of a quartz container and loaded into a high vacuum chamber. Then, the container was heated up to 620 °C and kept for 1 h, then additional thermal treatment was followed at 650 °C for typically 10 min.

Results and Discussion: Figure 1 (a) and (b) show SEM images of a Ca-silicide layer on the Si (111) substrate. It is found that Kirkendall voids were formed between the Si substrate and the upper CaSi layer, and the $CaSi_2$ were grown around the voids. The plan view of the surface shows the surface morphology of the $CaSi_2$ on the Si substrate after the removal of the upper CaSi layer. Figure 1(c) and (d) show cross sectional TEM images of the $CaSi_2$ and the Si substrate. It is found that $CaSi_2$ were grown with the epitaxial relationship of $CaSi_2\{00.1\}$ //Si{111} as shown in Figs.1(c) and (d).

The thermal treatment temperature and treatment time dependences of structural and morphological properties of the $CaSi_2$ was also investigated. In addition, the substrate orientation dependence of the morphological and structural properties of $CaSi_2$ will be shown. Moreover, the growth evolution of the $CaSi_2$ domains will be discussed.

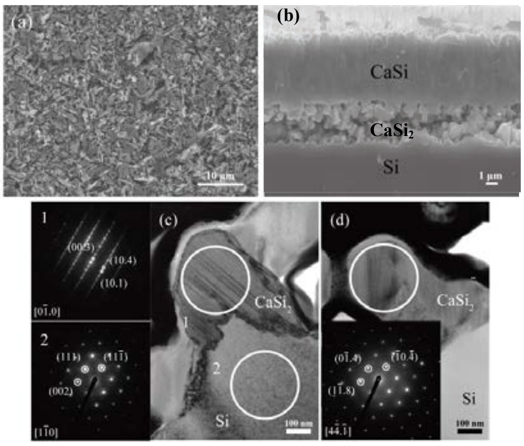

Fig.1 (a) Plan and (b) cross-sectional SEM images of $CaSi_2$ grown on Si substrates, (c),(d) TEM images of $CaSi_2$ and Si substrates. SAD patterns are also shown.

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