

# Control of Nano Structure by Multi Films for Nano-structured Thermoelectric Materials

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Thermoelectric generators, with which one can directly convert waste heat to useful electric power, have attracted considerable attention as one of the most efficient techniques leading to a low carbon, sustainable society. The figure of merit  $ZT$  of constituent thermoelectric materials is generally used as a measure for the efficiency of energy conversion in TE generators, and its value has not reached a large magnitude exceeding 2 for the last half century, despite that  $ZT \geq 4$  is strongly required for automobile exhaust heat utilization system. This large gap between the required values and obtained ones strongly let us believe that a thermoelectric generator is not usable in practical applications. We need to employ new, innovative techniques leading to a breakthrough for developing high-performance thermoelectric materials. In this study, we tried to control nano-structured particles in amorphous thermoelectric materials so as to drastically improve the thermoelectric properties by means of molecular beam epitaxy for obtaining high performance thermoelectric materials.

Keywords: thermoelectric materials, nano-structured thermoelectric, quantum effect

## 1. Introduction

For constructing an energy-saving, sustainable society, it is necessary to reduce the consumption of fossil fuels and the emission of CO<sub>2</sub> gas. Thermoelectric materials can generate electric power (electric energy) from waste heat (thermal energy), and have been drawing attention as one of the most efficient techniques for energy utilization.

The efficiency of energy conversion  $\eta$  in thermoelectric generators is an increasing function of the dimensionless figure of merit  $ZT = S^2\sigma T/\kappa$  of component materials.\*<sup>1</sup> Here  $S$ ,  $\sigma$ ,  $\kappa$ , and  $T$  represent the Seebeck coefficient,\*<sup>2</sup> electrical conductivity, thermal conductivity and absolute temperature, respectively. It is, therefore, of great importance to develop materials possessing a large magnitude of  $ZT$  for obtaining a large  $\eta$ . Note here that the value of  $ZT$  is 1 to 2 for the practical materials, with which  $\eta$  becomes approximately equal to 10%. In sharp contrast to the practical values,  $ZT \geq 4$  is required<sup>(1)</sup> to effectively improve the fuel efficiency in automobiles.

The control of  $ZT$  is a main target in developing thermoelectric materials. The Seebeck coefficient, electrical conductivity, and electron thermal conductivity are determined by the electronic structure, such as the density of states and group velocity in the vicinity of the Fermi level.<sup>(3),(4)</sup> Therefore, the performance of thermoelectric materials and devices would be improved using techniques leading to the variations in electronic structure.

It was therefore proposed that a quantum well, quantum wire, or quantum dot (nano-particles) that affect the electronic structure are usable for making variations in electronic structure to control thermoelectric properties.<sup>(5)-(8)</sup> However, adequate improvement in  $ZT$  by the quantum effect\*<sup>4</sup> has not been reported yet.<sup>(8)-(14)</sup> Small volume fraction of nano-structures\*<sup>3</sup> could be one of the reasons for the absence of significant effects on the thermoelectric properties. It might be also related with the inappropriate energy range of quantum states that is far apart from the Fermi level. The

absence of quantum states due to the too large size of particle could be also one of the reasons,<sup>(10),(15),(16)</sup> because the experimentally obtained diameter of nano-particles is ~5 nm, while a smaller particle size of 3 nm or less is required for the formation of quantum states.<sup>(5)-(7),(11)</sup>

These considerations let us strongly believe that the precise control of both the volume fraction and size of nano-particles is of great importance to achieve the sufficient increase of  $ZT$  with the quantum effect.

Recently, Makino and Okamoto et al. reported that the heat treatment of amorphous thermoelectric materials enables us to obtain densely precipitated nano-particles<sup>(15)-(17)</sup> in the amorphous phase. More recently, Okamoto et al. reported that a significant increase in the Seebeck coefficient was realized with the metallic electrical conduction kept when a super-lattice consisting of amorphous Si and amorphous Ge, in both of which a small amount of Au was doped, were annealed with the appropriate conditions.<sup>(18)</sup> In this thermoelectric thin film, however, the size and volume fraction of the nano structure were not sufficiently controlled, resulting in poor reproducibility.<sup>(19)</sup> The typical particle diameter were ~5 nm, and the volume fraction was ~10%.<sup>(15),(16),(18)</sup>

According to the reported facts, we tried in this study to control the diameter and volume fraction of nano-particles more precisely on the basis of the thin-film multi-layering technology.<sup>(20)</sup>

## 2. Nano Structures in Si/Ge Thin Films

### 2-1 Experimental method

We deposited ~1 nm of Si, ~1 nm of Ge, ~0.1 nm Au, and ~1 nm Ge in this sequence on the sapphire substrate by means of molecular beam epitaxy (MBE). The thickness of Au was determined so as the overall composition of Au to become 3%. This set of layers was repeatedly deposited

until the total film thickness became ~220 nm. We then annealed the thin-films at 300, 400, or 500°C for 15 minutes for making the size-controlled Si-Ge nano-particles precipitated in the samples. The crystalline Si-Ge nano-particles of a few nm in diameter were homogeneously scattered in the amorphous SiGe (a-SiGe), as schematically drawn in Fig. 1.

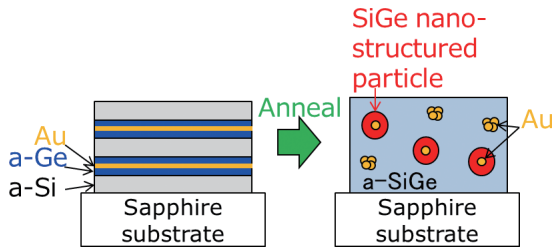


Fig. 1. Concept-figure of the formation of nano-structure

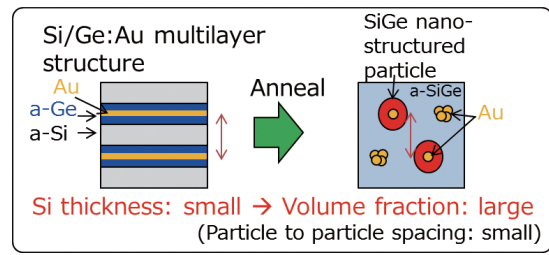
The averaged diameter of the nano-particles were evaluated by the full width at half maximum of X-ray diffraction and transmission electron microscope (TEM), and the volume fraction by Raman scattering measurement. Since these crystalline nano-particles were embedded in the amorphous phase, the volume fraction of crystals, which was determined from the Raman scattering data, represented that of nano-particles.

### 2-2 Experimental results

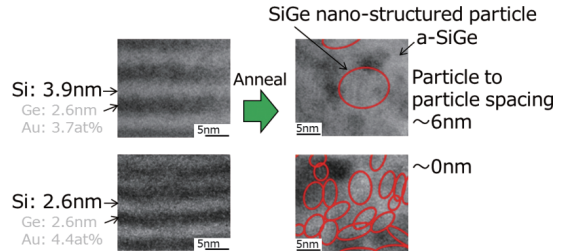
As the first step, we tried to gain deep insight into the mechanism of the formation of nano-particles for precisely controlling their size. Since the eutectic temperature of Au-Ge systems are 356°C, each Au layer would be easily mixed with the surrounding Ge-layers to form crystalline particles. This phenomena is known as the metal induced crystallization.<sup>(16)</sup> The Ge-Au nano-particles would incorporate Si atoms from the surrounding amorphous matrix to form the Si-Ge-Au nano-particles. If this speculation were valid, the volume fraction of the nano-structured particles could be controlled by the thickness of Si layers as schematically shown in Fig. 2.

In order to quantitatively evaluate the volume fraction of nano-particles, the estimated volume fraction was plotted as a function of Si thickness (Fig. 3). The volume fraction of the nano-structured particles linearly decreased with increasing thickness of the Si layer, provided that the thickness of the amorphous Ge layer was kept constant. The same tendency was observable for the Ge-layer's thickness dependence. By carefully considering these tendencies, we tried to derive an empirical equation for predicting the diameter and volume fraction of the nano-particles for precisely controlling.

Si-Ge nano-particles presumably formed during the mixing of Ge-Au nucleus and the surrounding Si. We firstly assumed that the nucleation occurs only at the Au-Ge mixing but the further nucleation is negligibly small at the mixing of Au-Ge nucleus and surrounding Si. This is explained, in other words, that an increase in the volume fraction is predominated by the growth of existing nano-particles



(a) Plan of controlling volume fraction of nano-particles



(b) Example of cross-sectional TEM showing an example of controlling volume fraction of nano-particles

Fig. 2. Plan of controlling volume fraction of nano-particles and an example of cross-sectional TEM

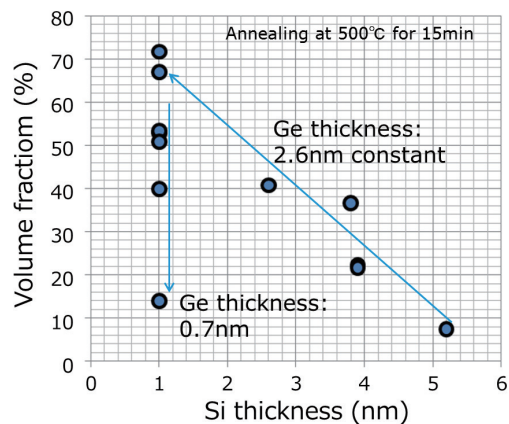


Fig. 3. Volume fraction of nano-particles dependence on Si thickness

rather than the nucleation. We also assumed that the particle size of the SiGe crystal has a limit. On the basis of these assumptions, we propose the following equation to describe the time evolution of the diameter,  $\phi$ , of the nano-particles.

$$\frac{d\phi(t)}{dt} = c \cdot CAu \{a \cdot (R_{Si/Ge})^b - \phi(t)\} \quad \dots \dots \dots (1)$$

Increasing rate is proportional to Au composition  $C_{Au}$ .

Nucleus that can be crystallized

Max. value to which particles can increase (The power of b is to make Si/Ge ratio an appropriate parameter ratio.)

Already crystallized particle (This is enlargement.)

Here  $\phi$ ,  $t$ ,  $C_{Au}$ ,  $R_{Si/Ge}$ ,  $a$ ,  $b$ , and  $c$  represent the particle diameter, the annealing time, the Au concentration, the Si/Ge ratio, the correction coefficient, the multiplier correction factor, and the parameter of particle diameter increase, respectively. When this equation is solved, the time evolution of particle diameter,  $\phi$ , is given by the following equation.

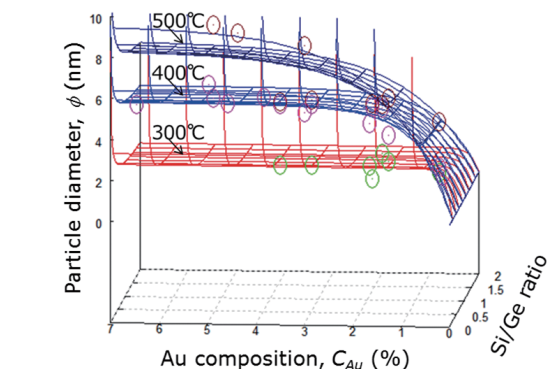
$$\phi(t) = a \cdot (R_{Si/Ge})^b \{1 - \exp(-c \cdot C_{Au} \cdot t)\} \dots\dots (2)$$

Equation (2) suggests that the particle diameter,  $\phi$ , increases with the annealing time,  $t$ , and has a limit value. It should be also mentioned that the increasing rate depends on Au concentration,  $C_{Au}$ . The volume fraction,  $\eta$ , is deduced from the following equation because nucleation was not assumed during the grain growth.

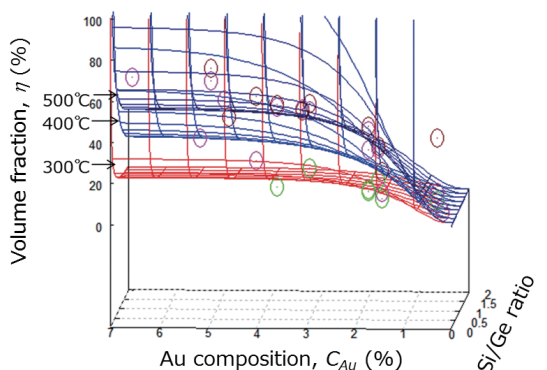
$$\eta(t) \propto \phi(t)^3 \dots\dots\dots (3)$$

Since we fixed annealing time  $t = 15$  minutes in the present experiments, the particle diameter,  $\phi$ , and volume fraction,  $\eta$ , should be a function of the Au concentration,  $C_{Au}$ , and Si/Ge ratio,  $R_{Si/Ge}$ .

In order to confirm the validity of those equations, the particle diameter and volume fraction of the specimens annealed at 300, 400, and 500°C for 15 min each were plotted in Fig. 4 (a) and (b) as a function of  $C_{Au}$  and  $R_{Si/Ge}$ . We also performed the function fitting with using  $a$ ,  $b$ , and



(a) Diameter of nano-structured particles vs. Au composition and Si/Ge ratio



(b) Nano-structured particles' volume fraction vs. Au composition and Si/Ge ratio

Fig. 4. Control of the diameter and volume fraction of nano-structured particles

$c$  as the fitting parameters. The measured values and function show good consistency, indicating that the size and volume fraction of nano-particles in the Si-Ge-Au thin films can be quantitatively predicted within the fitting range, that is, the particle diameter is 3 nm or more and the volume fraction is 20% or more.

For developing high performance Si-Ge-Au thermoelectric materials, we have to reduce the lattice thermal conductivity and optimize the electron transport properties through the electronic structure. For this purpose, we precisely managed the nano-structure of Si-Ge-Au alloys using Eqs. (3) and (4).

Figure 5 shows the relationship between the thermal conductivity and the size of nano-particles. Thermal conductivity drastically and linearly decreased with reducing size of nano-particles. The contribution of electron thermal conductivity,  $\kappa_{ele}$ , was roughly estimated using the Wiedemann-Franz law,<sup>\*5</sup> i.e.  $\kappa_{ele} = LT\sigma$  ( $L$  is Lorentz constant,  $L = 2.44 \times 10^{-8}$  W/SK<sup>2</sup>, and  $T = 300$  K). As a result,  $\kappa_{ele}$  was estimated to be  $\sim 0.02$  W/mK. This value is much smaller than the minimum lattice thermal conductivity of 0.2-10 W/mK.<sup>(21)</sup> Therefore, it can be argued that the contribution of the electron thermal conductivity is small enough to be ignored, and the contribution of the lattice thermal conductivity is predominant. Thus, it is definitely proved that the nano-particles effectively scatter the wave packet of phonons, and that we can manage the lattice thermal conductivity of Si-Ge-Au thermoelectric thin films.

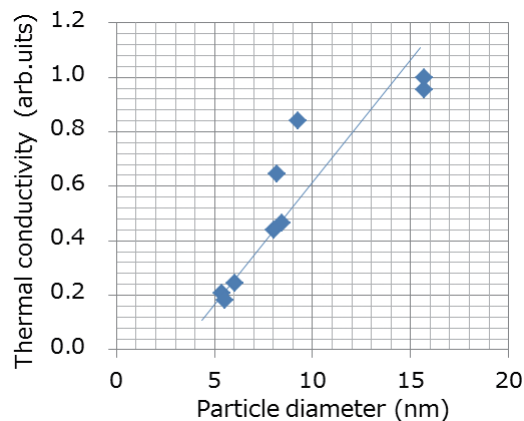


Fig. 5. Thermal conductivity vs. particle diameter

Finally, we mention here the Seebeck coefficient and the electrical conductivity of the present samples (Fig. 6). The measured data were plotted in Fig. 6. Generally speaking, the electrical conductivity decreases when the Seebeck coefficient increases. This tendency was observable in the present samples. However, we should stress here that the slope of curvature was much smaller than the ordinary case and the electrical conductivity dependence of the Seebeck coefficient becomes negligibly small in the highest electrical conductivity region. Although the mechanism is not very clear now, the present samples are char-

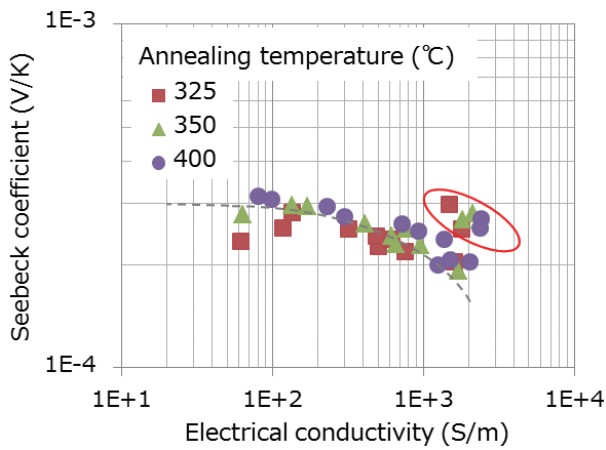


Fig. 6. Thin film's Seebeck coefficient vs. electrical conductivity (at room temperature)

acterized by this tendency.

We should also emphasize that a group of samples exist in the area surrounded by the red line. These samples do not follow the universal line. This variation of the data should be accounted for with the finite variation in the electronic structure near the Fermi level. The modified size and volume fraction of nano-particles definitely led to the variation of the electronic structure to significantly affect the electron transport properties.

We are now loaning to reveal the variation of the electronic structure near the Fermi level caused by the nano-particles by means of ultra-high-resolution photoemission spectroscopy and low temperature specific heat measurements. The results must provide us with the guiding principle for significantly increasing the power factor.

### 3. Conclusion

In this study, in order to construct a guiding principle for controlling the thermoelectric properties of Si-Ge-based alloys, we tried to manage the grain size and volume fraction of nano-particles precipitated in the amorphous phase. Empirical equations were proposed for describing the grain size and volume of nano-particles, and the proposed equations showed good consistency with the experimentally determined values. This means that we can manage the nano-structure in the Si-Ge-Au thin films. We also found that the lattice thermal conductivity is a function of the grain size. The variation of electron transport properties was not able to be accounted for with the rigid band model but with a finite variation of electronic structure near the Fermi level. These results definitely indicate that we can manage both the electron transport properties and lattice thermal conductivity by using the controllable nano-structure.

In the future, we plan to identify the variation of the electronic structure using ultra-high-resolution photoemission spectroscopy. These results must provide us with the guiding principle for significantly increasing the figure of merit  $ZT$ .

## 4. Acknowledgments

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### Technical Terms

\*1 Dimensionless figure of merit,  $ZT$ : A dimensionless figure representing the performance of a material directly connected to the efficiency by which heat is converted into electricity. The efficiency of thermoelectric conversion,  $\zeta$ , is given by the following equation.

$$\zeta = \frac{T_h - T_l}{T_h} \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + T_l/T_h}$$

where  $T_h$ ,  $T_l$ , and  $T$  are the high and low temperature sides of a temperature difference and  $(T_h + T_l)/2$ , respectively. From this equation, it is indicated that the conversion efficiency,  $\zeta$ , becomes higher monotonously as  $ZT$  gets higher. Therefore, in the development of thermoelectric materials, it is necessary to make  $ZT$  higher.

\*2 Seebeck coefficient: If temperature difference,  $\Delta T$ , is given to a substance and voltage,  $\Delta V$ , is generated at both ends of that temperature difference, the substance's Seebeck coefficient is given by  $-\Delta V/\Delta T$ . In other words, the Seebeck coefficient is the physical quantity that represents the degree of voltage generated by a temperature difference.

\*3 Nano structure: A crystal structure on the order of a few nm. Applying an electronic energy difference to a crystal structure and the material surrounding it causes electrons to be trapped in the crystal structure. From this, it can be expected that the quantum effect is made apparent.

\*4 Quantum effect: Localizing electrons (or holes) in the local space (approximately a few nm) in a substance causes the characteristics of wave to be manifested, resulting in a noticeable change in, for example, the value of energy in which electrons can exist. This also causes the number of electrons that can exist per energy, i.e. the density of states, to change drastically. In this study, part of the quantum effect in a crystal is applied to control the density of states.

\*5 Wiedemann-Franz law: A rule that shows there is a linear relationship between electrical and thermal conductivities and that is often applied to metallic materials. Intrinsically, this rule can be applied as long as the density of states is linear in terms of energy. On the other hands, the density of states of semiconductor materials is not linear, but is approximately parabolic. However, the parabola is also given as linear in the primary approximation if it is in a narrow energy range close to the Fermi level that contributes to the electron thermal conductivity. Therefore, it is possible to hold discussions by understanding the approximation range.



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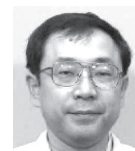
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