Thermoelectric Properties of Amorphous Ge/Au and Si/Au Thin Films

Akiko Miyata* Non-member
Makoto Abe* Non-member
Yoichi Okamoto* Non-member
Toshio Kawahara* Non-member
Jun Morimoto* Non-member
Narumi Inoue** Member

Thermoelectric Properties of Ge/Au and Si/Au thin films have been measured as functions of Au concentration and annealing cycles. Ge/Au and Si/Au thin films were prepared by the alternating deposition of Ge or Si and Au in the ultra-high vacuum chamber. In the Ge/Au thin films, the annealing cycles dependence of electrical resistivity decreases as Au concentration increases. The Ge/Au thin films both of 0 and 5 mass % Au have large thermoelectric power. High Au concentration samples are recrystallized even in the heating phase of 1st annealing cycle. From the difference of the atomic radius, Au should be the origin of amorphous phase. The best condition for high thermoelectric properties must be in low Au concentration. For the electrical resistivity of Si/Au thin films, there are almost no dependence of the annealing cycles. Au mainly plays the role of carrier source for the change of the electrical resistivity with Au concentration. We can conclude that the mechanism of the anomalously large thermoelectric power of Si-Ge-Au thin films comes out from the amorphous phase of Si and Ge.

Keywords : thermoelectrics, thin film, SiGe, amorphous

1. Introduction

Recently, many researchers have been interested in thermoelectric materials from the points of the saving energy and the environmental protection problems. The thermoelectric power generation is the technique to use the waste heat, and the thermoelectric materials with improved characteristics are strongly required. The excellence of thermoelectric materials is evaluated by the figure of merit $Z$. $Z$ is defined by the following equation,

$$Z = \frac{P}{\kappa} = \frac{\alpha^2 \rho}{\kappa} \quad (1)$$

where $P$, $\alpha$, $\rho$, and $\kappa$ are power factor, thermoelectric power, electrical resistivity and thermal conductivity, respectively. The power factor $P$ indicates the electrical power generation capability and is commonly used for materials such as thin films whose thermal conductivity is difficult to measure.

Some theoretical reports predicted that low-dimensional structure could cause the enhancement of $Z^{(1)}$~(7). Especially, Hicks and Dresselhaus theoretically predicted the improvement of the thermoelectric properties by introducing the multi-quantum-well structure$^{(8)}$~(2). Many researchers have an interest in their theoretical prediction because it shows great potential for enhancing the thermoelectric properties. Therefore there are many reports on quantum well and/or quantum wire structures$^{(8)}$~(10).

We have already reported that Si-Ge-Au amorphous superlattice thin films have the maximum value of the thermoelectric power over $10^{-2}$ V/K, the anomalously large thermoelectric power of the samples is thought to from the Si/Ge amorphous phase, and it depends on the constitution of thin film$^{(11)}$~(12). The as deposited thin films have the heterogeneous artificial superlattice structures, but the superlattice structure degradates by annealing at 450 K ~ 550 K for 15 min. We have confirmed that these films are homogeneous amorphous thin films when we measure the thermoelectric properties except heating phase of the first measurement$^{(12)}$. Amorphous phase can generally be recrystallized by the thermal annealing. However it is difficult to evaluate quantitatively the processes of the recrystallization by X-ray diffraction for our Si-Ge-Au samples, and we cannot discuss the relation between the change of the thermoelectric properties and the change of the crystallography. But we have succeeded to detect the apparent differences in the electronic band structure of Si-Ge-Au thin films using by PAS (photoacoustic spectroscopy) as a function of annealing cycles$^{(13)}$.

Generally, amorphous materials have various states of free energy minimum corresponding to the atomic configuration. So amorphous materials can have a variety of feasibility compared with crystal materials. It is well known that even pure Si and Ge form amorphous phase and show Mott transition whose band structure is called pseudogap when the metal element is added. There are many reports that the pseudogap system is expected to have a large enhancement in the thermoelectric power because the density of state nearby Fermi level causes a sharp decrease$^{(14)}$~(15).

Au doped Ge thin films also have large thermoelectric power about $10^{-3}$ V/K$^{(11)}$. Moreover the amorphous Si-Ge-Au bulk samples fabricated by the melt spinning method had $Z$ one order of magnitude larger than that of conventional Si-Ge crystal materials$^{(16)}$. The thermoelectric properties of Si-Ge-B thin film also show the extremely large power factor$^{(17)}$. And there is report about very high thermoelectric power in Si-Ge alloy film$^{(18)}$. Au
doped Ge and Si are also possible to have high thermoelectric power by the electronic structure calculation\(^{(19)}\). There are still many unsolved parts of the mechanism of high thermoelectric properties in the Si-Ge materials with.

In this paper, we attempt the evaluation of thermoelectric properties for two system thin films of Si, Ge and Au, that are Ge/Au and Si/Au thin films. We investigate how Au play a role in the anomalously high thermoelectric properties of the Si-Ge-Au thin film and approach the explication of the mechanism of this large thermoelectric power.

2. Experiments

The sample preparation was the same as described in our previous reports\(^{(11)}\)\(^{(12)}\). Alternating layered superlattice thin films were prepared by the sequential evaporation of the two components from three of Si (High Purity Chemicals Lab.; 99.999%), Ge (Furuuchi Chemicals; 99.99% up) and Au (High Purity Chemicals Lab.; 99.9 % up) onto the sapphire substrate in an ultra high vacuum system at 300 K. The thickness of thin films were almost 300 nm. Base pressure of the stainless steel chamber with a liq. N\(_2\) shroud was around 1\( \times 10^{-8}\) Pa, but rose up to 1 ~ 5 \( \times 10^{-6}\) Pa during the operation of the two electron beam guns. The evaporation rates and the layer thickness were controlled by a computer (NEC; PC-9801) with two sets of crystal oscillator thickness monitor (INFICON; XTC). The deposition rates of both evaporation source were held constant at 0.05 nm/sec. The crystal oscillator thickness monitors were calibrated by using surface morphology micrometer (Veeco; Dektak-3030) and X-ray low angle diffraction. The measurement of electrical resistivity and the thermoelectric power were performed in parallel direction to the film by four-probe method for the applied voltage range of -5 V to +5 V during the annealing. For the measurement of the temperature dependence of electrical resistivity and thermoelectric power, samples were heated and cooled between room temperature and 1000 K at the rate of 10 K/min in 1 atm inert gas flow. The thermoelectric power was measured by the conventional DC method with the temperature difference \(\Delta T\) at least 10 K.

The crystal properties of samples were studied by using X-ray diffraction analysis (Philips; X'Pert MRD High Resolution X-ray Diffractometer), where copper K\(_{\alpha}\) was used.

3. Results and Discussions

Figure 1 shows the X-ray diffraction profiles in the high angle region for as deposited Ge/Au and Si/Au thin films. The X-ray diffraction profiles of Ge/Au thin films with the different Au concentration in the high angle region are almost in the same situation. Especially, only two samples of 30 and 50 mass % Au show extra 1 peak. We may deduce that the recrystallization progressed as Au concentration increased. There are no differences in all diffraction profiles of Si/Au thin films. We couldn't distinguish the effects of Au addition on the structure of samples.

Figure 2 shows the typical temperature dependence of the power factor for some Si-Ge-Au thin film samples and Ge/Au, Si/Au thin film samples as a comparison\(^{(13)}\). The power factor of the Si-Ge-Au thin films are 10\(^{1}-10^{3}\) times larger than the value of the bulk SiGe materials\(^{(19)}\). On the other hand, Ge/Au and Si/Au films have almost the same power factor of the conventional SiGe bulk. As mentioned before, the power factor consists of \(\rho\) and \(\alpha\), these depend on the various parameters. So, we discuss the electrical resistivity and the thermoelectric power as functions of the Au concentration and annealing cycles respectively.

Figure 3 shows the Au concentration dependence of electrical resistivity as a function of the annealing cycles for Ge/Au thin films at 1000 K. At lower Au concentration region, the differences of electrical resistivity with annealing cycles are large. The differences decrease with Au concentration increase. At Au concentration of 50 mass %, there are no differences in electrical
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We deduce the Ge/Au thin films with lower Au concentration are recrystallized among 1st to 8th annealing cycles. Here, Sasaki, et al, reported that Au/Ge amorphous superlattice thin films (Au; 50 wt. %, Ge; 50 wt. %) were easy to diffuse the superlattice structure even at room temperature for a few days, and finished to recrystallize even at room temperature within one to two months (21). Therefore, the Ge/Au thin film of 50 mass % Au concentration is recrystallized even in the heating phase of 1st time annealing cycle and it is in the deep quasi-stable amorphous phase. Also from X-ray diffraction profiles in Fig. 1, the crystallization of Ge/Au films is found easier to progress than that of Si/Au.

So, from the difference of the atomic radius, we can say Au atoms act as the origin of amorphous phase which concerns the high thermoelectric properties. But, if Au concentration exceed the optimum quantities, the recrystallization progresses. And the electrical resistivity becomes large as the scattering center increases.

Figure 4 shows the Au concentration dependence of electrical resistivity as a function of the annealing cycles for Si/Au thin films at 1000K. The electrical resistivity changed complicatedly for the Au concentration, and there are almost no dependence on the annealing cycles. Therefore there are two possibilities can be considered, one is that the recrystallization of the amorphous structure didn’t occur in this region of annealing condition (temperature, time, atmosphere and number of cycles), and another is that the recrystallization progresses enough and films are in the deep quasi-stable phase even in the heating phase of 1st time annealing cycle. There is the report which discussed about annealing cycle dependence of thermoelectric property. That is the thermoelectric property changes by annealing cycles from 1 to 15 cycles, without obvious change of X-ray diffraction profile (22). So the slight change of quasi-stable amorphous phase is responsible to this thermoelectric property change. Also we have reported that band structure of Si-Ge-Au thin films changes by annealing (13). For the annealing cycles carrier concentration and scattering factor almost don’t change. Au plays the role as a source of carrier from the change of the electrical resistivity for Au concentration.

Figure 5 shows the best values of the thermoelectric power for Ge/Au and Si/Au films, and the measurement temperature is summarized in Table 1. We discuss the thermoelectric power of these films in relation to the electrical resistivity because the thermoelectric power has large fluctuations. Si/Au films (Au : 0, 5 and 30 mass %) have large thermoelectric power. From the result of the electrical resistivity for Si/Au films, we can deduce the band structure of Si/Au films change delicately by annealing cycles because the thermoelectric power change though carrier concentration and scattering factor doesn’t change (13).

Table 1. Measurement conditions of the best values of thermoelectric power

<table>
<thead>
<tr>
<th>Au concentration (mass %)</th>
<th>Ge/Au</th>
<th>Si/Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8th down 370 K (p)</td>
<td>7th down 860 K (p)</td>
</tr>
<tr>
<td>5</td>
<td>2nd down 400 K (p)</td>
<td>9th up 645 K (p)</td>
</tr>
<tr>
<td>10</td>
<td>9th down 420 K (n)</td>
<td>4th up 380 K (n)</td>
</tr>
<tr>
<td>30</td>
<td>1st up 610 K (p)</td>
<td>2nd down 900 K (p)</td>
</tr>
<tr>
<td>50</td>
<td>7th down 980 K (n)</td>
<td>1st up 640 K (p)</td>
</tr>
</tbody>
</table>
Ge/Au films (Au: 0 and 5 mass %) have large thermoelectric power and Ge/Au (Au: high concentration) have ordinary thermoelectric power. From this fact, it is considered that the diffusion and the recrystallization are easy to take place, and amorphous structure collapse, then the high thermoelectric properties are not generated when Au concentration exceed the optimum quantities. From the result of the electrical resistivity for Ge/Au films, the best condition for high thermoelectric properties should be in low Au concentration. But addition of Au makes the amorphous phase unstable. Therefore it is difficult to determine the best Au concentration. It is challenging task to find out the optimum concentration of Au for the practical use.

4. Conclusion

For Ge/Au thin films, Au is the main cause of amorphous phase which contributes to the high thermoelectric properties. However, when Au concentration exceeds the optimum quantities, the recrystallization progresses and the electrical resistivity also increases because the scattering centers increase. Consequently it prevents from the high thermoelectric properties. So, the best condition for the high thermoelectric properties should be low Au concentration.

For Si/Au thin films, Si mainly plays the role of the source of carriers, but the thermoelectric power is reduced with the increasing Au concentration.

The mechanism of the anomalously large thermoelectric power of Si-Ge-Au thin films is concluded to be in the amorphous phase of Si and Ge.

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Akiko Miyata (Non-member) was born in Nagasaki, Japan, and she received B. Engr. degree in National Defense Academy in 1999. She is now a graduate student of National Defense Academy. Her research interests are thermoelectric materials.

Makoto Abe (Non-member) was born in Aomori, Japan, and he received B. Engr. degree in National Defense Academy in 2003.

Yoichi Okamoto (Non-member) was born in Tokyo, Japan, and he received Doctor degree in Tsukuba University in 1991. He is now Associate Professor of National Defense Academy department of Materials Science and Engineering. His major research fields are thermoelectric materials and artificial superlattice. The Physical Society of Japan, The Japan Society of Applied Physics and The International Thermoelectric Society member.
Toshio Kawahara (Non-member) was born in Osaka, Japan, on January 17, 1966. He received a Ph. D. degree in Physics from Kyoto University in 1996, and is presently a research associate at National Defense Academy. He has worked on optical properties and thermoelectric properties of semiconductors. The Japan Society of Applied Physics, The Physical Society of Japan, Japan Institute of Electronics Packaging member.

Jun Morimoto (Non-member) was born in Okayama, Japan in 1950. He received his B.S. degree in physics from Saitama University in 1973 and Ph. D. degree in information processing from Tokyo Institute of Technology in 1983. He is now Professor at Dept. of Materials Science and Engineering, National Defense Academy. His research includes photoelectric and thermoelectric properties of semiconductors. He is a member of The Japan Society of Applied Physics, The Physical Society of Japan, Materials Research Society and American Physical Society.

Narumi Inoue (Member) was born in Tokyo, Japan, on August 15, 1948. He received his B.S. and M.S. in communication engineering from Shinsyu University in 1972 and 1974, respectively, and then his Ph. D. from Colorado State University in 1980. He is Professor of Electrical and Electronic Engineering Department at National Defense Academy. He has worked on laser processings, infrared detection and energy-conversion devices. The Japan Society of Applied Physics, The Laser Society of Japan, American Institute of Physics member.