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Thermal diffusivity measurement of low-*k* dielectric thin film by temperature wave analysis

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Abstract

Thermal diffusivity of thin film with low dielectric constant (k), what is called low-k dielectric thin film, 0.31–1.14 μm, including hydrogen-silsesquioxane (HSQ), methyl-silsesquioxane (MSQ), and poly(arylen ether) was examined by temperature wave analysis. The phase shift of temperature wave was observable up to 100 kHz. Thermal diffusivity of HSQ was 4.7×10^{-7} m^2 s^{-1}, on the other hand it was not higher than 1.1×10^{-7} m^2 s^{-1} for MSQ or poly(arylen ether) at room temperature. Temperature dependence of thermal diffusivity/thermal conductivity of MSQ was obtained, thermal diffusivity decreased but thermal conductivity increased in a heating scan at 30–150 °C. It was shown that the thermal diffusivity of low-k thin film was correlated with the chemical and the physical structures, the latter was formed in the spin-coating and the curing process.
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Keywords: Low-k dielectric thin film; Thermal diffusivity; Thermal conductivity; Temperature wave analysis; Spin-coating

1. Introduction

Thermal diffusivity of thin film having the low dielectric constant (k), what is called low-k dielectric thin film, is examined by the method of temperature wave analysis [1–11] in this study. The materials as so-called "spin-on low-k dielectrics" [12,13], have the relative low dielectric constant $k < 4.0$, considerably less than that of conventional silicon dioxide (SiO_2). Low-k dielectric thin films are used as electrical insulators in microprocessor industry and will be required to reduce the interconnect network capacitance which is effectively reducing the RC time constant in the device. For this purpose siloxane based materials, such as methyl-silsesquioxane (MSQ), hydrogen-silsesquioxane (HSQ) with porous structure, and some polymer resins are developed. However, it has been reported that low-k materials are less mechanically stable [14] having the lower thermal conductivity [15–20] than silicon dioxide (SiO_2). This raises a problem in performing thermal management of microelectronic devices [21].

In replacing SiO_2 with low-k materials, the characteristics of thermal conductivity and thermal diffusivity have to be properly evaluated in order to understand the relationship between electrical and thermal performances. In this stage the measurement method for thermal conductivity and thermal diffusivity of thin films is of significant practical interest. However, the precise measurement of thermal diffusivity of thin films less than 1 μm thickness has not yet been introduced. The 3ω [22–32] method is most successful and examined widespread for measuring thermal conductivity of thin films.

This study examines the validity of temperature wave analysis (TWA) for measuring thermal diffusivity of several kinds of spin-on low-k dielectric thin films. It has been reported that the sensing position in TWA method is advantageous for detecting the small change of thermal diffusivity in phase transitions [8–10], re-orientation of polymer stretched films [11,33], and thermosetting process [34]. This method has also been applied to the measurement of spin-coated polyimide film, in case of 0.12–2 μm thickness, in the frequency range

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up to 100 kHz [35]. In this study the influence of the film forming process on the thermal diffusivity is also examined.

2. Experimental

The low-k dielectric films were prepared by spin-coating method. The flat silica glass plate (thickness 2 mm) with polishing surface, on which a thin metal layer was sputtered in an area size of 1 mm × 4 mm, was used as a substrate for spin-coating. The surface of the substrate plate was pretreated in the O_2 plasma ashing before used in the spinning process. An electric resistance of sputtered thin metal layer was controlled at 50–250 Ω that was used as a sensor for detecting the temperature wave. After the film was formed on the substrate with some heat treatments for curing, another thin metal layer was sputtered directly on the top surface of the film as a heater element for generating a temperature wave. The sensor and the heater elements were set in parallel to each other.

The low-k dielectric materials examined in this study were as follows: three types of methyl-silsesquioxane (MSQ), HSG-R7 (relative dielectric constant $k = 2.8$, $\rho = 1.7\,g/cm^3$), RZ25 ($k = 2.5$, $\rho = 1.5\,g/cm^3$), and 6210 ($k = 2.1$, $\rho = 1.1\,g/cm^3$) supplied by Hitachi Chemical Co., Ltd., hydrogen-silsesquioxane (HSQ), T12 ($k = 2.9$–3.4, $\rho = 2.0\,g/cm^3$), supplied by TOK, and poly(arylen ether), Flare ($k = 2.85$, $\rho = 1.4\,g/cm^3$), supplied by Honeywell Electronic Materials.

The low-k thin films were prepared by spin-coating with the low-k resin in a carrier solvent, followed by melting and flowing and finally by curing in N_2 ambient. The film thickness was controlled both by changing the concentration of the solvent and the number of rotations in spin-coating, 500–4000 rpm. The spin-coating and the curing processes were as follows. For MSQ, first the solution at a selected concentration was applied on silica glass by spin-coating at a selected number of rotation for 10 s at room temperature. The applied film was dried by hot plate baking for 5 min each at 150 and 200 °C, proceeded by curing at 450 °C for 30 min in N_2 ambient. For HSQ, after spin-coating at several rotation numbers for 10 s at room temperature, the baking conditions were at 150 and 200 °C for 10 min each, proceeded by curing at 400 °C for 60 min in N_2 ambient. For poly(arylen ether) at 500 rpm for 5 s first and then at various rotating speeds for 45 s each at room temperature. The baking conditions were for 5 min at 85 °C, for 10 min at each 150, 200, 250 °C, proceeded by curing at 400 °C for 60 min in N_2 ambient.

Fig. 1 shows the relationship between the thickness of the spin-coated low-k dielectric thin film, MSQ-6210, HSQ-T12, and Flare, and a number of spin rotation. A thinner spin-coated film is formed by a higher number of spin rotation in each carrier solvent.

Fig. 2a shows a schematic diagram of the measuring system. The instrument consists of a specimen holder put in a hot stage, a function synthesizer (NF1942) inputting a.c. current on a heater, a two-phase digital lock-in amplifier (Stanford Research, SR830), a temperature control unit, and a d.c. source for bias current onto a sensor. Temperature wave is generated with different frequency on the front surface of the specimen. The power on the heater is optimized considering the electric resistance value of the heater element and the frequency, not higher than 100 mW. The periodical change of temperature on the rear surface is converted to the electric resistance variation of the sputtered sensor. Lock-in amplifier detects the amplitude decay and the phase delay between

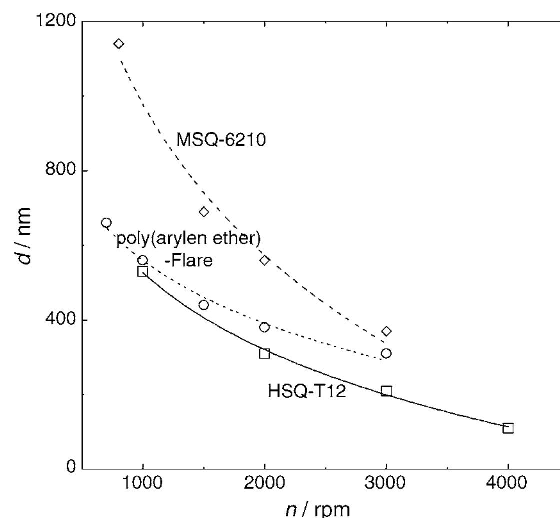

Fig. 1. The relationship between the number of spinning rotation (n) and the thickness (d) of the spin-coated low-k dielectric films: (◇) MSQ-6210, (□) HSQ-T12, (○) poly(aryl ether)-Flare.

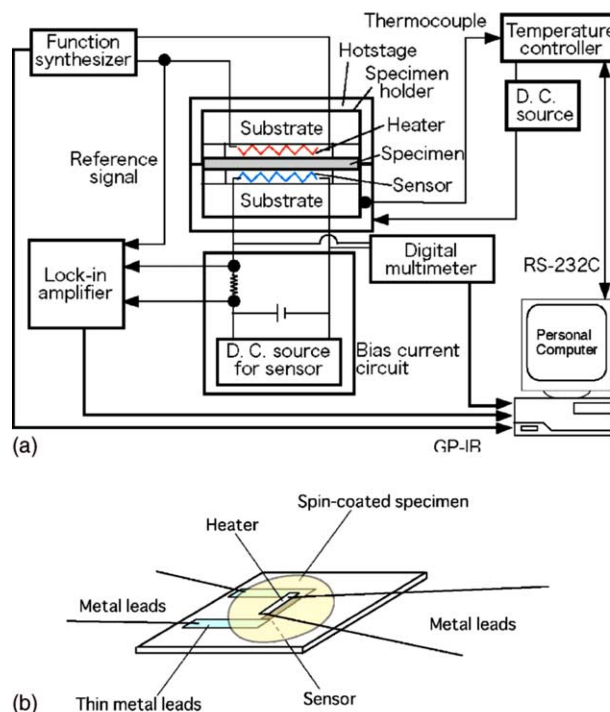

Fig. 2. (a) Schematic diagram of the measuring system. (b) A spin-coated film on the substrate with the sputtered sensor and the heater.

the heater and the sensor as a function of frequency of temperature were. Fig. 2b shows an example of the spin-coated specimen with the sputtered sensor and the heater.

A temperature scan measurement of thermal diffusivity as thermal analysis was performed at a fixed frequency, measuring the phase shift in heating and cooling. The scanning rate was 0.2–0.5 K/min with the frequency selected considering the thermally thick condition.

Heat capacity was determined with the power-compensation DSC, Perkin Elmer DSC7, scanned by 10 K/min in N_2 atmosphere. The calibration of heat capacity was performed with a certified sapphire crystal (Al_2O_3) disk. The specimens were prepared in an aluminum-pan by the same procedure of spin coating and baking.

3. Computational procedure

The specimen with thickness d is put between two substrates having semi-infinite thickness and known thermal properties. Assuming the one-dimensional heat flux, the temperature wave generated on the front surface ($x=0$) propagates in the thickness direction to the rear surface, detected by the sensor attached on the rear surface ($x=d$). The one-dimensional heat diffusion equation leads to the solution of temperature oscillation at $x=d$ as follows:

$$T(d,t) = \frac{\lambda\hat{\boldsymbol{k}}\cdot j_0}{\cosh(\hat{\boldsymbol{k}}d)[2\lambda\hat{\boldsymbol{k}}\lambda_s\hat{\boldsymbol{k}}_s + \{(\lambda\hat{\boldsymbol{k}})^2 + (\lambda_s\hat{\boldsymbol{k}}_s)^2\}\tanh(\hat{\boldsymbol{k}}d)]} \tag{1}$$

where $\hat{\boldsymbol{k}}$ is defined as [38–40]

$$\hat{\boldsymbol{k}} = \sqrt{\frac{\omega}{2\alpha}} + i\sqrt{\frac{\omega}{2\alpha}} = (1+i)\boldsymbol{k} \tag{2}$$

and T is the ac temperature, t the time, j_0 the heat flux on the heater, λ the thermal conductivity, α the thermal diffusivity, ω the angular frequency. Subscript 's' means the property of substrates and the other for the specimen. The thermal diffusion length μ is defined as

$$\frac{1}{\mu} = \boldsymbol{k} = \sqrt{\frac{\omega}{2\alpha}} \tag{3}$$

The term of phase shift becomes

$$\Delta\theta = -\boldsymbol{k}d - \tfrac{1}{4}\pi + \beta \tag{4}$$

with β, ξ defined as

$$\tan\beta = \frac{(\xi-1)^2\exp(-2\boldsymbol{k}d)\sin(-2\boldsymbol{k}d)}{(\xi+1)^2 - (\xi-1)^2\exp(-2\boldsymbol{k}d)\cos(2\boldsymbol{k}d)} \tag{5}$$

$$\xi = \frac{\lambda\boldsymbol{k}}{\lambda_s\boldsymbol{k}_s} = \frac{c\sqrt{\alpha}}{c_s\sqrt{\alpha_s}} \tag{6}$$

Thermal diffusivity α can be determined from the phase shift ($\Delta\theta$) by curve fitting based on Eqs. (4) and (5) with the fitting parameters ξ and $\boldsymbol{k}$d. If the conditions: (i) $\boldsymbol{k}$d > 1 or (ii) $\xi \sim 1$ is satisfied, Eq. (1) becomes to a simple form of

$$T(d,t) = \frac{\sqrt{2}j_0\lambda\boldsymbol{k}\exp(-\boldsymbol{k}d)}{(\lambda\boldsymbol{k}+\lambda_s\boldsymbol{k}_s)^2}\exp\left\{i\left(\omega t - \boldsymbol{k}d - \frac{\pi}{4}\right)\right\} \tag{7}$$

and the phase shift $\Delta\theta$ on the sensor is:

$$\Delta\theta = -\boldsymbol{k}d - \tfrac{1}{4}\pi \tag{8}$$

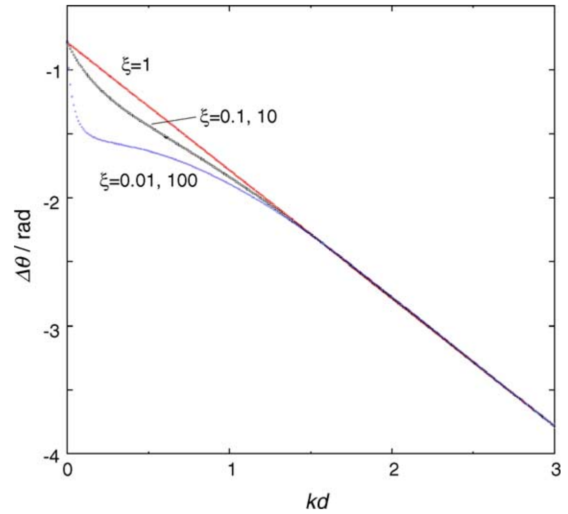

Fig. 3. The simulated results on the effect of ξ on the relationship between $\Delta\theta$ and $\boldsymbol{k}$d: $\xi=1$, $\xi=0.1$, 10, $\xi=0.01$, 100.

In this case thermal diffusivity α is determined from the linear slope in the plot of $\Delta\theta$ versus $\omega^{1/2}$. Fig. 3 shows the simulated results on the effect of ξ on the relationship between $\Delta\theta$ and $\boldsymbol{k}$d. The simulated curves show that the linearity in the plot of $\Delta\theta$ and $\boldsymbol{k}$d can be obtained in a wider frequency range when ξ approaches the value of 1. In this study the phase component of temperature wave is used for the calculation of thermal diffusivity of low-k dielectric thin film.

4. Results and discussion

Fig. 4 shows the phase shift ($\Delta\theta$) of spin-coated low-k dielectric thin films, MSQ-RZ25 ($d=0.85$ μm) and 6210 ($d=1.14$ μm), plotted as a function of square root of frequency of temperature wave. The frequency f_c, at which $\boldsymbol{k}$d = 1 is satisfied for each specimen, is shown by the arrows in Fig. 4. The plots show the linear relationship in the wide frequency range, including the frequency smaller than f_c, as expected in Eq. (4), and the simulation results in Fig. 3. It is noteworthy that a linear relationship is observed up to 90 kHz, which is near to the limitation of the frequency of the Lock-in amplifier used in this study.

The thickness of the sputtered metal thin layer as a sensor is several ten nanometers by the photographs taken by atomic force microscopy (AFM) [35]. The heat capacity of the sensor is negligible small and the electric impedance being mostly

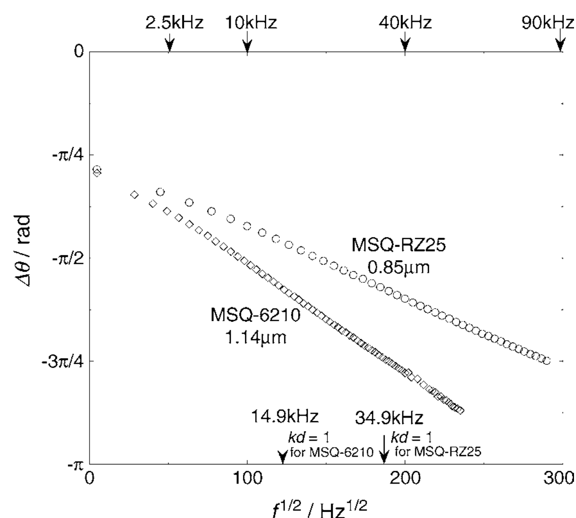

Fig. 4. Phase delay $\Delta\theta$ plotted as a function of square root of frequency of temperature wave of spin-coated low-*k* dielectric films: (◇) MSQ-6210; 1.15 µm, (◯) MSQ-RZ25 0.85 µm.

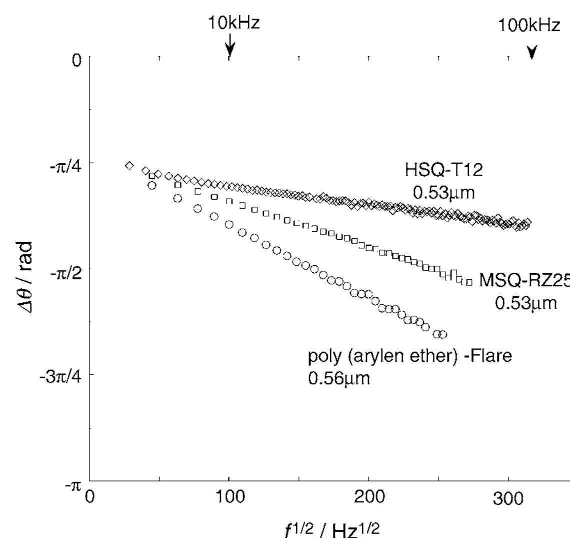

Fig. 5. Phase delay $\Delta\theta$ plotted as a function of square root of frequency of temperature wave of spin-coated low-*k* dielectric film: (◇) HSQ-T12 0.53 µm, (□) MSQ-RZ25 0.53 µm, (◯) poly(arylen ether), Flare 0.56 µm.

constant up to 100 kHz. From the linear part of the curvature of each plot in Fig. 4 thermal diffusivity can be calculated.

Fig. 5 shows the comparison of phase shift plot of three different types of low-*k* thin films, HSQ, MSQ, and poly(arylen ether); HSQ-T12: 0.53 µm, MSQ-RZ25: 0.53 µm, Flare: 0.56 µm. Different slopes can be found in the linear part of the curves, meaning the definite difference of thermal diffusivities between three types of low-*k* films, originated in the chemical structure. Poly(arylen ether), Flare, shows the smaller thermal diffusivity than siloxane, HSQ and MSQ.

The results of the measurements of thermal diffusivity, α, at room temperature are given in Table 1 along with the values of thickness, d, mass density, ρ, and relative dielectric constant, k. In the measured thermal diffusivities in Table 1, HSQ-T12 shows the highest value, $4.7 \times 10^{-7}\,\mathrm{m^2\,s^{-1}}$, but MSQ and poly(arylen ether) do not show the thermal diffusivity higher than $1.1 \times 10^{-7}\,\mathrm{m^2\,s^{-1}}$.

For MSQ the thickness dependence is not simple, it decreases in the both limits. The gradual cone-shaped thickness dependence of thermal diffusivity of MSQ suggested the hypothesis; when the specimen thickens up to 1 µm, a crack or a defect could be formed in the film and this unsteady structure would cause the decrease of thermal diffusivity. On the other hand, when the specimen thins near to 0.1 µm, the molecular anisotropy effect that was formed in the spin-coating process would not be neglected, and then thermal diffusivity would be decreasing with decreasing the thickness.

Table 1
Thermal diffusivity of low-*k* dielectric thin films

Specimen	d (nm)	Thermal diffusivity ($\times 10^{-7}\,\mathrm{m^2\,s^{-1}}$)	Relative dielectric constant at 10 kHz	Density (g/cm^3)
MSQ-R7	650	1.1	2.8	1.7
	550	1.1		
	360	0.76		
MSQ-RZ25	850	0.56	2.5	1.5
	780	1.0		
	530	0.77		
	410	0.77		
MSQ-6210	1140	0.62	2.1	1.1
	690	0.91		
	560	1.1		
	370	0.85		
HSQ-T12	530	4.7	2.9–3.4	2
	310	4.1		
Poly(arylen ether)	660	0.14	2.85	1.4
Flare	560	0.41		
	440	0.91		
	380	0.83		
	310	0.94		

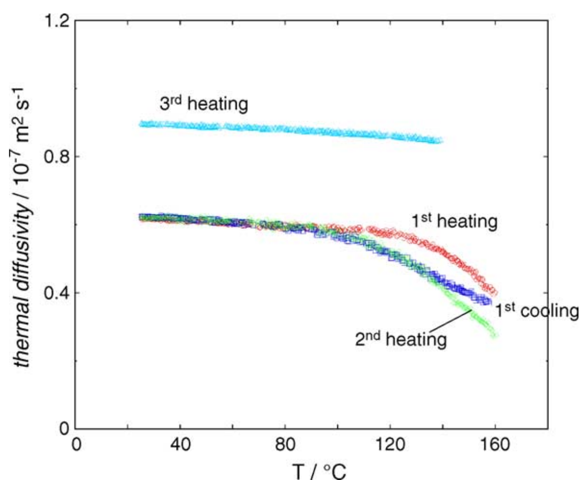

Fig. 6. Thermal diffusivity of MSQ-6210, 1.14 μm in heating/cooling scan at a rate of 0.5 K/min: (◯) first heating, (□) first cooling, (◊) second heating, (Δ) third heating. The frequency was 20.224 kHz.

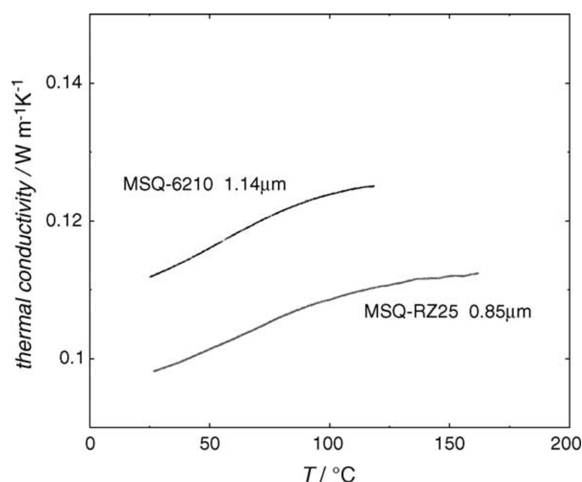

Fig. 7. Thermal conductivity of MSQ-6210 (after third heating) 1.14 μm and RZ25 0.85 μm.

The thickness dependence of thermal diffusivity of Flare also suggests the in-plane molecular anisotropy by the spin-coating method. It is well known that the thermal diffusivity of solid polymer is strongly affected by the molecular anisotropy [11,33] formed in the mechanical stresses. For polyimide films formed by spin-coating it was reported that the anisotropy was observed in refractive indices affected by several factors [36,37], such as residual stress and volume expansion coefficient.

Fig. 6 shows the temperature dependence of thermal diffusivity in heating and cooling at 0.5 K/min of MSQ-6210 measured at frequency of 20.224 kHz. The first heating/cooling and the second heating were performed up to 160 °C and then the specimen was annealed at 200 °C. Thermal diffusivity shows a steep decline above 100 °C in first and second heating. After annealing at 200 °C, thermal diffusivity at 30 °C increases up to 0.9×10^{-7} m^2 s^{-1} and in the third heating the steep decline of thermal diffusivity above 100 °C is not observed, instead thermal diffusivity decreases gradually. It is known that thermal diffusivity correlates with the microstructure of the materials, and the results in Fig. 6 suggest that some kinds of porous structure or defects in the spin-coated thin film changes in the thermal treatment following the further curing process. The fact that the thermal diffusivity of 1.14 μm film increases near to the value obtained at smaller thickness, such as 0.69 μm, suggests that some kinds of cracks or defects formed in the thick specimen is treated in the additional thermal treatment after second heating.

From the temperature scan data of thermal diffusivity and heat capacity, thermal conductivity of MSQ is calculated in Fig. 7, assuming the density change in the temperature range from 30 to 160 °C can be negligible. The thermal conductivity of MSQ in this study increases with increasing temperature. The nearly identical temperature dependence of the thermal conductivity of HSQ and MSQ was previously reported by the 3ω method [15]. The calculated thermal conductivities of MSQ and HSQ at room temperature are listed in Table 2. These data suggest that the heat transport property depends not only on the chemical structure but also on the processing conditions, such as the number of rotating of spin-coating

Table 2
Thermal conductivity of low-*k* dielectric thin film

Specimen	*d* (nm)	Thermal diffusivity ($\times 10^{-7}$ m^2 s^{-1})	λ (W m^{-1} K^{-1})	C_p (J g^{-1} K^{-1})
MSQ-RZ25	850	0.58	0.099	1.14
	780	1.0	0.17	
	530	0.77	0.13	
	410	0.77	0.13	
MSQ-6210	1140	0.62	0.077	1.13
	1140[a]	0.90	0.11	
	690	0.91	0.11	
	560	1.1	0.14	
	370	0.85	0.11	
HSQ-T12	530	4.7	0.26	0.272
	310	4.1	0.22	

[a] 1140 after annealing at 200 °C.

or the heat treatment process. It is shown that the method of temperature wave analysis is useful to detect the small change of thermal diffusivity corresponding to the processing conditions of low-k thin films with the thickness of sub-micron.

5. Conclusion

The applicability of temperature wave analysis to measure the thermal diffusivity of low-k dielectric thin film was examined. It was shown that the temperature sensor of sputtered thin metal layer was sensitive enough to detect the phase shift of temperature wave at high frequency up to 100 kHz. As predicted in the mathematical simulation, the linear part of $\Delta\theta$ versus $f^{1/2}$ plot was found experimentally.

Temperature dependence of thermal diffusivity and thermal conductivity of MSQ were obtained, thermal diffusivity decreased but thermal conductivity increased with increasing temperature. This tendency is in good accordance with the temperature dependence of thermal conductivity of HSQ and MSQ previously reported. It is suggested that the thermal diffusivity is influenced not only by the microstructure originated in the chemical structure but also by the formed structure in the spin-coating and the curing processes. The method of temperature wave analysis is useful to observe the small change of thermal diffusivity in these processes.

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