Formation of various epitaxial nanodots in Si films for thermoelectric materials

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Abstract. Nanostructures are expected to enhance thermoelectric properties of Si-based materials. For enhancement, the simultaneous achievement of low $\kappa$ and high $\sigma$ is required. In our previous study, we have demonstrated drastic reduction of $\kappa$ in Si by introducing epitaxial connected Si NDs resulting in the smallest $\kappa$ in Si. We have also reported that Si films containing Ge NDs exhibited the bulklike $\sigma$ and the drastic $\kappa$ reduction compared with that of bulk Si. However, $S$ was not controlled in this nanostructure. In general, introduction of interfaces or high $S$ materials can increase $S$ of the total film. In addition to control of $\kappa$ and $\sigma$, $S$ can be controlled by tuning the material and size of NDs. In this work, we developed the formation method of the various material and size of introduced NDs.

1. Introduction

Thermoelectric conversion has been attracted as one of the energy harvestings. Thermoelectric conversion efficiency depends on dimensionless figure of merit $ZT (=S^2\sigma T/\kappa)$. $S$ is Seebeck coefficient, $\sigma$ is electrical conductivity, $\kappa$ is thermal conductivity and $T$ is absolute temperature. For its enhancement, $ZT$ has to be increased. The conventional approach to enhance $ZT$ is to use heavy elements (Te, Pb, etc.) for $\kappa$ reduction while maintaining high $\sigma$. However, these materials are often composed of rare metals, which are high cost and toxic. On the other hand, Si-based materials, which are eco-friendly and low cost materials, indicated high $\kappa$ because they are composed of light elements, resulting in low $ZT$. Therefore, they are now very far from practical use.

Recently, introducing nanostructures has been expected to enhance thermoelectric performance of Si based materials. Nanostructuring was expected to cause phonon scattering, resulting in $\kappa$ reduction. We have demonstrated drastic reduction of $\kappa$ in Si by introducing epitaxial connected Si NDs resulting in the smallest $\kappa$ in Si [1]. We have also reported that Si films containing Ge NDs exhibited the bulk-like $\sigma$ and the drastic $\kappa$ reduction compared with that of bulk Si. In this structure, epitaxial Ge NDs worked as phonon scattering centers and epitaxial Si layers worked as electric conduction layers. This result indicated the possibility of the independent control of the thermal and electric conductivities [2,3]. However, $S$ was not controlled in this nanostructure. In general, introduction of interfaces or high $S$ materials can increase $S$ of the total film. In addition to control of $\kappa$ and $\sigma$, $S$ can be controlled by tuning the material and size of introduced NDs. In this work, we developed the formation method of the various material and size of NDs.

2. Experimental

We fabricated three types of Si films containing different NDs (Ge, Si, $\beta$-FeSi₂) on undoped Si substrates (>1000 $\Omega$cm). Si substrates were introduced into molecular beam epitaxy chamber after chemical treatment. Clean Si surfaces were formed by depositing Si buffer layer at 550 °C. Ultrathin SiO₂ films were formed on clean Si surfaces by oxidizing at 600 °C at $2\times10^4$ Pa, and then nanowindows were formed in the ultrathin SiO₂ films by depositing 1 monolayer of Ge or Si ($Si + SiO₂ \rightarrow 2SiO↓$ or $Ge + SiO₂ \rightarrow GeO↓ + SiO↑$). Then, epitaxial Ge, Si or $\beta$-FeSi₂ NDs were formed by depositing Ge, depositing Si or codepositing Fe and Si ($Fe : Si =1 : 2$) [4-6]. Epitaxial Si layers were then formed on NDs by Si deposition. By repeating these formation processes: the ultrathin SiO₂ film,
NDs, and Si layers (= one formation cycle), we fabricated Si films containing various NDs. At these processes, we conducted in-situ observation of the surface structures by reflection electron diffraction (RHEED) and performed ex-situ observation of the samples by scanning transmission electron microscopy (STEM).

3. Results and Discussion
Figures 1 (a)-(c) show the RHEED patterns of Ge, Si and β-FeSi2 NDs of first formation cycle, respectively. These patterns indicated epitaxial growth of (001)Ge/(001)Si, (111)Si// (111)Si and (110)β-FeSi2// (111)Si or (101)β-FeSi2// (111)Si. Ge, Si and β-FeSi2 NDs samples were fabricated by repeating 8, 6 and 6 formation cycles. We confirmed epitaxial growth of these NDs continued.

We fabricated the larger size β-FeSi2 NDs (36 ML) than our previous study (18 ML, 10 nm)[6]. The cross-sectional STEM image of β-FeSi2 NDs (36 ML) sample was shown in Fig. 2. We found that multilayered structures of β-FeSi2 NDs /Si layers were formed, and that the ND size was about 20 nm, which is larger than our previous study[6]. The epitaxial relationship of (110)β-FeSi2// (111)Si or (101)β-FeSi2// (111)Si was also confirmed by fast Fourier transformation analysis of STEM images.

In general, formation of stacking structure of NDs is difficult due to the silicidation. However, in the case of the present formation using ultrathin SiO2 film, ultrathin SiO2 films can work as barrier of intermixing, resulting in the success in the formation of stacking structure of various NDs.

4. Conclusion
We fabricated various epitaxial nanodots in Si films. The formation of Ge, Si and β-FeSi2 NDs samples was confirmed by RHEED and STEM. Also, large size β-FeSi2 NDs sample was controlled by large deposition amount.

These various structures can be expected to show various thermoelectric properties.

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Figure 1. RHEED patterns of (a)Ge, (b)Si, and (c)β-FeSi2 NDs at first cycle.
Figure 2. STEM image of $\beta$-FeSi$_2$ NDs (36 ML) samples

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