

Annealing Cycle Dependence of Thermal Conductivity for Si–Ge–Au Thin Film Analyzed by Thermal Microscopy

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The thermal effusivity of a Si–Ge–Au thin film was measured using a thermal microscope. A thin-film sample with sixty-seven artificial intervals each comprising Si (2.0 nm)/Au-doped Ge (2.5 nm) was prepared and annealed more than 20 times. The dependence of the thermal conductivity of the film on the number of annealing cycles was determined using the obtained experimental thermal effusivity data, bulk density, and specific heat capacity. The film thickness (~300 nm) was greater than the thermal diffusion length of the samples. The thermal conductivity of the Si–Ge–Au thin film was satisfactory considering the number of annealing cycles. Thus, we elucidated the annealing effect of thermal conductivity for the Si–Ge–Au thin film.

1. Introduction

The heavy dependence of many countries on fossil fuels is a matter of serious public concern. One strategy to address this environmental crisis is to step up research on sustainable energy and to develop thermoelectric materials. The effectiveness of a material in thermoelectric applications is determined by the dimensionless figure of merit, ZT , which is expressed as⁽¹⁾

$$ZT = S^2\sigma T/\lambda, \quad (1)$$

where S , σ , T , and λ are the Seebeck coefficient, electrical conductivity, absolute temperature, and thermal conductivity, respectively. A “good” thermoelectric material is defined as one with a large Seebeck coefficient, high electrical conductivity, and low thermal conductivity.

It is well known that good thermoelectric materials, which contain metal atoms and semimetal atoms, should possess the following structures: (1) a structure with a large number of atoms in the unit cell of crystals, (2) a superlattice structure, and (3) a structure containing large

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atoms bonded loosely in the cage crystal structure of a large unit cell. Recently, Okamoto and others have suggested that the extremely high power of a Si–Ge–Au superlattice thin film is related to structural change and thermal conduction.^(2–10) On the other hand, we have measured the thermal effusivities of thin films by the thermoreflectance method using thermophysical microscopy (TM).⁽¹¹⁾

With this background, the thermal effusivity of a Si–Ge–Au film was measured by TM. Moreover, the dependence of the thermal conductivity of the film on the number of annealing cycles was determined using the obtained experimental thermal effusivity data, bulk density, and specific heat capacity.

2. Experimental Methods

2.1 Samples

The detailed sample preparation procedure is described in Refs. 3–10. Thin films comprising Au-doped Ge layer and Si layer were prepared by an independent shutter operation with the simultaneous evaporation of these two components onto glass substrates in an ultrahigh-vacuum system. The base pressure of the stainless-steel chamber with a liquid N₂ shroud was approximately $\sim 10^{-8}$ Pa, but increased to up to $\sim 10^{-6}$ Pa during the operation of two electron beam guns. The evaporation rate and layer thickness were controlled by a computer with two sets of crystal oscillator thickness monitors. The deposition rate of both evaporation sources was maintained at approximately 0.05 nm/s. The crystal oscillator thickness monitors were calibrated using a surface morphology micrometer and X-ray low-angle diffraction system. The sample was prepared with sixty-seven artificial intervals each comprising Si (2.0 nm)/Au-doped Ge (2.5 nm). One annealing cycle was performed at a heating rate of 10 K/min, after which the temperature was maintained at 673 K for 10 min, cooled at 10 K/min, and then maintained at room temperature for 10 min in N₂ gas flow at atmospheric pressure. The film thickness (~ 300 nm) was greater than the thermal diffusion length of the samples. The structure of the Si–Ge–Au thin film is illustrated in Fig. 1.

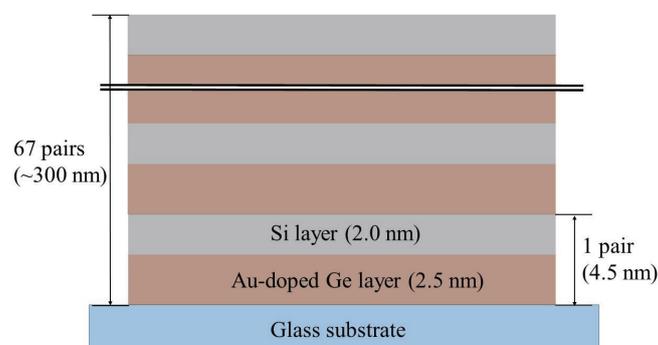


Fig. 1. (Color online) Schematic of structure of the Si–Ge–Au thin film.

2.2 Thermal effusivity measurements

For the thermal effusivity measurements, it was necessary to sputter a Mo film, which was approximately 100 nm thick, onto the surface of the sample. Figure 2 shows the TM apparatus, which is described in detail in Ref. 12. Detailed information on typical TM and data processing for determining the thermal effusivity at one point of a sample is available in our previous publication;⁽¹³⁾ only a brief outline is provided here. The Mo thin film was first sputtered onto the sample to serve two functions: as a laser-beam refractor for temperature measurements and as a heat absorber. A small area of the sample surface was heated by an intensity-modulated laser beam, and the temperature response was monitored by another laser beam on the basis of thermorefectance. The thermal effusivity was derived from the phase lag between the thermal wave and the thermorefectance signal.

Each of the two laser beams used in the setup was coaxially aligned and focused on the sample surface. A compensating network based on a differential scheme was used to reduce the fluctuations caused by the instability of the probe laser. The diameters of the heating and detection areas were 23.4 and 7.2 μm , respectively. To justify the use of a one-dimensional heat-transfer model in the analysis of the measurement data, the area heated by the heating laser beam must be larger than the area used for the reflectivity measurements. The spatial resolution of the apparatus was determined from the sum of the diameter of the probing laser beam and the thermal diffusion length. In this study, the modulation angular frequency of the heating laser beam was 2 MHz. The sample surface could be viewed using a CCD camera built into the microscope's optical system. The heating laser beam with a sinusoidally modulated signal and angular frequency ω was incident on the sample surface. The temperature response of the

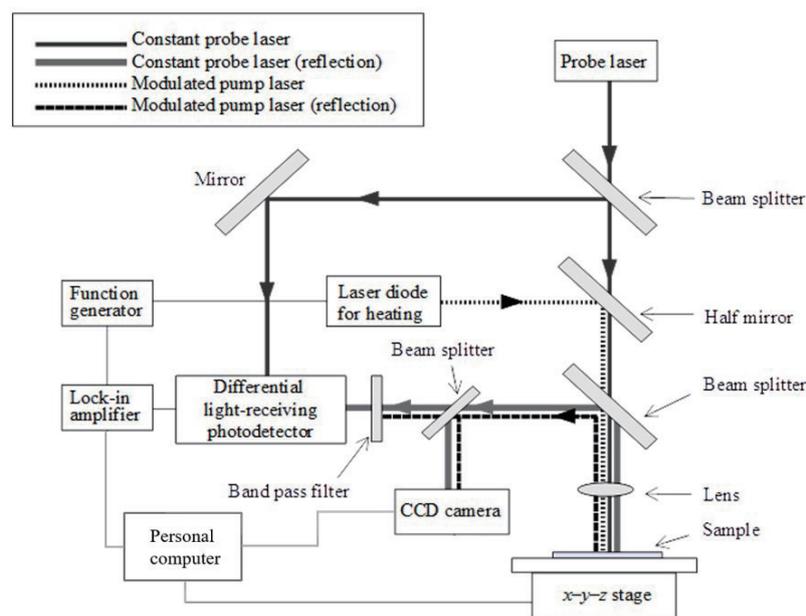


Fig. 2. Illustration of thermal microscope apparatus.

sample surface to the heat input from the laser was measured by monitoring the variation in the intensity of the reflected beam of the second temperature-sensing laser that was operating at constant energy. The measurements were carried out at room temperature, and the temperature oscillated with a phase lag of θ relative to the phase of the heating laser. The thermal effusivity of the sample, b_s , was derived using Eqs. (2) to (4) below. The analytical formulation was based on the assumption that the contact thermal resistance of the coating/sample interface was negligible in a two-layered system and the temperature distribution in the sample reached a steady state. The analysis was based on one-dimensional heat flow in a semi-infinite layer:

$$\theta = \frac{3}{4}\pi + \arctan \left(\frac{\cosh^2 \sqrt{\frac{\omega\tau_f}{2}} \left(\tanh \sqrt{\frac{\omega\tau_f}{2}} + \beta \right) \left(\tanh \sqrt{\frac{\omega\tau_f}{2}} + \beta^{-1} \right)}{\cos^2 \sqrt{\frac{\omega\tau_f}{2}} (\beta - \beta^{-1}) \tan \sqrt{\frac{\omega\tau_f}{2}}} \right), \quad (2)$$

where

$$\tau_f = d^2/\alpha_f, \quad (3)$$

$$\beta = b_s/b_f, \quad (4)$$

and τ , α , and d represent the characteristic time for heat diffusion, thermal diffusivity, and thickness of the Mo layer, respectively. The subscripts “s” and “f” are modifiers that indicate whether a variable represents a parameter of the sample or the Mo film, respectively. The value of θ in Eq. (2) was measured using a lock-in amplifier. The thermophysical properties of the Mo film and the values of α_f and b_f were determined in separate experiments.

2.3 Evaluation of thermal conductivity

The thermal conductivity of the sample, λ_s , can be obtained from b_s using Eq. (5) if the bulk density ρ_s and the specific heat capacity C_{ps} are known:

$$\lambda_s = b_s^2 / \rho_s C_{ps}. \quad (5)$$

The bulk density and specific heat capacity of the Si–Ge–Au thin-film sample are summarized in Table 1. The bulk density was evaluated on the basis of the additive law using

Table 1
Bulk density and specific heat capacity of the Si–Ge–Au thin-film sample.

Sample	Bulk density (kgm ⁻³)	Specific heat capacity (Jkg ⁻¹ K ⁻¹)
Si–Ge–Au	5767	300

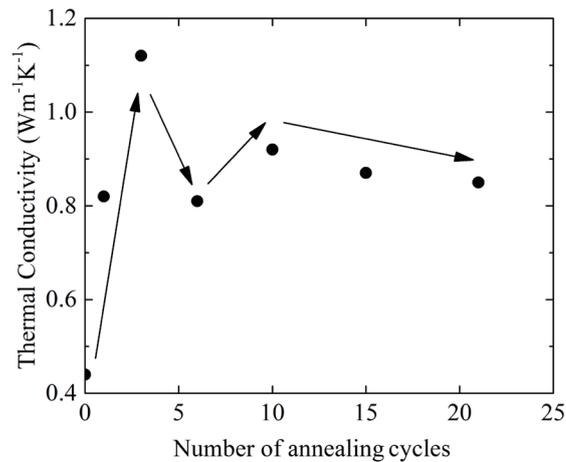


Fig. 3. Dependence of the thermal conductivity of Si-Ge-Au thin film on the number of annealing cycles.

the values for the solid state for Si, Ge, and Au in Ref. 14 at 298 K. The specific heat capacity was evaluated on the basis of Kopp's law using values for the solid state for Si, Ge, and Au in Ref. 14 at 298 K. In this study, the mass fractions of the sample were 22, 70, and 8, respectively, for Si, Ge, and Au.

3. Results and Discussion

Figure 3 shows the dependence of the thermal conductivity on the number of annealing cycles (0–21) for the Si-Ge-Au thin film. For no annealing cycles, the thermal conductivity was relatively low, because the sample was in the form of an amorphous artificial superlattice thin film. For two annealing cycles, the thermal conductivity was relatively high, owing to the degradation of the superlattice. Following degradation, the superlattice became a simple amorphous thin film. The thermal conductivity decreased once for six annealing cycles, increased once for ten cycles, and slightly decreased for more than ten annealing cycles. This decrease in the thermal conductivity may be ascribed to the generation of a nanocrystalline nucleus, followed by a growth and increase in the number of nanocrystal grains. The thermal conductivity of the simple Si-Ge-Au amorphous thin film was approximately $1.1 \text{ Wm}^{-1}\text{K}^{-1}$, since the initial annealing led to the degradation of the artificial superlattice. Subsequently, the thermal conductivity decreased with increasing number of annealing cycles because of the phonon scattering effect due to the growth and increase in the number of nanocrystal grains.^(2–10)

4. Conclusions

In this study, the dependence of thermal conductivity on the number of annealing cycles was determined for a Si-Ge-Au thin film. The following conclusions were drawn:

1. For no annealing cycles, the thermal conductivity was relatively low because the sample was an amorphous artificial superlattice thin film.

2. The thermal conductivity slightly decreased with increasing number of annealing cycles for more than 10 cycles. This can be attributed to the nucleation and growth of nanocrystals.

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