Photoacoustic Spectra and Thermoelectric Properties of Amorphous Si/Au/Ge/Au Superlattice
アモルファス Si/Au/Ge/Au 層周期超格子の光音響スペクトラルと熱電特性

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1. Introduction

Recently, many researchers have been interested in thermoelectric materials from the viewpoint of the energy and environmental conservation. The thermoelectric power generation is the technique to use the wasted heat. But energy conversion efficiency is lower than conventional generator.

Generally, thermoelectric materials are evaluated by dimensionless figure of merit \( ZT = \frac{\alpha^2 T}{\rho \kappa} \), where \( \alpha \), \( \rho \), \( T \) and \( \kappa \) are thermoelectric power, electrical resistivity, absolute temperature and thermal conductivity, respectively. One of the criteria for the practical use of the thermoelectric materials is \( ZT > 1 \).

We have reported extremely large thermoelectric power of Si-Ge-Au amorphous thin film which maximum \( ZT \) value reached around 10. It was reported that quasi-stable amorphous phase and/or mixture of microcrystal would be responsible for large thermoelectric power. But the mechanism is not clarified sufficiently.

In this work, to make the mechanism clearer, we present thermoelectric properties and PA (photoacoustic) spectra of amorphous Si/Au/Ge/Au superlattice with various Au concentrations. And we attempt to discuss influence of Au in the thin film.

2. Experiments

The sample preparation procedure was almost same as previous papers. Samples were prepared by alternate deposition of Si, Ge and Au in the ultra high vacuum system. They have 4 layers of Si/Au/Ge/Au as 1 period. The artificial intervals and total number of periods were kept in 10 nm and 30, respectively. So all the samples thickness was 300 nm. We denoted the samples as (thickness of Si layer in nm/ thickness of Au layer in nm/ thickness of Ge layer in nm/ thickness of Au layer in nm/ number of intervals). All samples were (5.0 - x/ x/ 5.0 - x/ x/ 30), where x is ranging 0 to 0.7. The layered structure was collapsed easily by annealing at 673 K.

The thermoelectric power and resistivity were measured by four terminal methods during annealing cycles. Annealing temperature was set at 673 K, and one annealing cycle was heat up and cool down between room temperature and 673 K at a rate of 10 K/min. The concentration ratio of the sample was measured by X-ray fluorescent analyzer (RIGAKU; RIX2100).

For the optical absorption measurement, conventional microphone PAS (photoacoustic spectroscopy) was used. The wavelength of excitation light was scanned from 400 nm to 1600 nm with the steps of 5 nm. The optical system of the PAS was tuned for the sensitivity not for the resolution.

3. Results and Discussion

Fig. 1 shows Au concentration dependence of thermoelectric power at second annealing cycle. In this figure, all data were replotted from ref. 5. The regions 1 and 3 have positive and negative thermoelectric power, respectively. Region 2 of Au concentration ranges from 6 to 8 % is transition region. So thermoelectric power of the thin films changes from positive to negative with Au concentration increased. Obviously, conduction type of Si-Ge-Au thin films can be affected by Au concentration.

Fig. 2 shows the PA spectra of as-deposited samples at room temperature with various Au layer thickness. The PA spectra exhibit absorption spectra of the films. The peaks at around 1400 nm come from the absorption of surface adsorbed water. In absorption spectrum of (5.0/ 0/ 5.0/ 0/ 30), two clear peaks are observed at around 1400 nm (marked by “A”) and 1100 nm (marked by “B”). Peaks A and B would represent the band gap of amorphous Si and amorphous Ge, respectively. Peaks A and B shift to longer wavelength with Au concentration.
increased. In ref. 7, it is reported that the band gap of amorphous Si decreases with increasing Au concentration, since Au atoms in amorphous Si make strong potential fluctuations. It is considered that Au atoms in amorphous Ge act similarly. So the shift of peaks A and B would correspond to change of band gap of amorphous Si and amorphous Ge by Au impurity.

In the samples that contain Au, the small peaks (marked by “C”) are found at around 1100 nm. The band gap of amorphous Ge would not be responsible for peak C, because the peak position does not change by Au quantity. Also, small shoulders on water peak at around 1400 nm (marked by “D”) are observed. There are two impurity levels associated with Au in crystal Si. One is acceptor level, which exists about 0.02 eV above Fermi energy. The other is donor level, which locates about 0.27 eV under Fermi energy. And band gap of amorphous Si is approximately 1.7 eV. Therefore, we can estimate gap from valence band to acceptor level is 0.87 eV (= ~1430 nm) and the gap from donor level to conduction band is 1.12 eV (= ~1100 nm). These gaps were made from Au impurity in amorphous Si. Therefore, it is considered that peaks (peak C) and shoulders (peak D) indicate donor and acceptor level due to Au impurity in amorphous Si. And the formation state of both donor and acceptor level may be responsible for change of conduction type of the thin film with Au concentration and temperature.

4. Conclusion

From the measurements of thermoelectric properties and PAS, we conclude followings.

Conduction type of the thin film is affected by the formation state of both donor and acceptor level by Au impurity.

The electronic energy band gaps of amorphous Si and amorphous Ge decrease with increasing Au concentration. But they have different Au concentration dependence.

References