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Dielectric properties of chemically vapour-deposited Si_3N_4

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The dielectric properties of chemically vapour-deposited (CVD) amorphous and crystalline Si_3N_4 were measured in the temperature range from room temperature to 800° C. The a.c. conductivity ($\sigma_{a.c.}$) of the amorphous CVD-Si_3N_4 was found to be less than that of the crystalline CVD-Si_3N_4 below 500° C, but became greater than that of the crystalline CVD-Si_3N_4 over 500° C due to the contribution of d.c. conductivity ($\sigma_{d.c.}$). The measured loss factor (ε'') and dielectric constant (ε') of the amorphous CVD-Si_3N_4 are smaller than those of the crystalline CVD-Si_3N_4 in all of the temperature and frequency ranges examined. The relationships of $\varepsilon'' \propto \omega^{n-1}$, $(\varepsilon' - \varepsilon'_\infty) \propto \omega^{n-1}$ and $\varepsilon''/(\varepsilon' - \varepsilon'_\infty) = \cot(n\pi/2)$ were observed for the amorphous and crystalline specimens, where ω is angular frequency and n is a constant. The values of n of amorphous and crystalline CVD-Si_3N_4 were 0.8 to 0.9 and 0.6 to 0.8, respectively. These results may indicate that the a.c. conduction observed for both of the above specimens is caused by hopping carriers. The values of loss tangent (tan δ) increased with increasing temperature. The relationship of $\log(\tan\delta) \propto T$ was observed. The value of tan δ for the amorphous CVD-Si_3N_4 was smaller than that of the crystalline CVD-Si_3N_4.

1. Introduction

Amorphous silicon nitride (Si_3N_4) is increasingly being used in semi-conductor devices because of its superior insulative properties. There have been many reports on the electrical properties of the amorphous silicon nitride in recent years [1, 2]. However, all of these have dealt with thin films of several hundred nanometres thickness. Using these thin films, it is rather difficult to determine the intrinsic electrical characteristics of the amorphous Si_3N_4 accurately because of the "size effect" [3]. To eliminate the "size effect", larger specimens of Si_3N_4 are needed. The electrical properties of crystalline Si_3N_4 fabricated by the methods of reaction-sintering or hot-pressing, have also been reported [4–7]. The dielectric constants of the reaction-sintered and hot-pressed body are known to be smaller due to the effects of pores and glass-phase in the grain boundaries, respectively. Furthermore, the Maxwell–Wagner type dielectric loss [8] (which is not the intrinsic character of the bulk material) is frequently observed in those sintered bodies due to the existence of inhomogeneous texture or secondary phases. In order to truly clarify the intrinsic electrical properties of the amorphous and crystalline Si_3N_4, high-purity and high-density specimens must be used.

We have previously reported the direct current (d.c.) conductivity of the amorphous and crystalline Si_3N_4 measured from the samples of several millimetres thickness prepared by chemical vapour deposition (CVD) [9]. In the present work, the dielectric properties of amorphous and crystalline Si_3N_4 under an alternate current (a.c.) field were measured and the conduction mechanisms for both types of material are discussed.

2. Experimental procedure

The plate-like amorphous and crystalline CVD-Si_3N_4 of about 1 mm thick were prepared on a graphite substrate heated by electric current. $SiCl_4$, NH_3 and H_2 were used as source gases. The details of the preparation procedures have been reported earlier [10]. Table I summarizes the sample preparation conditions and some of the properties of the resulting samples used in the present work. The samples were ultrasonically cut to a disc of 10 mm diameter. Both of the surfaces of the samples were shaved flat. For the present measurements, a thickness of about 0.7 mm was used.

Fig. 1 shows schematically the apparatus used for the measurements of the dielectric properties. A.c. conductivity ($\sigma_{a.c.}$) and the dielectric constant (ε') were measured by using a transformer bridge (Ando; TR-10C). The apparent loss factor (ε''_{app}) and loss tangent (tan δ) were calculated as follows

$$\varepsilon''_{app} = \sigma_{a.c.}/\omega \qquad (1)$$

$$\tan\delta = \varepsilon''/\varepsilon' \qquad (2)$$

where ω is the angular frequency ($\omega = 2\pi f$, f = frequency). The measurements were made in the frequency range of 60 Hz to 3 MHz. The d.c. conductivity ($\sigma_{d.c.}$) was also measured by using the three-point method for a comparison. Detailed procedures for the $\sigma_{d.c.}$ measurements were previously reported [9]. Fig. 2 shows a schematic drawing of the sample heating apparatus used in this study. A silver paste (Tokuriki: P-382) was used as electrodes and a gold wire (0.1 mm diameter) and a platinum wire (0.5 mm diameter) were used as lead wires. The measurements were made in an argon atmosphere in the temperature range from room temperature to 800° C.

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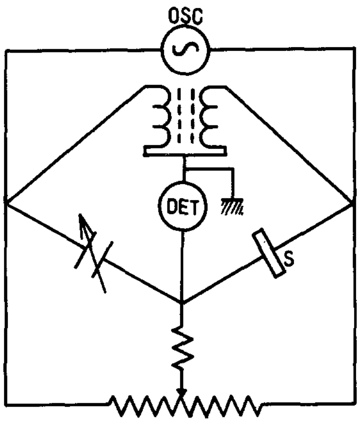

Figure 1 Schematic drawing of the device used for measurements of dielectric properties. S, specimen; OSC, oscillator; DET, detector.

3. Results and discussion

Figs 3a and b show the temperature dependence of $\sigma_{\text{a.c.}}$ for amorphous and crystalline CVD-Si_3N_4, respectively. For comparison purposes, the $\sigma_{\text{d.c.}}$ variation is also indicated by broken lines. The slope of $\sigma_{\text{a.c.}}$ for both specimens decreased with decreasing temperature and with increasing frequency. At the temperatures below 600° C, the $\sigma_{\text{a.c.}}$ of the amorphous CVD-Si_3N_4 is considerably smaller than that of the crystalline CVD-Si_3N_4 for the entire frequency range examined.

It is well known that the $\sigma_{\text{a.c.}}$ may be represented as

$$\sigma_{\text{a.c.}} = \sigma_{\text{d.c.}} + A\omega^n \qquad (3)$$

where A and n are constants [11]. As is clear from Fig. 3, the contribution of $\sigma_{\text{d.c.}}$ to $\sigma_{\text{a.c.}}$ became greater at higher temperature ranges for both specimens, with $\sigma_{\text{a.c.}}$ of the amorphous CVD-Si_3N_4 becoming nearly equal to $\sigma_{\text{d.c.}}$ at about 800° C. The values of the band gap calculated from the temperature dependence of the $\sigma_{\text{d.c.}}$ for the amorphous and crystalline CVD-Si_3N_4 were 3.6 and 3.8 eV, respectively. Thus, the band gap of the amorphous CVD-Si_3N_4 is slightly smaller than that of crystalline CVD-Si_3N_4. The amorphous material is known to have a concentration of state density at the edge of the conduction and valence bands. Hence, the band gap of an amorphous material is generally smaller than that of its crystalline phase [12]. The value of the band gap of the amorphous CVD-Si_3N_4 obtained in the present work is smaller than the values reported by Kendall (4.0 eV) [2], Bean *et al.* (4.4 eV) [13] and Brown *et al.* (4.5 eV) [14]. It is unclear whether this difference is due to the size effect [3] (the difference between bulk material and thin film) or the difference in the amorphous structure. The band gap of the crystalline CVD-Si_3N_4 obtained in this study is closely in agreement with that of the hot-pressed Si_3N_4 (containing 5 wt % MgO) reported by Thorp and Sharif [7].

The apparent loss factor ($\varepsilon''_{\text{app}}$) is expressed by

$$\varepsilon''_{\text{app}} = \sigma_{\text{d.c.}}/\omega + A\omega^{n-1} \qquad (4)$$

The measured $\varepsilon''_{\text{app}}$ consists of the loss from $\sigma_{\text{d.c.}}$ and that from the real polarization. The loss due to $\sigma_{\text{d.c.}}$ increases with increasing temperature and decreasing frequency. The contribution of $\sigma_{\text{d.c.}}/\omega$ to the $\varepsilon''_{\text{app}}$ can be graphically removed from $\varepsilon''_{\text{app}}$ because the relationship between $\log \varepsilon''_{\text{app}}$ and $\log f$ has the slope of -1 in the low-frequency region [15]. Figs 4a and b show the relationship between the real loss factor ε'' and the frequency of amorphous and crystalline CVD-Si_3N_4, respectively.

ε'' varied with frequency in both specimens as follows

$$\varepsilon'' = A\omega^{n-1} \qquad (5)$$

where n takes values between 0.75 to 0.85 for the amorphous CVD-Si_3N_4 and 0.62 to 0.76 for the crystalline CVD-Si_3N_4. In many amorphous materials n is nearly equal to 0.8. This result provides evidence that the a.c. conduction is driven from a hopping conduction [16].

According to Austin and Mott [17], ε'' can be expressed as in Equation 6 when a hopping conduction model is used near the Fermi level

$$\varepsilon''(\omega) = 1/3\pi e^2 kT\,[N(E_f)]^2\alpha^{-5}\,[\ln(\nu_{\text{ph}}/\omega)]^4 \qquad (6)$$

where e is the electron charge, k is the Boltzmann constant, T is the absolute temperature, $N(E_f)$ is a state density at the Fermi level (E_f), ν_{ph} is a wave number of phonons, $\alpha = \ln(\nu_{\text{ph}}/\omega/2R)$ (R is a hopping distance). The value of n is theoretically 0.8 at $1 \ll \nu_{\text{ph}}$ because $[\ln(\nu_{\text{ph}}/\omega)]^4$ depends approximately on $\omega^{-0.2}$ [17].

The value of n for the amorphous CVD-Si_3N_4 is found to be equal to 0.8 in the present work. This result indicates that the a.c. conduction mechanism of the amorphous CVD-Si_3N_4 is due to the hopping near the Fermi level. The value of n for the crystalline CVD-Si_3N_4 ranges between 0.62 and 0.76. This value is slightly smaller than that of the amorphous CVD-Si_3N_4. When the value of n is $0.6 < n < 1$, the

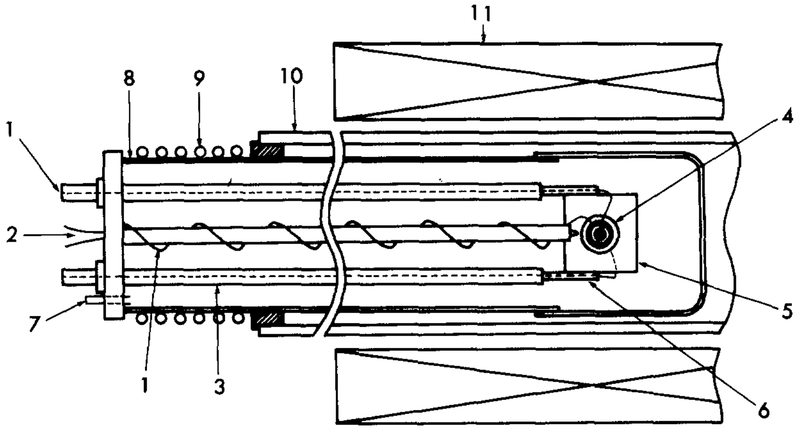

Figure 2 Schematic drawing of the device for heating specimens. (1) Platinum lead wire, (2) Pt-Pt 13% Rh thermocouple, (3) stainless steel tube for shielding, (4) specimen, (5) quartz plate, (6) quartz tube for insulating, (7) gas inlet, (8) stainless steel tube for holding, (9) water jacket, (10) quartz tube, (11) electric furnace.

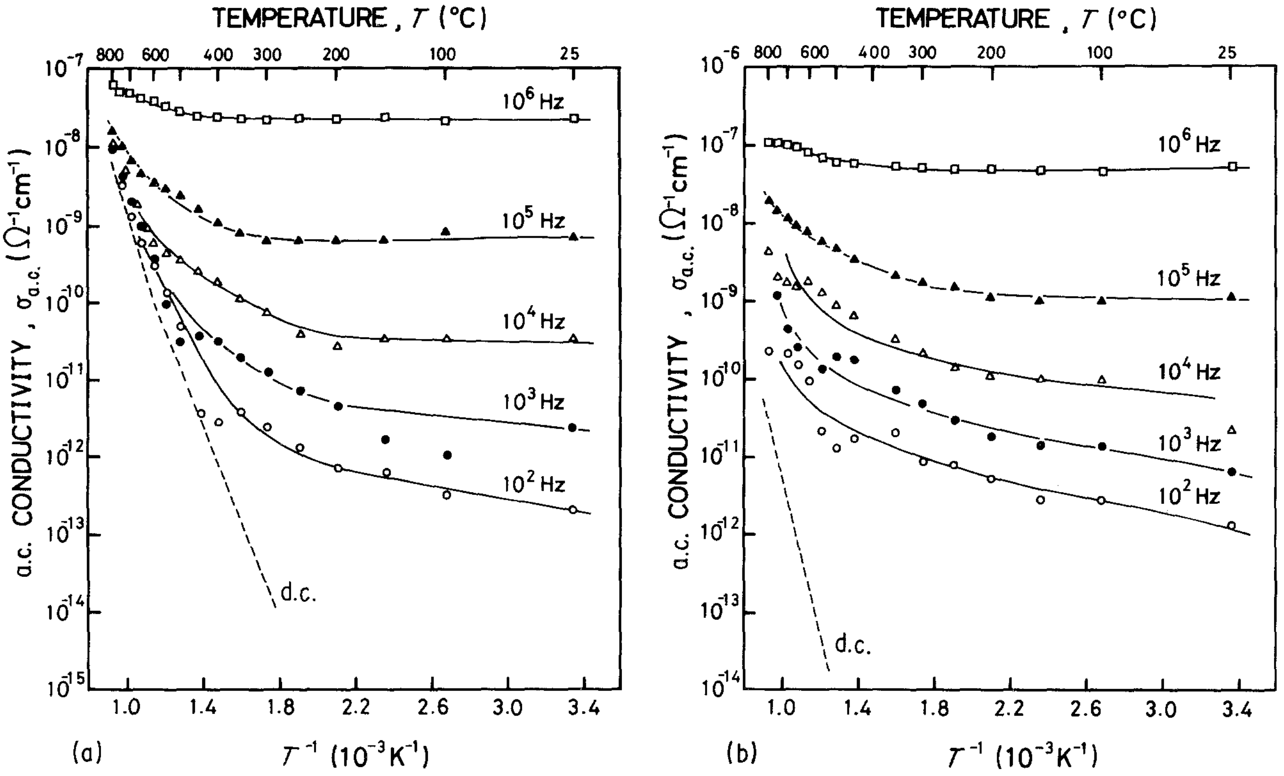

Figure 3 Temperature dependence of $\sigma_{a.c.}$ for the (a) amorphous and (b) crystalline CVD-Si_3N_4.

conduction mechanism is also considered to be hopping [18]. Various n values between 0.6 and 0.9 were reported for many crystalline materials such as silicon and β-alumina [19]. The values of n for hot-pressed Si_3N_4 ranged from 0.57 to 0.92 and its a.c. conduction mechanism is considered to be hopping [6]. Therefore, the a.c. conduction mechanism of the crystalline CVD-Si_3N_4 may also be due to hopping. Because the localized state near the Fermi level does not exist in the crystalline materials, Equation 6 cannot be applied to this case. Although, the conduction mechanism for amorphous material has been formulated by Mott and Davis [16], the explanation of the hopping conduction mechanism for crystalline material has not yet been established.

The frequency dependency of ($\varepsilon' - \varepsilon'_\infty$) for the amorphous and crystalline CVD-Si_3N_4 was given in Figs 5a and b, respectively. The values of the ε' at room temperature for the amorphous and crystalline CVD-Si_3N_4 were 8.66 and 8.36, respectively. ε' has no dependency on frequency at room temperature and takes on a value nearly equal to ε'_∞. Because ε'_∞ does not usually vary with the temperature [20], the value of ε' at room temperature can be considered to be a good approximation for ε'_∞. The value of ε'_∞ calculated from the Cole–Cole plot [21] by extrapolating the frequency

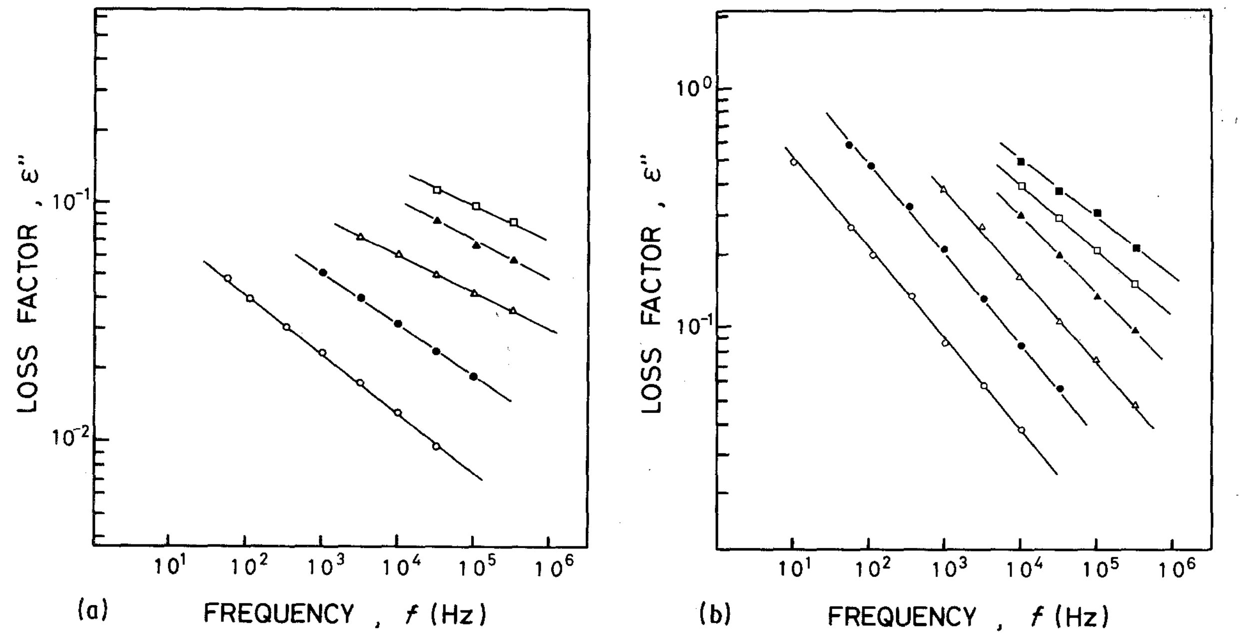

Figure 4 Frequency dependence of loss factor ε'' for the (a) amorphous and (b) crystalline CVD-Si_3N_4. Temperature (°C): (■) 800, (□) 700, (▲) 600, (△) 500, (●) 400, (○) 300.

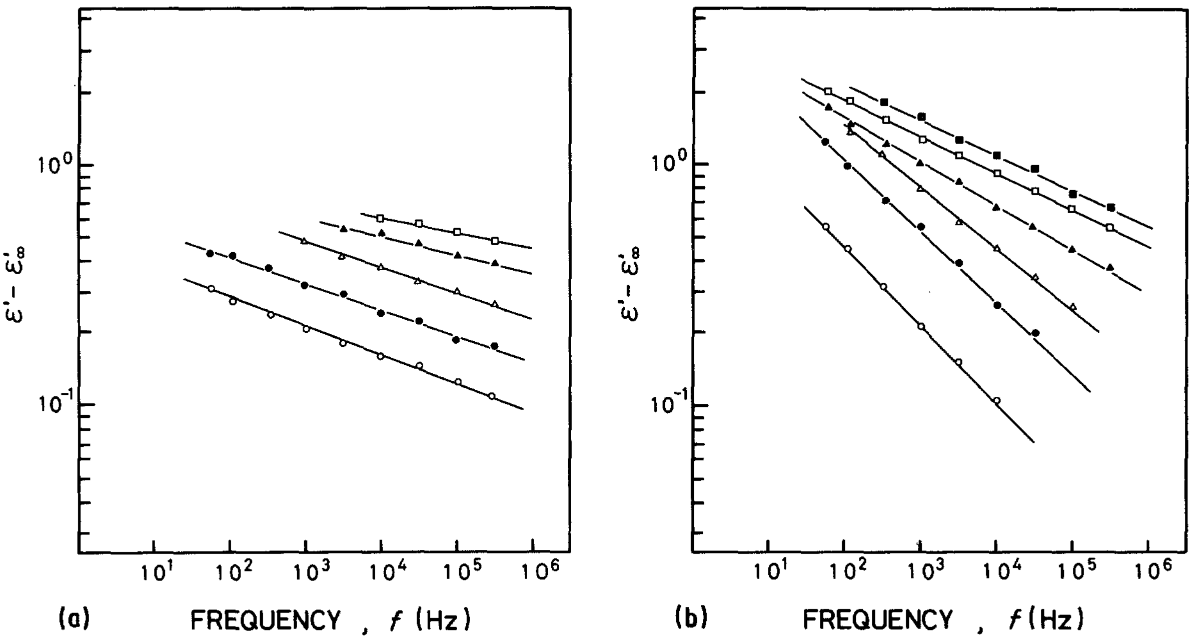

Figure 5 Frequency dependence of ($\varepsilon' - \varepsilon''_\infty$) for the (a) amorphous and (b) crystalline CVD-Si_3N_4. For key, see Fig. 4.

to infinity, were almost in agreement with the values of ε' at room temperature.

The value obtained from the relation $(\varepsilon'_\infty)^{0.5}$ is equal to the refractive index when the dielectric polarization is caused only by electrons [22]. The refractive indices of both amorphous and crystalline Si_3N_4 films (thickness 1 μm) at the wavelength of 450 nm were reported to be 2.03 and 2.06, respectively [23]. Both of these values are smaller than the values obtained from $(\varepsilon'_\infty)^{0.5}$ given by the present work. This result suggests that the atomic polarization [22], in addition to the electrical polarization, is contributing to the value of ε'_∞. Because the value of ε'_∞ increases with increasing density, the Lorentz-Lorenz relationship [24] can be used to explain the larger value of ε'_∞ for the crystalline CVD-Si_3N_4 as compared to the value ε'_∞ of the amorphous CVD-Si_3N_4.

The density of the crystalline CVD-Si_3N_4 is shown to be larger than that of the amorphous CVD-Si_3N_4 in Table I. Fig. 5 indicates a linear relationship between $\log(\varepsilon' - \varepsilon'_\infty)$ and $\log f$, or the relationship $(\varepsilon' - \varepsilon'_\infty) \propto \omega^{n-1}$. The values of n in the expression obtained from Fig. 5 were 0.88 to 0.94 for amorphous and 0.68 to 0.85 for crystalline CVD-Si_3N_4. These values were slightly larger than those obtained from the relationship of $\varepsilon'' \propto \omega^{n-1}$. The same tendency was observed in the hot-pressed Si_3N_4. Thorp and Sharif [6] explained that this difference is due to the contribution of hopping carriers to ε'' being less than that to ε'. The ε'' to $(\varepsilon' - \varepsilon'_\infty)$ ratio satisfied the Kramers–Kronig relationship [19] given by Equation 7 for both specimens

$$\varepsilon''(\omega)/[\varepsilon'(\omega) - \varepsilon'_\infty] = \cot(n\pi/2) \qquad (7)$$

This relationship can be applied to either non-Debye dipolar or to hopping carrier system [19]. The n values calculated from Equation 7 and from the relationships of $(\varepsilon' - \varepsilon'_\infty) \propto \omega^{n-1}$ and $\varepsilon'' \propto \omega^{n-1}$ are listed in Table II. The n values calculated from Equation 7 were nearly in agreement with the values obtained from other methods. This result supports the conclusion that the a.c. conduction mechanism of the amorphous and crystalline CVD-Si_3N_4 is due to hopping.

The ε' values at room temperature reported in the past, as well as ones obtained in the present work, are summarized in Table III. Values of ε' of the amorphous Si_3N_4 thin films were between 5 and 7 [14, 25–28]. These values are smaller than that of the amorphous CVD-Si_3N_4 found in the present work. The earlier data were obtained from samples of thin films (several tens to hundreds of nanometres thickness) deposited on semi-conductor silicon substrates and may not show the intrinsic value of the bulk material. This is due to the effect of the space capacity existing at the Si–Si_3N_4 or Si_3N_4–metal electrode interface. On the other hand, the thickness of the amorphous CVD-Si_3N_4 used in the present work was about 1 mm, which is almost 1000 times thicker than the previous specimens. Therefore, the value obtained in the present work can be considered as the intrinsic value of the bulk amorphous CVD-Si_3N_4.

ε' of the crystalline CVD-Si_3N_4 obtained in the

TABLE I Deposition conditions and some properties of CVD-Si_3N_4

Specimen	T_{dep}* (°C)	P_{tot}† (torr)	Density ($g\,cm^{-3}$)	Hardness‡ ($kg\,mm^{-2}$)	Thermal conductivity ($cal\,cm^{-1}\,sec^{-1}\,K^{-1}$)
Amorphous	1300	30	3.00	2800	0.02
Crystalline§	1400	40	3.18	3200	0.10

*Deposition temperature.
†Total gas pressure in the CVD furnace.
‡Vickers microhardness at room temperature (100 g load).
§α-type hexagonal structure. The (222) plane is preferably oriented to the deposition surface.

TABLE II Comparison of the n values of the amorphous and crystalline CVD-Si_3N_4 obtained by different equations at various temperatures

Temperature (°C)	n from $\varepsilon' - \varepsilon''_\infty$		n from ε''		n from $n = \left(\frac{2}{\pi}\right)\cot^{-1}\left(\frac{\varepsilon''}{\varepsilon' - \varepsilon'_\infty}\right)$	
	Amorph.	Cryst.	Amorph.	Cryst.	Amorph.	Cryst.
800	–	0.84	–	0.76	–	0.75
700	0.94	0.84	0.85	0.72	0.86	0.77
600	0.93	0.81	0.83	0.68	0.88	0.77
500	0.89	0.74	0.84	0.64	0.90	0.76
400	0.89	0.70	0.79	0.62	0.92	0.76
300	0.88	0.68	0.75	0.62	0.93	0.74

present work is in good agreement with that of the crystalline CVD-Si_3N_4 prepared by Galasso [29]. ε' of the hot-pressed Si_3N_4 is slightly smaller than that of the crystalline CVD-Si_3N_4 because the silicate phases contained in the hot-pressed Si_3N_4 at its grain boundaries have smaller values of ε' than that of the CVD-Si_3N_4 [30]. Ordinarily, ε' of the silicates is between 3 and 5. ε' of the reaction-sintered Si_3N_4 is larger than that of the crystalline CVD-Si_3N_4 when free silicon remains in the body ($\varepsilon'_{Si} = 11.9$), and is smaller when any voids exist in the body. According to the rule of mixtures [31], ε' decreases as the void volume increases.

Fig. 6 shows the temperature dependence of tan δ for the amorphous and crystalline CVD-Si_3N_4 at the frequency of 10 kHz. A log–linear relationship between tan δ and temperature is observed below 650° C for both specimens. A similar relationship was reported in soda-glass and borosilicate-glass [32]. The relationship can be given by Equation 8

$$\tan\delta = A\exp(aT) \qquad (8)$$

where both A and a are constants and T is an absolute temperature. This relationship can be explained by Gevers' theory which assumes that the relaxation time of the displacement process has a certain activation energy and the activation energy is distributed according to the gaussian distribution [33]. The deviation from the linear relationship observed above 650° C, was caused by a significant increase of the dielectric loss by the d.c. conduction. The tan δ of the amorphous CVD-Si_3N_4 is less than that of the crystalline CVD-Si_3N_4 because the ε'' of the amorphous CVD-Si_3N_4 is less than that of the crystalline CVD-Si_3N_4 as shown in Fig. 4.

4. Conclusions

The dielectric properties of thick plates (about 1 mm thick) of amorphous and crystalline Si_3N_4 prepared by chemical vapour deposition under $SiCl_4 + NH_3 + H_2$ gases were measured in the temperature range from room temperature to 800° C. The following results were obtained.

1. The temperature dependence of the a.c. conductivity ($\sigma_{a.c.}$) for the amorphous and crystalline CVD-Si_3N_4 decreased with decreasing temperature and with increasing frequency. $\sigma_{a.c.}$ of the amorphous CVD-Si_3N_4 was three to ten times smaller than that of the crystalline CVD-Si_3N_4 in the temperature range from room temperature to 500° C. On the other hand, $\sigma_{a.c.}$ of the amorphous CVD-Si_3N_4 was larger than that of the crystalline CVD-Si_3N_4 above 500° C due to the contribution of the d.c. conductivity ($\sigma_{d.c.}$).
2. Both ε' and ε'' of the amorphous CVD-Si_3N_4 were smaller than those of crystalline CVD-Si_3N_4 in the entire temperature and frequency ranges examined.
3. The relationships of $\varepsilon'' \propto \omega^{n-1}$, $(\varepsilon' - \varepsilon'_\infty) \propto \omega^{n-1}$ and $\varepsilon''/(\varepsilon' - \varepsilon'_\infty) = \cot(n\pi/2)$ were observed for both amorphous and crystalline specimens. The values of n found for the amorphous (0.8 to 0.9) and crystalline (0.6 to 0.8) CVD-Si_3N_4 indicate that the a.c. conduction mechanism of both specimens is due to hopping.
4. The tan δ of the amorphous CVD-Si_3N_4 was

TABLE III Dielectric constants (ε') of various Si_3N_4 (at room temperature)

ε'	Frequency (Hz)	Structure	Preparation method	Source materials	References
4.8–5.8	10^5	Amorph.	CVD	$SiCl_4 + NH_3$	[25]
7	10^5	Amorph.	CVD	$SiH_4 + NH_3$	[26]
7.4	–	Amorph.	CVD	$SiH_4 + NH_3$	[14]
6	–	Amorph.	CVD	$SiH_4 + N_2H_4$	[27]
6–7	–	Amorph.	SP*	$Si + N_2$	[28]
5.6–6.2	–	Amorph.	SP	$Si + N_2$	[28]
8.4	10^3	Cryst.	CVD	$SiF_4 + NH_3$	[29]
5.6	8×10^9 to 10^{10}	Cryst.	RS†	–	[4]
9.4	–	Cryst.	RS	–	[5]
7–8	5×10^4 to 3×10^7	Cryst.	HP‡	–	[30]
7.98	10^5	Cryst.	HP	–	[6]
8.36	10^2 to 3×10^5	Amorph.	CVD	$SiCl_4 + NH_3$	Present work
8.66	10^2 to 3×10^5	Cryst.	CVD	$SiCl_4 + NH_3$	Present work

*Sputtering method.

†Reaction-sintering method.

‡Hot-pressing method.

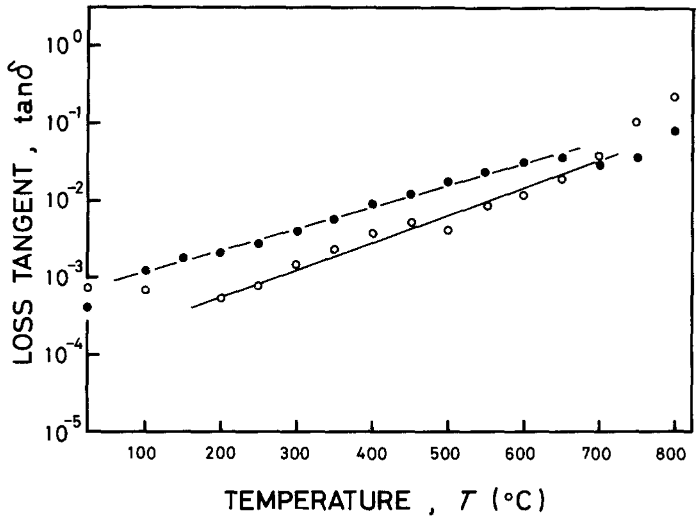

Figure 6 Temperature dependence of tan δ for the (○) amorphous and (●) crystalline CVD-Si_3N_4 (f = 10 kHz).

smaller than that of the crystalline CVD-Si_3N_4 in the temperature range from room temperature to 600° C.

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