Measurement of Thermal Radiative Properties of Silicon Wafers with Oxide Film and Nitride Film at 950°C*

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The normal spectral emissivity, reflectance and transmittance of silicon wafers were measured at a temperature of 950°C and wavelengths of 0.7 to 9 μm. The samples were seven silicon wafers with oxide films of 2.2 to 628 nm film thickness and nitride films of 48 to 193 nm film thickness with small dopant density. It was found that the emissivities of specular surfaces of silicon wafers with very thin oxide films at wavelengths of 0.7 to 8 μm were 0.6 to 0.7, the reflectances were 0.1 to 0.3 and the transmittances were 0 to 0.2. The emissivity of silicon wafers with oxide films of more than 75 nm film thickness and nitride films of more than 48 nm film thickness changed from 0.6 to 1.0 according to film thickness and wavelength. The emissivities and reflectances of silicon wafers were calculated using the free carrier absorption theory considering the interference phenomenon. Calculated results agreed with experimental results.

Key Words: Thermophysical Property, Thermal Radiation, Electric Equipment, Silicon Wafer, Oxide Film, Spectral Emissivity, High Temperature

1. Introduction

In semiconductor device processing, silicon wafers are heated to 800 ~ 1 000°C to diffuse impurity atoms and to form oxide film[1]. Much research[2]~[5] on the prevention of thermoplastic deformation and achieving of uniform heating has been reported. However the availabe data on thermal radiative properties of silicon wafers at high temperature are insufficient, and hence every analytical study conducted thus far has used a different value of emissivity from 0.2 to 0.7[6]. In addition, a pyrometric temperature measurement technique for silicon wafers in a diffusion furnace was reported[7] but the measured value changed to a maximum of 70°C according to change of the emissivity[8]. Consequently it was necessary to obtain thermal radiative properties of silicon wafers with various films systematically.

Allen[9] measured the spectral emissivity of single-crystal silicon at temperatures of 730 to 1 410°C (melting point) and a wavelength of 0.65 μm. The results were that the emissivity of a smooth surface was 0.59 and that of a sandblasted surface was 0.79 at a temperature of 950°C.

Liebert[10] measured the normal spectral emissivity and transmittance of *p*-type and *n*-type silicon wafers at temperatures of 610 and 800°C and wavelengths of 4 to 15 μm. The results showed that the emissivity changed from 0.6 to 0.8 according to wavelength and impurity atom concentration and the transmittance was zero. The emissivities at both temperatures were almost same. In addition, Liebert calculated the emissivity using the Hagen-Rubens theory and the free carrier absorption theory. The latter theory agreed with experimental results.

Sato[11] measured the normal spectral emissivity of *n*-type silicon wafers without oxide film at temperatures of 70 to 800°C. The emissivity was 0.6~0.7 at

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temperatures of 600 to 800°C and wavelengths of 0.4 to 15 μm. The measured emissivity was close to the theoretical formula using optical properties.

Myers et al.[12][13] measured the normal spectral emissivity, reflectance and transmittance of polysilicon at a temperature of 1 000°C and wavelengths of 0.7 to 15 μm. Their measuring method was the same as that in this work. The results were that the emissivity was 0.7 to 0.8, the reflectance was 0.2 to 0.3 and the transmittance was zero.

Thermal radiative properties of silicon wafers with different film thicknesses were measured at room temperature as follows. All samples were heavily doped with impurity atoms, because the emissivity of pure silicon is small at room temperature and wavelengths of 1.1 to 8 μm[14].

Senitzky and Weeks[15] measured the spectral reflectance of n-type silicon wafers with epitaxial silicon films of 0.5 to 3 μm film thickness at wavelengths of 5 to 50 μm. The reflectance changed sinusoidally from 0 to 0.6 according to the film thickness. The analytical results considering the interference effect of multiple reflection inside the film agreed with the experimental results.

Pettibone et al.[16] measured the spectral emissivity of p-type silicon wafers with oxide films of 0 to 800 nm film thickness at wavelengths of 2 to 8 μm. The emissivity changed sinusoidally from 0.7 to 0.94 according to the film thickness. The analytical results considering the interference effect of multiple reflection inside the film agreed with the experimental results.

The object of this paper is to systematically obtain thermal radiative properties of silicon waters with films which are used in semiconductor device processing at high temperature. The normal spectral emissivity, reflectance and transmittance of four silicon wafers with oxide (SiO_2) films of 2.2 to 605 nm film thickness and three silicon wafers with nitride (Si_3N_4) films of 48 to 193 nm film thickness are measured at a temperature of 950°C and wavelengths of 0.7 to 9 nm. The emissivity of a specular surface and a rough surface of a wafer are compared. The emissivity of a quartz plate 1 mm thick is measured to check the accuracy. In addition, the emissivity and reflectance of silicon wafers are calculated using the free carrier absorption theory considering the interference effect of multiple reflection inside the film, and the findings are compared with the experimental results.

2. Nomenclature

e : electron charge 1.6×10^{-19}C
k_2 : extinction coefficient of silicon substrate
L : radiative emissive power W
m^* : effective mass of electron kg
m_e : mass of electron 9.11×10^{-31} kg
N : carrier concentration m^{-3}
n_1 : refractive index of film
n_2 : refractive index of silicon substrate
r : direct current resistivity Ωm
T : temperature K
z : wafer thickness m
δ : film thickness m
ε : emissivity
ε_0 : electrical permittivity of vacuum 8.85×10^{-12} C^2/Nm^2
ε_∞ : relative dielectric constant in absence of contribution from free carrier at very high frequencies
λ : wavelength m
μ : mobility of electron m^2/Vs
ρ : reflectance
ρ_1 : reflectance at boundary between air and film
ρ_2 : reflectance at boundary between film and silicon substrate
τ : transmittance
τ_r : relaxation time s
ω : frequency s^{-1}

3. Experimental Apparatus

The integral blackbody method developed by Myers et al.[13] was used to determine thermal radiative properties of semitransparent materials at high temperature. Figure 1 shows a schematic horizontal cross section of the apparatus. A sample holder (stainless steel, 57 mm in outer diameter and 20 mm in length) with samples was installed at the center of a tubular heater (60 mm in inner diameter, 550 mm in length and with temperature fluctuation of less than ± 1°C). Two cavity holes (10 mm in diameter and 15 mm in depth) and two through holes (10 mm in diameter) were aligned. The samples (two pieces 12 mm in diameter) were attached in front of one cavity hole and one through hole. The normal spectral emissive power from each hole was meaured by a spectrophotometer (Japan Spectroscopic Co., Ltd., Model

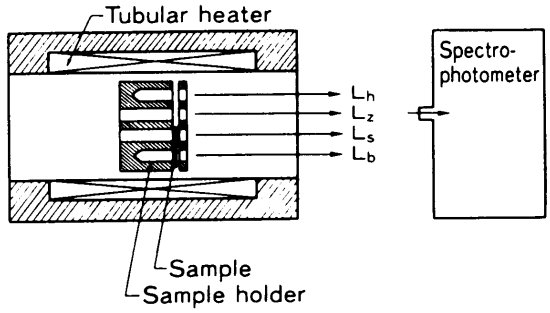

Fig. 1 Experimental apparatus

CT-25GT). The sensors were a silicon photodiode at wavelength smaller than 1 μm and a vacuum thermocouple at wavelength larger than 1 μm. The temperature of the samples was measured by a thermocouple (Pt-Pt 13 % Rh) which was attached to the sample holder. When the normal spectral emissive power of the cavity hole without sample L_h, that of the through hole without sample L_z, that of the through hole with sample L_s and that of the cavity hole with sample L_b are measured, the normal spectral emissivity ε, reflectance ρ and transmittance τ are determined by Eqs. (1)～(3)[13].

$$\varepsilon=(L_s-L_z)/(L_h-L_z) \quad (1)$$

$$\rho=(L_h-L_b)/(L_h-L_z) \quad (2)$$

$$\tau=(1-\varepsilon-\rho) \quad (3)$$

In this measuring method the cavity hole must be the blackbody. The emissivity of an oxide stainless steel cavity hole of 10 mm in diameter and 15 mm in depth is estimated to be 0.97[17] and so the error is about 3 %. Also, both sides of the sample must be nonscattering. Surface roughness of one side of the silicon wafers used in this work was less than 0.1 μm (called a specular surface in this paper) and that of the other side was about 1 μm (called a rough surface). However, most measurements are of specular surfaces and the transmittance of silicon wafers at high temperature is small (shown later); thus the error is small.

Table 1 shows the list of samples. The silicon wafers were p-type or n-type with small concentrations of impurity atoms (about $10^{21}\ m^{-3}$). The oxide films and the nitride films were formed by a diffusion furnace and a chemical vapor deposition reactor. Film thickness was measured by ellipsometry. As samples were held in air at high temperature, oxide film thickness changed during the experiment. The error of the emissivity caused by the change of oxide film thickness was less than ±0.05. The oxide film of sample No. 1 before the experiment was formed in air at room temperature.

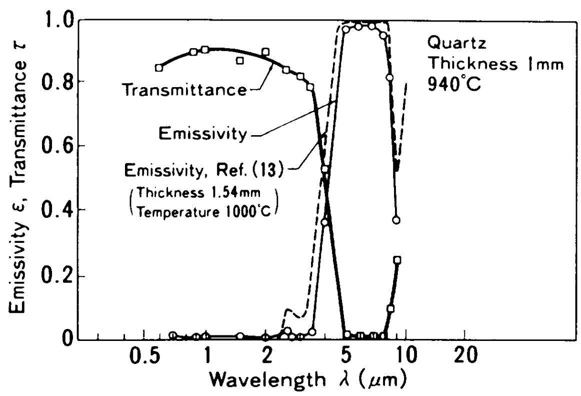

Fig. 2 Normal spectral emissivity and transmittance of quartz

4. Experimental Resuls

4.1 Quartz plate

Figure 2 shows the normal spectral emissivity and transmittance of a quartz plate 1.0 mm thick at a temperature of 940°C. In Fig. 2 the broken line shows Myers et al.'s data[13] of a quartz plate 1.5 mm thick at a temperature of 1 000°C. The emissivity of our results and Myers et al.'s data agree, except in the range of wavelengths from 3 to 5 μm where the transmittance

Table 1 List of samples

No.	Material	Plate thickness (mm)	Film thickness (nm) Before experiment	Film thickness (nm) After experiment
1	Silicon wafer with oxide film	0.475	2.2	51
2		0.475	75	99
3		0.55	305	323
4		0.475	605	628
5	Silicon wafer with nitride film	0.55	48	48
6		0.475	141	141
7		0.50	193	193
8	Quartz	1	—	—

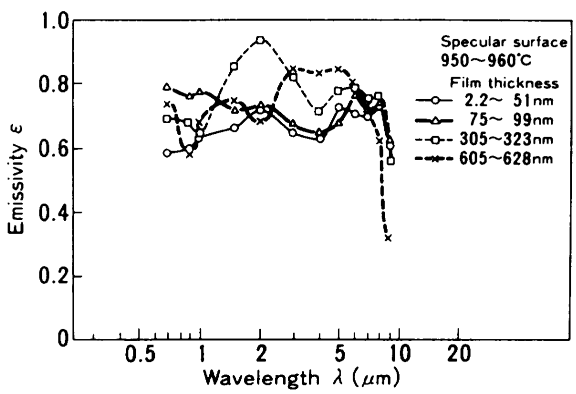

Fig. 3 Normal spectral emissivity of silicon wafers with oxide film

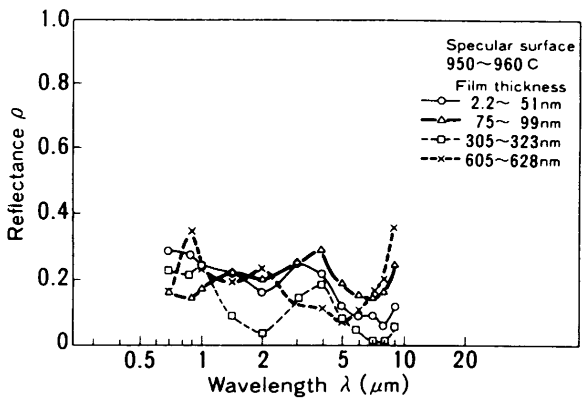

Fig. 4 Normal spectral reflectance of silicon wafers with oxide film

depends on plate thickness. Thus, the error of the emissivity in this work is less than ±0.05.

4. 2 Silicon wafers with different film thicknesses

Figures 3~5 show the normal spectral emissivity, reflectance and transmittance of four silicon wafers with different oxide film thicknesses at a temperature of about 950°C. The specular surfaces of wafers were measured. The emissivity of the silicon wafer with an oxide film of 2.2 to 51 nm film thickness (symbolized by ○ in figures and referred to as the base wafer in this paper) is 0.6 to 0.7 at wavelengths of 0.7 to 8 μm, the reflectance is 0.1 to 0.3 and the transmittance in 0 to 0.2. The silicon wafer with oxide film of 75 to 99 nm film thickness (symbolized by △) has larger emissivity and smaller reflectance than the base wafer at wavelength of less than 1.5 μm. The silicon wafer with oxide film of 305 to 323 nm film thickness (symbolized by □) has larger emissivity and smaller reflectance than the base wafer at wavelengths of 1.5 to 3 μm. The silicon wafer with oxide film of 605 to 628 nm film thickness (symbolized by ×) has larger emissivity and smaller reflectance than the base wafer at wavelengths of 3 to 5 μm. The transmittance changes are small even though the film thickness changes.

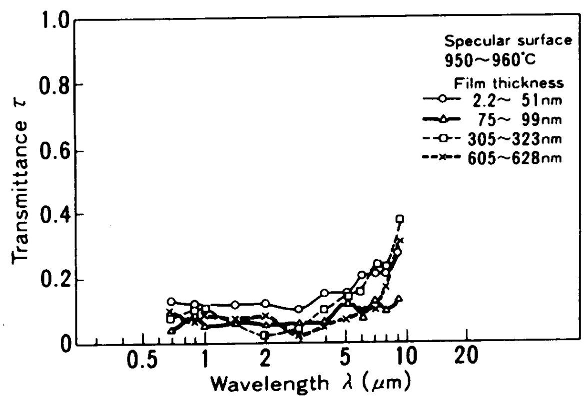

Fig. 5 Normal spectral transmittance of silicon wafers with oxide film

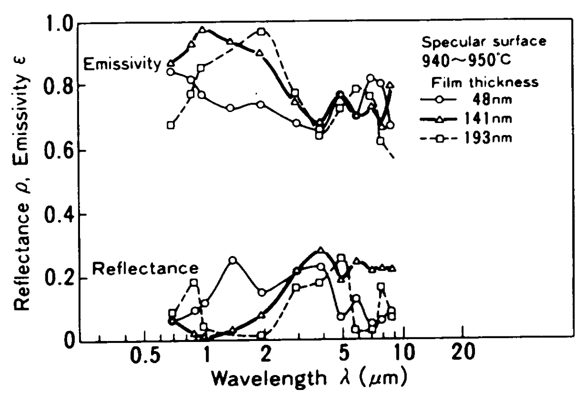

Fig. 6 Normal spectral emissivity and reflectance of silicon wafers with nitride film

Figures 6 and 7 show the normal spectral emissivity, reflectance and transmittance of three silicon wafers with different nitride film thicknesses at a temperature of about 950°C. The silicon wafer with nitride film of 48 nm film thickness (symbolized by ○) has larger emissivity and smaller reflectance than the base wafer at a wavelength less than 1.5 μm. The silicon wafer with nitride film of 141 nm film thickness (symbolized by △) has larger emissivity and smaller reflectance than the base wafer at a wavelength less than 3 μm. The silicon wafer with nitride film of 193 nm film thickness (symbolized by □) has larger emissivity and smaller reflectance than the base wafer at wavelengths of 1 to 3 μm. The reason for the change in the emissivity and the reflectance is the interference effect of multiple reflection inside the film[15][16], which will be shown later.

Reference (14) shows that the normal spectral emissivity ε of a silicon wafer with small concentration of impurity atoms was 0 to 0.1 at room temperature and a wavelength of 1.1 to 8 μm, the reflectance ρ was 0.1 to 0.3 and the transmittance τ was about 0.5. The data were obtained in different experiments and so the total of ε, ρ and τ was not 1.0. Comparing the data at room temperature with our results, it is concluded that the emissivity increases and the reflectance decreases at high temperature. The reason is that the free carrier concentration increases at high temperature. The transmittance changes little even though temperature changes.

4. 3 Surface roughness of silicon wafer

Figure 8 shows the normal specular emissivity and reflectance of the specular surface and the rough surface of the base wafer. The emissivity of the rough surface is larger than that of the specular surface by 0.07. This result is similar to that of an earlier work[9].

5. Analysis

The normal specular reflectance ρ of a wafer with

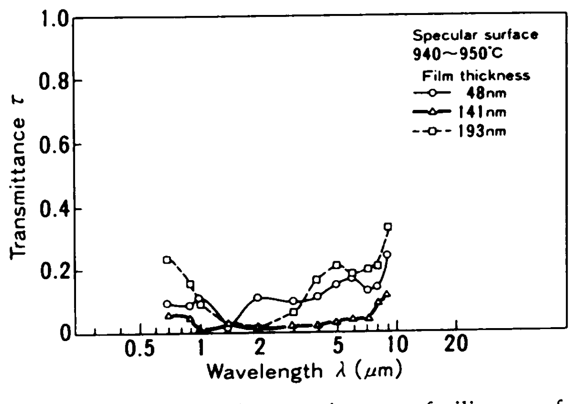

Fig. 7 Normal spectral transmittance of silicon wafers with nitride film

a film of thickness δ at a wavelength λ is calculated by Eq. (4) considering the interference effect of multiple reflection inside the film[15]. Here absorption in the film and reflection at the back side of the wafer are neglected.

$$\rho=\{\rho_1+\rho_2+2\sqrt{\rho_1\rho_2}\cos(4\pi n_1\delta/\lambda)\}/\{1+\rho_1\rho_2+2\sqrt{\rho_1\rho_2}\cos(4\pi n_1\delta/\lambda)\} \quad (4)$$

The reflectance at the boundary between air and the film ρ_1 and the reflectance at the boundary between the film and the silicon substrate ρ_2 are related to the optical properties as shown in Eqs. (5) and (6) using the electromagnetic theory. Here the extinction coefficient of the film is assumed to be zero.

$$\rho_1=(n_1-1)^2/(n_1+1)^2 \quad (5)$$

$$\rho_2=\{(n_2-n_1)^2+k_2^2\}/\{(n_2+n_1)^2+k_2^2\} \quad (6)$$

As the refractive index n_1 of SiO_2 and Si_3N_4 changes little according to temperature, the value at room temperature[18] is used. The wavelength where the extinction coefficient of the film is negligible is 0.1 to 8 μm for SiO_2 and more than 0.2 μm to the unknown upper limit for Si_3N_4[18]. The refractive index n_2 and the extinction coefficient k_2 of silicon are calculated by Eqs. (7) and (8) using the free carrier absorption theory. Absorption due to band-to-band transitions occurs at wavelengths lower than 1.1 μm and absorption due to Si-O lattice vibration occurs at a wavelength of 9 μm[11]. The wavelength where the free carrier absorption is dominant is 1.1 to 8 μm.

$$n_2^2-k_2^2=\varepsilon_\infty-Ne^2\tau_r^2/\{m^*\varepsilon_0(1+\omega^2\tau_r^2)\} \quad (7)$$

$$n_2k_2=Ne^2\tau_r/\{2\omega m^*\varepsilon_0(1+\omega^2\tau_r^2)\} \quad (8)$$

The relative dielectric constant in the absence of the contribution from the free carrier at very high frequencies is $\varepsilon_\infty=13$[10] and the effective mass of the electron is $m^*=0.27m_e$[10]. The carrier concentration N is calculated by Eq. (9) when temperature T is low and the concentration of impurity atoms is small[19]. The relaxation time τ_r is calculated by Eqs. (10) and (11) using the direct current resistivity r[10]. The mobility of electrons is $\mu=0.005$ m²/Vs at a temperature of 950°C[20].

$$N=3.87\times10^{22}T^{1.5}\exp(-7020/T) \quad (9)$$

$$\tau=m^*/(rNe^2) \quad (10)$$

$$r=1/(Ne\mu) \quad (11)$$

The reflectance of silicon wafers with oxide films and nitride films is calculated using Eqs. (4)～(11).

The transmissivity of a substrate of thickness z is $\exp(-4\pi k_2z/\lambda)$[11]. For the case of a silicon wafer of 0.5 mm thick at a temperature of 950°C and wavelengths 0.7 to 8 μm, the transmittance is zero. Then the emissivity is $\varepsilon=1-\rho$.

Figures 9 and 10 are calculated results of the spectral emissivity and the reflectance of silicon wafers with oxide films and nitride films. At a wavelength where the emissivity is maximized or the reflectance is minimized and the width changes, the calculation results agree with the experimental results of Figs. 3～6.

6. Conclusions

The normal spectral emissivity, reflectance and transmittance of silicon wafers with oxide films and

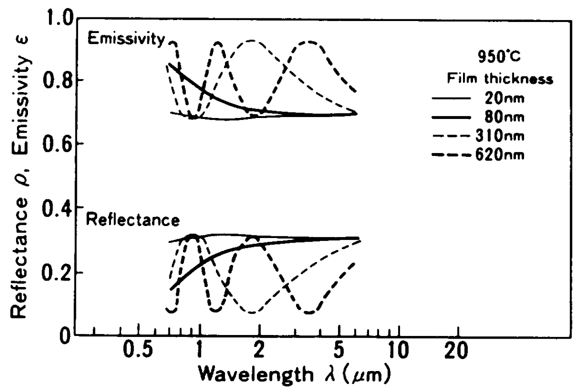

Fig. 9 Calculation results of emissivity and reflectance of silicon wafers with oxide film

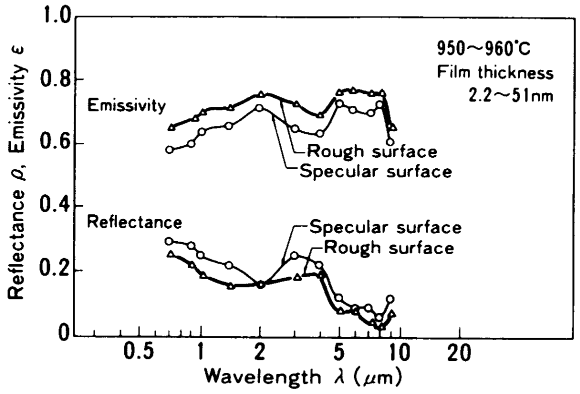

Fig. 8 Normal spectral emissivity and reflectance of specular surface and rough surface of silicon wafers with oxide film

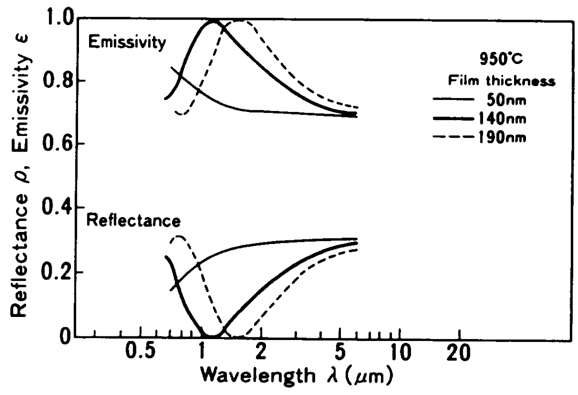

Fig. 10 Calculation results of emissivity and reflectance of silicon wafers with nitride film

nitride films were measured at a temperature of 950°C. The following conclusions were obtained.

(1) The emissivities of specular surfaces of silicon wafers with oxide films of less than 51nm thickness at wavelengths of 0.7 to 8 μm were 0.6 to 0.7, the reflectances were 0.1 to 0.3 and the transmittances were 0 to 0.2.

(2) The emissivities of silicon wafers with oxide films of more than 75 nm film thickness and nitride films of more than 48 nm film thickness changed from 0.6 to 1.0, and the reflectance changed from 0 to 0.3 according to film thickness and wavelength.

(3) The emissivity of a rough surface of a wafer was greater than that of a specular surface by 0.07.

(4) The emissivity and reflectance of silicon wafers were calculated using the free carrier absorption theory considering the interference effect of multiple reflection inside the film. The calculated results agreed with the experimental results.

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