High Dimensionless Figure of Merit $ZT = 1.38$ Achieved in p-Type Si–Ge–Au–B Thin Film

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We succeeded in obtaining amorphous Si–Ge thin films containing ~ 6 nm nanocrystals by means of a vapor deposition. The thermal conductivity was controllable using the particle size of the nanocrystals, and a very small value of thermal conductivity ~ 1 W/mK was obtained with an averaged particle size less than 6 nm. The electron transport properties were improved using Au-doping to form impurity levels near the valence band top, and B-doping to control the Fermi level. With the effect of this co-doping technique and nano-structuring, we estimated obtaining $ZT = 1.38$ at 1100 K. [doi:10.2320/matertrans.MT-M2019310]

(Received October 24, 2019; Accepted January 30, 2020; Published March 13, 2020)

Keywords: thermoelectric materials, nano structures materials, Co-doping method

1. Introduction

The consumption of fossil fuels and the emission of greenhouse gases are recognized as serious problems to prevent us from constructing a sustainable society. The thermoelectric generator, which is capable of transforming waste heat into useful electric power, has attracted much interest as a key technology to greatly reduce the problems mentioned above. Unfortunately, the efficiency of energy conversion in commercially available thermoelectric generators is limited to less than 10%. The efficiency of energy conversion in the devices is generally determined by the dimensionless figure of merit $ZT = S^2\sigma T/(\kappa_{lat} + \kappa_{ele})$ of their constituent thermoelectric materials.¹⁾ Here S , σ , κ_{ele} , and κ_{lat} represent the Seebeck coefficient, electrical conductivity, electron thermal conductivity, and lattice thermal conductivity, respectively. Practical thermoelectric materials, such as Bi_2Te_3 -based²⁾ and PbTe -based³⁾ alloys, show high ZT values exceeding 1.86 at 320 K and 2.20 at 915 K,⁴⁾ respectively. However, these materials contain rare, expensive, and toxic elements that prevent their use in a wide variety of applications. Therefore, research and development for new, cheap, nontoxic and high ZT thermoelectric materials is strongly desired.

The Si–Ge alloys are one of the nontoxic thermoelectric materials showing a ZT peak at high temperatures. They were used in Radioisotope Thermoelectric Generators for space missions in the 1960's. Unfortunately, their ZT values were limited by relatively high thermal conductivity $\kappa > 5.0$ W/mK to less than 0.50 for p-type and 0.90 for n-type.⁵⁾ Recently, nano-structuring^{6,7)} and nano-inclusion^{8,9)} approaches were employed to reduce the lattice thermal conductivity, and relatively low values of $\kappa < 2.3$ W/mK were reported for $\text{Si}_{0.80}\text{Ge}_{0.20}$ alloys without significant degradation of the power factor $PF = S^2\sigma$. As a result, the values for ZT were increased up to 0.95¹⁰⁾ and 1.30¹¹⁾ for p-type and n-type materials, respectively.

More recently, a significantly reduced $\kappa = 1.35$ W/mK over a wide temperature range from 300 K to 700 K was reported for the bulk nanostructured $\text{Si}_{0.65}\text{Ge}_{0.35}$ prepared by means of ball milling and pulse-current sintering methods.¹²⁾ Unfortunately, however, the power factor of their samples was lower than 0.03 W/mK² to limit their ZT to less than 0.012.

In order to improve the power factor in keeping with the small κ_{lat} of Si–Ge alloys, we considered a constructive modification of the electronic structure near the chemical potential (Fermi level)^{13,14)} as likely being one of the most effective methods. Heremans *et al.*¹⁵⁾ proposed the use of resonance states to modify the density of states $N(\epsilon)$, and reported that the ZT value of PbTe -based thermoelectric materials was considerably augmented from 0.7 (Na-PbTe) to 1.5 ($\text{Tl}_{0.02}\text{Pb}_{0.98}\text{Te}$) at 800 K by the use of a tiny amount of Tl, that was supposed to produce some resonant states near the chemical potential. Recently, this method was applied intentionally for n-type Si–Ge alloys, and successfully demonstrated a high ZT value of 1.88¹⁶⁾ by doping with Fe and P.

Another method to improve the ZT value was proposed: quantum well, quantum wire, or quantum dot that affect the electronic structure were suggested as effective ways for making variations in electronic structure to improve electron transport properties for higher ZT .^{17–20)} However, clear evidence for an effective improvement in ZT due to these quantum effects have not been reported yet.^{20–25)} The reason for their failure is likely to be related to the energy range of the characteristic electronic structure being apart from the narrow energy range where electron transport properties are determined, or the too small amount of quantum states to effectively affect the electron transport properties. For example, each quantum state produced by a nano-cluster of 1 nm in a diameter is negligibly small containing only less than 0.05 electrons per atom.

We considered that a new level containing sufficient states could be produced, provided that we employed *d*-orbitals of transition metal randomly distributed in the matrix. Besides,

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we planned to employ amorphous phase and nano-crystals for greatly reducing lattice thermal conductivity. We selected, in this study, a Si-Ge system as a typical material possessing a rather high bandgap, simple local atomic arrangements, and a potential to be amorphous phase or nano-crystalline phase.

Formation of amorphous phase Si-Ge was reported previously by means of low temperature molecular beam deposition,^{26–33)} and an annealing method for producing nanocrystals from amorphous materials was also reported. Recently, we employed this technique, and reported^{33,34)} that the thermal conductivity of Si-Ge nano-crystalline thin films was greatly suppressed into small values less than $1 \text{ Wm}^{-1}\text{K}^{-1}$, which is comparable with the limit of amorphous phase Si-Ge, by controlling the particle size to less than 6 nm. At that time,^{30–34)} SiGe:Au samples showed a maximum ZT value of approximately 0.6. This indicated that there is a limit to reducing lattice thermal conductivity as a technique to enhance a ZT value. Therefore we considered developing another technique, i.e. co-doping to control not only thermal lattice conductivity, but also electric properties.

In this study, we tried to control the electronic structure using Au as an impurity element, because it has d -orbitals in the vicinity of the valence band top. We also employed B to control the Fermi level. With the effect of the co-doping technique and the reduction of lattice thermal conductivity in association with amorphous and nano-crystalline structure, we estimated $ZT = 1.38$, which would be a best result for p-type Si-Ge materials.^{10,35–41)}

2. Experimental Procedures

We deposited multi-layered amorphous thin film in a sequence of $\sim 1 \text{ nm}$ Si, $\sim 1 \text{ nm}$ Ge, $\sim 0.1 \text{ nm}$ Au, and $\sim 1 \text{ nm}$ Ge on a sapphire substrate by means of molecular beam deposition. The thickness of Au was adjusted as the overall composition of Au became 3 mol%. This set of layers was repeatedly deposited until the total thickness of the film became $\sim 220 \text{ nm}$. All the deposited layers were confirmed to be amorphous phase by the halo pattern from x-ray diffraction. The thin-films were annealed at 300, 400, or 500°C for 15 minutes so as the size-controlled crystalline Si-Ge nano-particles would be homogeneously distributed in the matrix of amorphous Si-Ge (a-SiGe).

The averaged diameter of the crystalline nano-particles was evaluated by the Scherer equation from the full width at half maximum of x-ray diffraction peaks obtained by the Bragg-Brentano type diffractometer with $\text{CuK}\alpha$ radiation. It is further confirmed by using transmission electron microscopes. (These data is shown in supplementary figure A3). Since these crystalline nano-particles were embedded in the amorphous phase, the volume fraction of nano-crystals was determined using a Raman scattering measurement (as shown in supplementary figure A4).

The electrical conductivity and Seebeck coefficient was measured in the RZ2001i developed by Ozawa Science Co. Ltd. in a nitrogen atmosphere over a wide temperature range of 300 K to 1073 K. The electrical conductivity was measured by a 4-terminal method. The thermal conductivity was measured at room temperature using a time-domain thermo-

reflectance method, pico-TR assembled by picoTherm Corporation.

3. Results

3.1 Control of nano-structures in Si-Ge thin films and their thermal conductivity

Since the eutectic temperature of Au-Ge systems is very low at 356°C, each Au layer is supposed to mix easily with the surrounding Ge-layers to form crystalline particles. This phenomenon is known as metal induced crystallization.^{26–32)} The Ge-Au nano-particles formed as a result of metal induced crystallization would incorporate with Si atoms of the surrounding amorphous matrix to form Si-Ge-Au crystalline nano-particles. We as above, considered that, if it is the case, the volume fraction of the crystalline nano-particles could be controlled by the thickness of Si layers.

We confirmed the validity of this idea by the evaluation of the volume fraction vs. Si thickness as shown in Fig. 1. We plot here two series of samples: a series of constant Ge thickness (0.26 nm) and those with constant Si thickness (1.0 nm). The volume fraction of the nano-structured particles linearly decreased with the increasing thickness of the Si layer in the first series of samples, in which the thickness of the amorphous Ge layer was kept constant at 2.6 nm. The same tendency was observable in the second series of samples for the Ge-layer's thickness dependence with a constant Si sickness of 1.0 nm.

Fig. 1 Volume fraction of crystalline nano-particles vs. (a) Si thickness, and (b) Ge thickness.

Fig. 2 Evolution of thermal conductivity as a function of particle diameter of precipitating crystalline nano-particles.

Now we succeeded in controlling the grain size. We tried, in the next step, to reveal the grain size dependence of thermal conductivity. After making various samples of different averaged grain sizes, we measured their thermal conductivity using the TDTR method at room temperature. The resulting data are plotted in Fig. 2 as a function of grain size. The contribution of electron thermal conductivity, κ_{ele} , was roughly estimated using the Wiedemann-Franz (W.F) law, i.e. $\kappa_{ele} = L_0 T \sigma$ where $L_0 = 2.44 \times 10^{-8} \text{ W}\Omega/\text{K}^2$ is a constant known as the Lorentz number. (In the narrow energy range near the Fermi level that contributes to the electronic thermal conductivity, the state density is given as linear in the first-order approximation. After understanding that a first-order approximation gives a rough estimation, we would discuss that it could apply the W.F law. It emphasizes that this is only a rough estimate.) As a result, κ_{ele} was estimated to be very tiny less than $\sim 0.02 \text{ W/mK}$ for all samples at 300 K. This value is much smaller than the minimum lattice thermal conductivity $\sim 1 \text{ W/mK}$ of the present measurement, and therefore the contribution of electron thermal conductivity was safely ignored.

The estimated lattice thermal conductivity drastically and monotonically increased with an increase in the size of nano-particles. Notably, the lattice thermal conductivity of samples containing crystalline nanoparticles possessed essentially the same lattice thermal conductivity, provided that the averaged grain size was smaller than 6 nm.

3.2 Enhancing figure of merit of Si-Ge thin film with Au and B co-doping technique

From the experiment and analyses described above, we found the condition to reduce the lattice thermal conductivity of amorphous Si-Ge samples containing Au and crystalline nano-particles. In the next step, we tried to optimize the carrier concentration in our samples by introducing B additionally as another impurity element.

Figure 3 shows the Au concentration dependence of ZT at 1083 K of two series of samples at approximately 3 mol% B and 0 mol% B. By assuming the thermal conductivity measured at room temperature is constant over the whole temperature range, we estimated the value of ZT . This assumption is reasonable, partly because the samples show no bi-polar effect in the whole temperature range and partly

Fig. 3 Au concentration dependence of ZT at 1083 K. Two series of samples with different B concentration were plotted.

because the electron thermal conductivity is negligibly small even at high temperatures. Another piece of information was that the temperature dependence of thermal conductivity in the bulk of amorphous Si-Ge-Au-B with nano-crystals, similar to the thin films in this paper, showed thermal conductivity at RT higher than at higher temperatures. (Based on this result, the estimated ZT value of 1.38 described below might be underestimated.) The results of the bulk will be presented in the near future.

One can see that a finite variation of ZT was observed in both series of samples. In the case of 3 mol% B, ZT reached near 0.8 at 0 mol% Au, which is almost equal to the maximum ZT -value previously reported for p-type Si-Ge samples. Surprisingly, $ZT > 1$ is obtained for several samples doped with a few mol% of Au in the series of 3 mol% B. This fact indicates that the impurity states near the chemical potential are capable of improving the performance of thermoelectric materials.

The electrical conductivity, Seebeck coefficient, and power factor (PF) of the sample possessing the highest ZT are plotted in Fig. 4 as a function of temperature. The maximum value of ZT in this study was estimated to be 1.38 at 1100 K, where Seebeck coefficient, electrical conductivity, and thermal conductivity were $170 \mu\text{V/K}$, 4780 S/m , and 1.09 W/mK , respectively. The technique for improving thermoelectric performance by modifying electronic structure near the band gap and reducing lattice thermal conductivity with nano-structuring would be applicable for any other thermoelectric semiconductors.

4. Conclusion

In this study, in order to obtain high figure of merit, we prepared Si-Ge-based thin films with control of the size and volume ratio of crystalline nano-particles. We employed a few mol% Au as a dopant to form impurity states characterized by high magnitude near the chemical potential. It was found that the size and volume fraction of crystalline nano-particles are controllable using the thickness of Si- and Ge- and Au-layers at the initial deposition. The lattice thermal conductivity was reduced as low as the amorphous

Fig. 4 (a) Electrical conductivity, (b) Seebeck coefficient, and (c) power factor of $\text{Si}_{65}\text{Ge}_{28}\text{Au}_4\text{B}_3$ plotted as a function of temperature. Solid diamonds are the results of first measurement, and solid circles are the second measurement.

limit of 1 W/mK , provided that the size of crystalline nanoparticles was less than 6 nm . It was confirmed that the thermoelectric performance of Si-Ge thin film consisting of crystalline nano-particles embedded in the amorphous matrix was significantly improved with co-doping of Au and B, and $ZT = 1.38$ was estimated for $\text{Si}_{65}\text{Ge}_{27}\text{Au}_4\text{B}_3$ at 1100 K .

Acknowledgments

This study was conducted under a project commissioned by the New Energy and Industrial Technology Development Organization (NEDO). One of the authors, Toyota Technological Institute, was also financially supported by MEXT/JSPS KAKENHI Grant Number JP18H01695 and JP18K18961. We would like to express our gratitude to Prof. Dr. Okamoto of the National Defense Academy, Dr. Manabu Inukai, and Dr. Muthusamy Omprakash, who provided significant advice.

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Appendix

In order to quantitatively evaluate the volume fraction of nano-crystalline particles, we tried to derive an empirical equation for predicting the diameter and volume fraction of the crystalline nano-particles. Here, since B was a dopant and has no eutectic with Si–Ge in our experimental condition, there was no change in the size and volume fraction of the nano-crystalline between doped and non-doped B on Si–Ge: Au, we assumed that the influence of B on the nucleus of nano-crystalline particles was negligibly small. Si–Ge nano-particles were speculated to grow during the mixing of the Ge–Au nucleus and the surrounding Si. Therefore, we assumed here that although nucleation occurs not only at Au–Ge mixing further nucleation is negligibly small. We also assumed that the particle size of the Si–Ge crystals has a limit, and the development speed of the size of crystalline particle is proportional to the Au concentration. Using these assumptions, we proposed the following equation to describe the time evolution of the diameter ϕ of the nano-particles.

$$\frac{d\phi(t)}{dt} = cC_{Au}\{a(R_{Si/Ge})^b - \phi(t)\} \quad (A1)$$

Here ϕ , 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. By solving this differential equation, we obtain the time evolution of the particle diameter, $\phi(t)$, given by the following equation.

$$\phi(t) = a(R_{Si/Ge})^b \{1 - \exp(-cC_{Au}t)\} \quad (A2)$$

Equation (A2) suggests that the particle diameter, $\phi(t)$, increases with the annealing time, t , to be saturated into a constant value defined as its limit. The volume fraction, η , is deduced from the following equation because new nucleation was not assumed during the grain growth.

$$\eta(t) \propto \phi(t)^3 \quad (A3)$$

Since we fixed the annealing time $t = 15$ minutes in the present experiments, the particle diameter, ϕ , and volume fraction, η , are supposed to become a function of the Au concentration, C_{Au} , and Si/Ge ratio, $R_{Si/Ge}$.

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. A1(a) and (b) as a function of C_{Au} and $R_{Si/Ge}$. We also performed curve fitting using a , b , and 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, a particle diameter higher than 3 nm and a volume fraction exceeding 20%.

Fig. A1 (a) Averaged diameter and (b) volume fraction of crystalline nano-particles plotted as a function of Au concentration and Si/Ge ratio. The fitted curvatures at 573 K, 673 K, and 773 K were superimposed to the data.

Fig. A2 Optical absorption coefficient in Si–Ge doped with Au. One can see that the absorption signals around 1 eV increases with increasing Au composition.

We discuss, in the next step, the role of impurity states to increase *PF* of Si–Ge containing Au. Figure A2 shows the results of the optical absorption coefficient measurements that show the circumstantial evidence of the impurity level near the chemical potential in association with the doped Au. In order to clearly confirm the effect of only Au, this experiment was performed on non-B doped Si–Ge: Au. One

Fig. A3 (Left) Typical example of cross-section TEM image of an annealed sample showing the crystalline nano-grains as shown in red circles. The authors measured the averaged diameter of the crystalline nano-particles by the TEM. The standard deviation of the distribution of the diameter measured by the TEM is about 20% (population parameter of approximately 10 particles per an image).

(Right) Particle diameter measured by TEM vs the diameter by XRD. We can confirm the strong correlation between the both diameters measured by XRD and TEM. In the analysis of this paper, we mainly used the diameter measured by XRD. Because the error bar of about 10% of the diameter measured by XRD is not only smaller than that of TEM, but also the measurement area of about 10 mm square of XRD is larger than that of TEM.

can realize that the absorption signal near 1 eV increases along with Au concentration. This fact suggests that the doped Au produced impurity states in the energy gap. This formation of the impurity states must cause variation in electron transport properties especially when the chemical potential stays near the band gap. The mechanism leading to the large evolution in ZT should be related to the formation of impurity states. We are now planning to investigate the impurity states in more detail by means of high-resolution photoemission spectroscopy. The results will be presented in the near future.

Another supplementary information is added as Fig. A3, and A4.

Fig. A4 (Top) Typical example of Raman scattering signal from an annealed sample. A prefix to "a" indicates amorphous, "c" is crystalline. The authors evaluated the volume fraction of Si-Ge, i.e. the ratio of amorphous to amorphous plus crystalline in Si-Ge integral intensities by the Raman signal.

(Bottom) Distance between nano-particles measured by TEM vs volume fraction by Raman scattering measurement. The broken line is an eye guide. (TEM images are the projection onto 2 dimensional plane. Therefore it is difficult to measure true distance between the two nearest nanoparticles. Hence, the authors adopted the volume fraction, as this parameter containing true distance information.) The authors considered that this figure would give a certain validity of using the volume fraction for the evaluation of particle-distance controllability, because the distance measured by TEM shows strong correlation with the volume fraction.