The study for the annealing effects on the Si and Ge amorphous thin film by using photoacoustic spectroscopy

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We have already reported the anomalously high thermoelectric properties of the Si-Ge-Au amorphous thin films. These thermoelectric properties are changing slowly during the repeated annealing cycles. However, there are no obvious differences in X-ray diffraction profiles under the annealing cycles. On the other hand, the apparent differences in photoacoustic (PA) spectra with repeated annealing cycle were observed. In this paper, to clarify the mechanism of thermoelectric properties, we have evaluated the mono (Si) and binary (Au doped Ge) elements thin films instead of Si-Ge-Au thin films under the various times of the annealing cycles. The Si and Ge amorphous thin films were prepared by the deposition of non-doped Si and heavily Au doped Ge, respectively, in the ultra high vacuum. There are large differences in PA spectra of Si and Au doped Ge samples depending on the annealing cycles. The changes of optical properties in Si-Ge-Au thin films are mainly caused by those in Si thin films.
Key words: PAS, thermoelectric properties, Si, Au doped Ge, thin film

1. INTRODUCTION

Recently, there have been renewed interests in finding new, efficient thermoelectric materials from the point of the saving energy and the environmental protection problems. The thermoelectric power generation is the technique to use the waste heat, and thermoelectric technique is environment conservative technique. So, the thermoelectric technique should be developed and the thermoelectric materials with improved characteristics are strongly required. The thermoelectric materials are evaluated by the figure of merit $Z = P/\kappa = \alpha^2/(\rho\kappa)$, where P, α, ρ and κ are power factor, thermoelectric power, electrical resistivity and thermal conductivity, respectively. It is difficult to control α, ρ and κ independently, since these thermoelectric parameters complexly depend on many parameters, such as carrier concentration, carrier mobility and effective mass of carrier etc. The power factor P indicates the electrical power generation capability and is commonly used for the evaluation of materials such as thin films whose thermal conductivity is hard to measure.

We have already reported that Si-Ge-Au amorphous thin films show the maximum value of the thermoelectric power of over 10^{-2} V/K [1]. Though there have been reported about high thermoelectric power in Si-Ge alloy film [2], our Si-Ge-Au thin films have much larger than that of Si-Ge alloy film. The thermoelectric properties of Si-Ge-B thin film also show the extremely large power factor [3]. The anomalously large thermoelectric power of the Si-Ge-Au thin film is thought to be from the Si and/or Ge amorphous phase, and it depends on the deposition constitutions of thin film such as substrate temperature, concentration ratio and evaporation rates and so on [4]. The as-deposited thin films have the heterogeneous artificial superlattice

structure, but the superlattice structure collapses 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 for the first heating phase of the measurement [4]. Also, there is the report which discussed about annealing cycle dependence of thermoelectric property [5]. That is the thermoelectric property changes by annealing cycle from 1 to 15 cycles without obvious change of X-ray diffraction (XRD) profile. In general, amorphous phase recrystallizes with the thermal annealing. However it is difficult to evaluate quantitatively the process of the recrystallization by XRD 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 by photoacoustic spectroscopy (PAS) as a function of annealing cycle [6].

In this paper, we attempt the evaluation of the mono and binary elements thin films, that is Si thin films and Au doped Ge ones instead of Si-Ge-Au films to make easy to clarify the relation of the mechanism of thermoelectric properties to each material. Especially, we investigate the optical properties of Si thin films and Au doped Ge thin films as a function of annealing cycle.

2. EXPERIMENTS

The samples were prepared onto the sapphire substrate in the ultra high vacuum system at 300 K by the deposition of non-dope Si (Kojundo Chemical Lab.; 99.999 %) and heavily Au (Kojundo Chemical Lab.; 99.9 % up) doped Ge (Furuuchi Chemical; 99.99 % up), respectively. The thickness of thin films were 300 nm.

Base pressure of the stainless steel chamber with a liq. N_2 shroud was around 1×10^{-8} Pa, but rose up to $1 \sim 5 \times 10^{-6}$ 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 low angle XRD.

In this work, we have prepared two kinds of samples, Sample-Si and Sample-Ge for XRD and PAS. Samples were cut into small pieces and each piece were annealed in the infrared image furnace. Then we measured optical transmittance, absorption (Photoacoustic (PA) spectra) and XRD spectra. We labeled each piece such as "Sample-Si-3" that means a piece cut from Sample-Si and annealed three times.

For the optical absorption measurement, conventional PAS was used. The PAS experimental apparatus consisted of a 300 W halogen lamp coupled with a monochrometer (Jobin - Yvon, H20 - IR). The incident light beam was focused onto the thin film samples set in the PAS cell. The film thickness (300 nm) is apparently less than the thermal diffusion length of the samples. The PAS signal was detected by a microphone and amplified by a lock-in amplifier (NF Electronic Instruments; 5610B) system with the mechanical chopper of 21.2 Hz. This chopper frequency is decided only from experimental system characteristics.

For the optical transmittance measurement, we used the same PAS system as the detection where it is used in the optical absorption measurements. However, carbon black powder was set in the PAS cell instead of the samples. And the sample was set on the light beam axis, directly behind the mechanical chopper. All optical measurements were carried out at room temperature. The wavelength of the excitation light was scanned from 400 nm to 1600 nm with the steps of 5 nm. The PA signal intensity was normalized by the signal from the fixed quantity of carbon black to eliminate the effects of the spectral characteristics of the experimental apparatus.

The crystal properties of samples were studied by using XRD analysis (Philips; X'Pert MRD High Resolution X-ray Diffractometer), where copper $K\alpha_1$ was used. The XRD was measured over the range $2\theta = 0.5 \sim 80$ degrees. For the XRD measurement, the acceleration voltage and scan speed were 45 kV and 0.01 deg/min, respectively. From the result of the high angle XRD, the degree of recrystallization was evaluated.

3. RESULTS AND DISCUSSION

Figure 1 shows the "1-optical transmittance T" of Sample-Si-Ge-Au as a function of annealing cycles [6]. The ordinate means reversed normalized transmittance for the comparison with absorption spectra. As-deposited Sample-Si-Ge-Au is an opaque silver metallic color. Then in the visible light region, normalized "1-T" is almost unity. Normalized "1-T" gradually decreases with increasing wavelength above 800 nm. After annealing, the spectrum starts to show a sharp drop at

around 500nm. This sharp drop is enhanced by the annealing cycles. The valley at around 650 nm becomes deep with the annealing cycles.

Figure 2 shows the X-ray diffraction profiles in the high angle region for Sample-Si-0, Sample-Si-7, Sample-Ge-0 and Sample-Ge-2. Open triangles, closed triangles, open diamonds and closed diamonds indicate typical X-ray diffraction peaks for Si, Ge, Au and sapphire, respectively. There are no differences in all diffraction profiles of Si thin films (Sample-Si-0 $\sim$ 7). The Ge thin films except for Sample-Ge-0 show extra 1 peak at around 38 degrees which can be assigned to Au. We may deduce that the recrystallization progresses with the annealing for Sample-Ge because of the existence of Au peak in Sample-Ge-1~7.
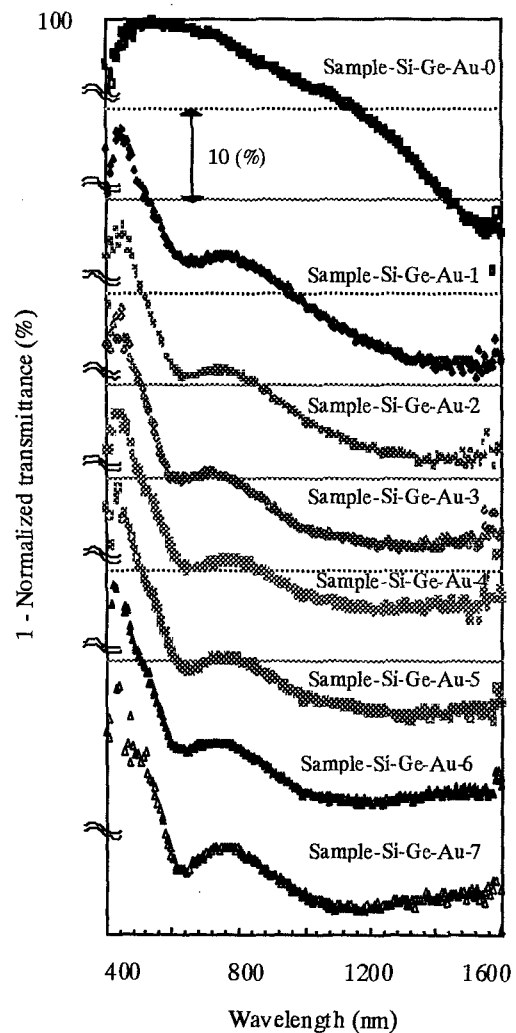

Fig. 1 "1 - normalized transmittance" of Sample-Si-Ge-Au. In the ordinate, data for each sample are shifted 10% to distinguish them easily. Doded lines indicate 100% position for each sample.

Figure 3 shows the "1-optical transmittance T" of Sample-Si as a function of annealing cycles. On the contrary, from the absorption spectra which is changed by the annealing, we cannot obtain the meaningful

information because the measured absorption of Sample-Si and Sample-Ge are very small and almost flat. Normalized "1-T" below 630 nm gradually decreases to the valley between 630 ~ 820 nm, then increases between 800 ~ 1000 nm and decreases above 1100 nm with the increasing wavelength. The valley shifts to lower wavelength as the annealing cycles increase.
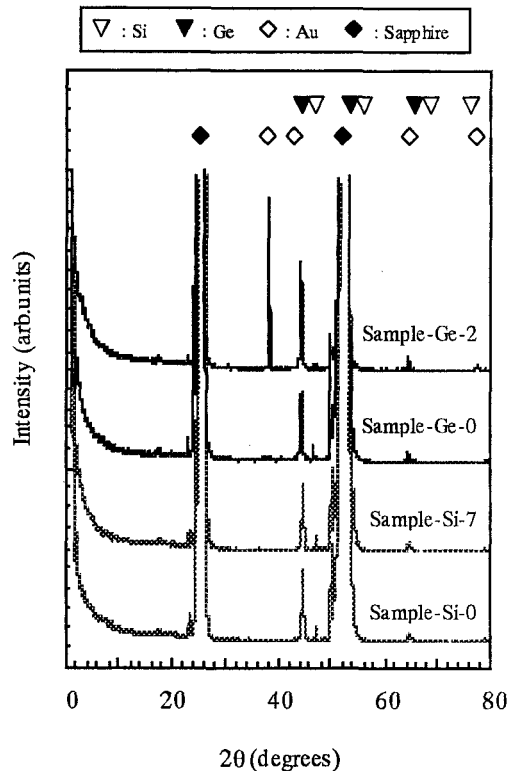

Fig. 2 High angle X-ray diffraction of Sample-Si and Sample-Ge.

Fig. 3 "1 - normalized transmittance" of Sample-Si. In the ordinate, data for each sample are shifted 50% to distinguish them easily. Doded lines indicate 100% position for each sample.

Figure 4 shows the annealing cycle dependence of these valley position in the energy scale. The valley (marked by arrow) has the similar energy to the reported optical bandgap of amorphous Si (1.5 ~ 2.0 eV) [7]. From the energy increase with annealing cycles, we can say that the energy corresponding to the valley shows the tendency to saturate. As mentioned before, thermoelectric property changes by the annealing cycle. So we can consider that the slight change of quasi-stable amorphous phase is responsible to this thermoelectric property change. Therefore, we can conclude that the tendency of energy shift is caused by the change of quasi-stable amorphous phase.

Figure 5 shows the "1-optical transmittance T" of Sample-Ge as a function of annealing cycles. Sample-Ge-0 is almost unity and an opaque silver metallic color. The color of Sample-Ge changes to transparent even after 1 annealing cycle and normalized "1-T" show the drastic decrease. After the 1st annealing, there appears small structure around 600 nm. Normalized spectra of Sample-Ge-1~7 do not depend on the annealing cycles.

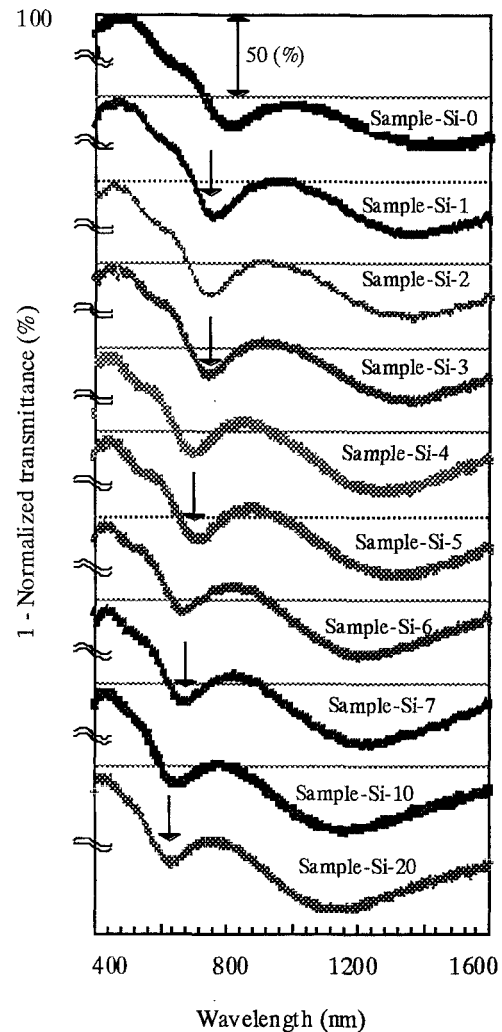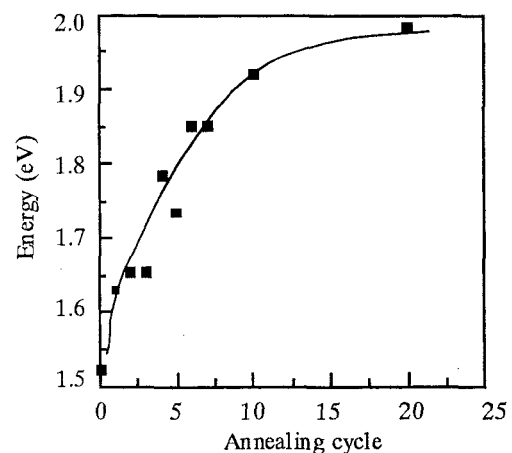Comparing with Figs. 3 and 5, Normalized "1-T" of

Fig. 4 The annealing cycle dependence of valley peak position in the Fig. 3 of energy.

Sample-Si-Ge-Au in Fig.1 is qualitatively equal to the summation of the spectrum of Sample-Si and Sample-Ge. The normalized "1-T" of Sample-Si-Ge-Au is mainly affected by that of Sample-Si.
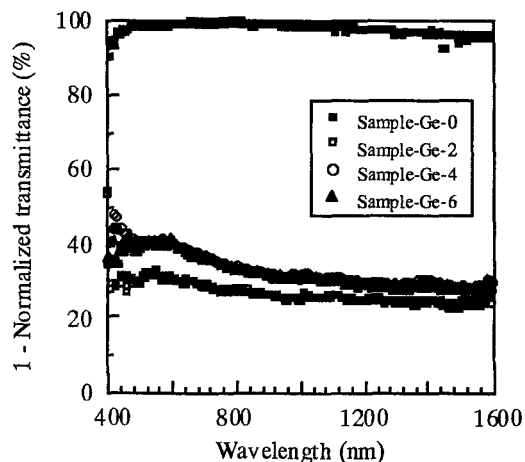

Fig. 5 "1 - normalized transmittance" of Sample-Ge.

4. CONCLUSION

We found the changes of optical properties of Si and Au doped Ge thin films in photoacoustic spectra as a function of the annealing cycle.

Though there cannot been seen any differences in X-ray diffraction, the apparent differences in absorption of Si and Ge thin films with the repeated annealing cycles were observed. The absorption of Si-Ge-Au thin film has the similar to the summation of that of Si and Au doped Ge. The optical properties of Si-Ge-Au thin films are mainly caused by that of Si thin films. So, we can deduce that the change of thermoelectric properties of Si-Ge-Au with annealing cycles could be mainly appeared in optical properties of Si and caused by the change of quasi-stable amorphous phase.

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