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Electrical properties of Si-N films deposited on silicon from reactive plasma

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Because reactive-plasma-deposited Si-N films might offer certain advantages in silicon integrated-circuit technology, we have evaluated their electrical properties and compared them with those of CVD Si_3N_4. Various films with compositions in the range $0.75 \leq Si/N \leq 1.9$ were studied using C-V and I-V measurements, the latter at temperatures up to 200°C. The dominant conduction mode appears to be Frenkel-Poole emission; this is consistent with the observed linear I-vs-$V^{1/2}$ relationship and magnitudes of various parameters. The resistivities (range 10^4–10^{21} Ω cm at 2×10^6 V/cm) and dielectric strengths (range 0.8×10^6 to 8×10^6 V/cm) are found to depend upon the film composition and on an as yet undefined structural parameter (for Si/N≈0.75). The interface between Si-N and Si is associated with a high density of surface charge ($>10^{12}$ cm^{-2}) and a large trapping instability.

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I. INTRODUCTION

Amorphous Si-N films with compositions ranging from Si/N = 0.75 (Si_3N_4) to ~2.0 have been prepared using reactive-plasma deposition (RPD) at low temperatures (275 °C).[1] This deposition process is characterized by exceptionally good step coverage, leading to the use of films with Si/N ~ 1.0 as the final passivation layer in many devices. Because these films might offer certain advantages in SIC (silicon integrated-circuit) technology, their electrical properties have been evaluated. It is found that the ability to vary the composition offers a potentially attractive means of tailoring certain electrical properties of Si-N dielectric films.

The electrical characteristics investigated include "bulk" properties such as resistivity, dielectric breakdown strength, Frenkel-Poole barrier height, thermal activation energy for current leakage, dynamic and static dielectric constant, and "interface" properties such as the surface charge and trapping. In order to put these data into perspective, we compare them with those on CVD Si_3N_4 made in a Nitrox (Applied Materials Technology, Inc.) reactor at 830 °C.

II. EXPERIMENTAL

The Si substrates were 2-in.-diam wafers of n-type (111) material doped with As to a resistivity of 7 Ω cm. They were cleaned and then coated with about 1000 Å of RPD Si-N film, using a radial flow reactor described previously.[1] The reacting gases were SiH_4 (1.70%) and NH_3 (2.39%) in Ar carrier gas, the total flow was 2.32 liters/min, the pressure was 0.95 mm, and the substrate temperature was 275 °C. Different film compositions were obtained by changing the rf power in the range 100–400 W. These are nominal values which were read off at meters located on the power supply. The true power to the plasma or the plasma density depends on the geometry of the system, and, at best, it would roughly follow the relative changes in nominal rf power.

The film composition was determined using Rutherford backscattering analysis on ~2000-Å films; Auger spectroscopy gave nearly identical results. No composition variation with thickness could be detected down to a depth resolution of ~150 Å. The various rf powers, resulting film compositions, and certain other properties are listed in Table I.

For electrical evaluation, ~20-mil-diam Al dots were evaporated onto the Si-N through a shadow mask. A back Al contact was formed on bare Si. Measurements were made in a test facility consisting of an Electroglas 910 prober equipped with a Temptronix TP 35 thermochuk (20–300 °C).[2] The apparatus

TABLE I. Electrical properties of various Si-N films.

Film composition (Si/N)	rf power (W)	ϵ_d [a] at 25 °C	$\mathcal{E}_a$ [b] (eV)	φ_B [c] (V)	ρ [d] (Ω cm)	E_m [e] (10^6 V/cm)	ϵ_s [f]
~0.75	400	2.9	0.26	1.3	5×10^{19}	8.1	5.8
0.76	350	2.7	0.24	1.4	3×10^{17}	6.4	6.5
0.8	300	2.8	0.3	1.2	3×10^{15}	5.0	6.8
1.0	250	2.5	0.4	1.2	4×10^{13}	3.9	6.4
1.15	200	2.5	...	...	9×10^{11}	3.1	7.0
1.4	150	2.0	...	...	10^{10}	2.3	6.7
1.9	100	1.8	...	...	4×10^4	0.8	7.8
0.75	CVD	1.9	0.5	1.7	8×10^{20}	7.2	7.2

[a] Dynamic dielectric constant.
[b] Thermal activation energy for conduction.
[c] Barrier height for Frenkel-Poole emission.
[d] Resistivity at 2×10^6 V/cm.
[e] Dielectric strength (field for a current of 4 μA).
[f] Static dielectric constant (1 MHz).

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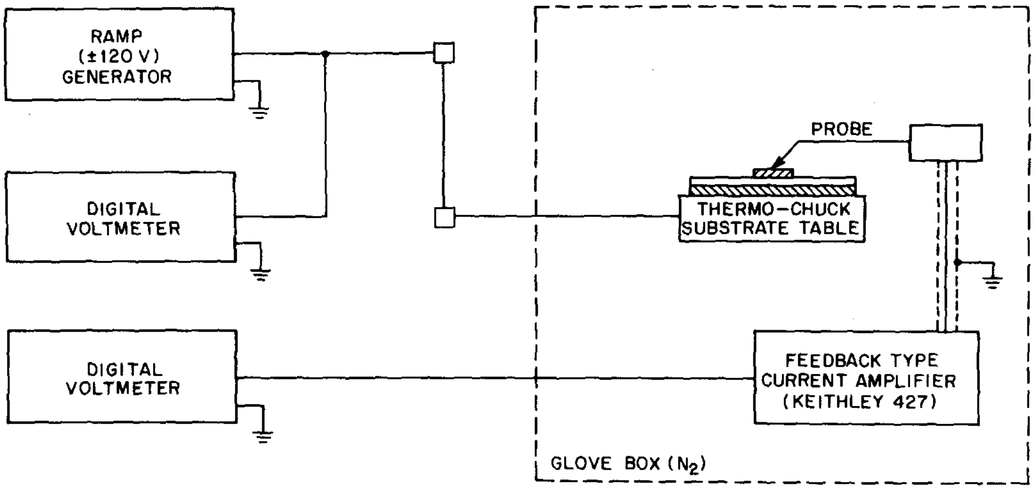

FIG. 1. Schematic of the setup for I-V measurements at different temperatures.

was enclosed in a dry-N_2 glove box. Usual C-V and I-V measurements were made, the latter as a function of temperature. Figure 1 shows a schematic of the setup for I-V measurements.

III. I-V CHARACTERISTICS

A. Conduction mode, barrier height, and activation energy

Figure 2 shows typical current-voltage characteristics at 25, 80, and 130 °C for an RPD Si-N film (400 W, Si/N = 0.75). Figure 3 shows an Arrhenius plot of leakage current for a constant field of 4.6×10^6 V/cm. The plots shown here are for the metal electrode biased positive, i.e., the semiconductor was forward biased, and the current was mainly limited by bulk conduction through the dielectric. Results for negatively biased field plates were similar at lower currents, but with increasing negative voltage, the current tended to saturate at a value determined by the reverse-biased semiconductor ($\sim 10^{-8}$ A). Reproducible and quick measurements could be made by starting at the highest field (corresponding to a current of 1—2 μA) and then going down in voltage; this requirement was probably imposed due to trapping instabilities which will be discussed in Sec. IV C.

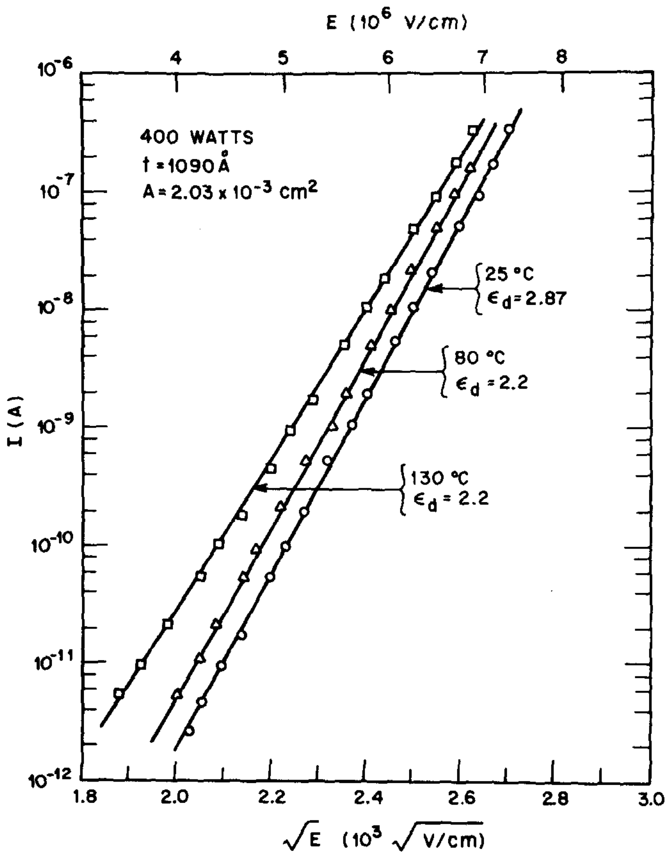

FIG. 2. Current-voltage characteristics of RPD Si-N film deposited at 400 W.

The linear relationship between the log of the current and the square root of the field, E (V/cm), is similar to that found for CVD Si_3N_4 where it has

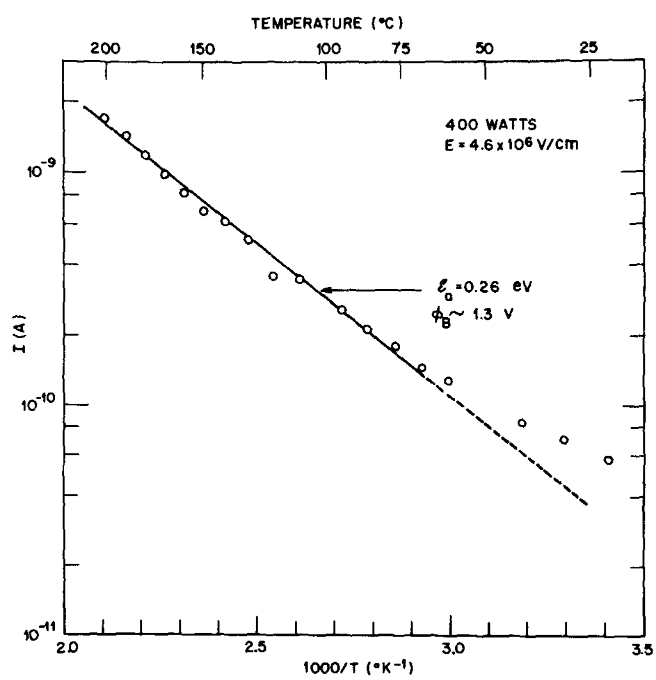

FIG. 3. Arrhenius plot of leakage current at 4.6×10^6 V/cm for the sample of Fig. 2.

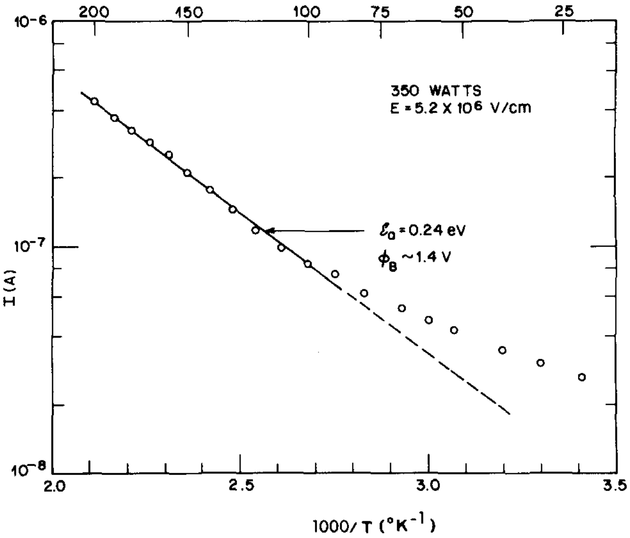

FIG. 4. Arrhenius plot of leakage current at 5.2×10^6 V/cm for the RPD Si-N film deposited at 350 W.

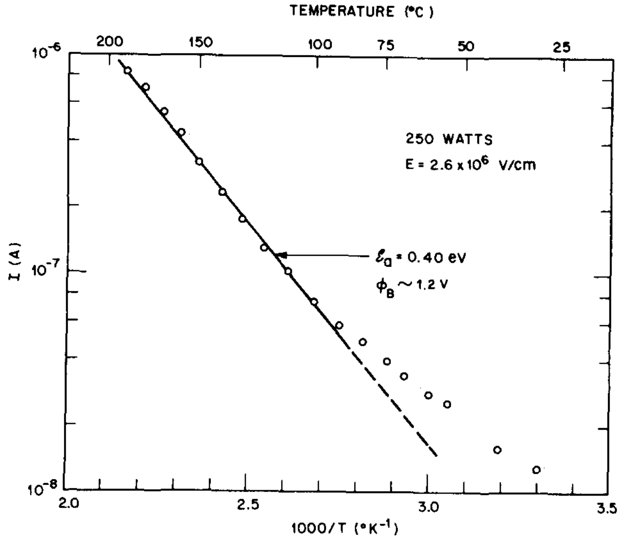

FIG. 6. Arrhenius plot of leakage current at 2.6×10^6 V/cm for the RPD Si-N film deposited at 250 W.

been shown[3–5] that conduction occurs through Frenkel-Poole emission (internal Schottky effect). This involves field-enhanced thermal excitation of electrons from traps into the conduction band of the dielectric. According to this mechanism,[6]

$$J=C_1E\exp\{-(q/kT)[\varphi_B-(qE/\pi\epsilon_0\epsilon_d)^{1/2}]\} \quad (1)$$

with

$$\epsilon_d=\frac{77.087}{T^2[(\text{slope})(\ln I/E^{1/2})]^2}, \quad (2)$$

$$\varphi_B=\mathcal{E}_a/q+[(5.746\times10^{-7})E/\epsilon_d]^{1/2}, \quad (3)$$

where J is the current density (A/cm^2), φ_B is the barrier height or depth of trap potential well, ϵ_0 is permittivity of free space, ϵ_d is a dynamic dielectric constant, C_1 is a function of density of traps, and $\mathcal{E}_a$ is the slope of Arrhenius activation-energy plot of $\ln I$ versus $1/T$. It should be mentioned that at high voltages a linear $\ln I$-vs-$V^{1/2}$ relationship also holds for the case of Fowler-Nordheim tunneling[7] which is the dominant conduction mode in SiO_2 and Al_2O_3 films. Here, $J\sim V^2\exp(-b/V)$, where b is a constant *independent* of temperature. Moreover, Sze[3] has pointed out that if one treats Fowler-Nordheim tunneling as internal Schottky emission, a large apparent ϵ_d of 10—50 would result.

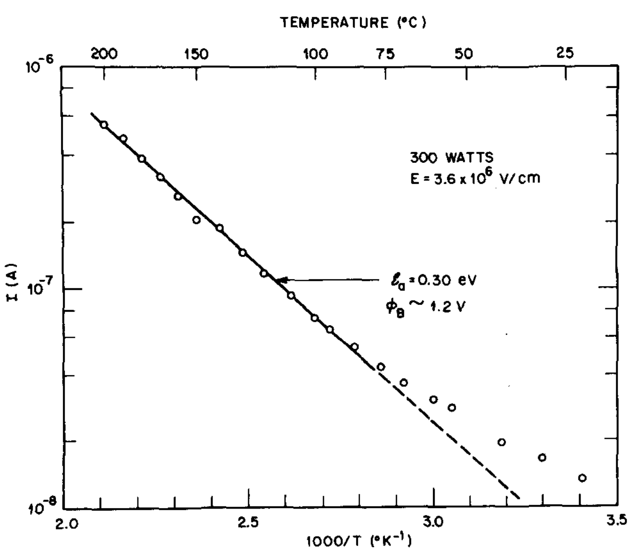

FIG. 5. Arrhenius plot of leakage current at 3.6×10^6 V/cm for the RPD Si-N film deposited at 300 W.

For the film investigated in Figs. 2 and 3, ϵ_d is quite low ($2<\epsilon_d<3$), and the leakage current has an appreciable temperature dependence ($\mathcal{E}_a=0.3$ eV above 60 °C). Both of these observations would favor the Frenkel-Poole emission model, at least at temperatures above 60 °C. However, it should be emphasized that the above model will not fit data over the full range of temperatures investigated. Thus, ϵ_d is not really constant at various temperatures, whereas the $\ln I$-vs-T^{-1} plot shows a significant deviation from linearity below 60 °C. At these lower temperatures, the temperature dependence of leakage current gets considerably weaker, and this might be taken as an indication of possible tunneling components in the leakage current.

A similar conclusion was reached for RPD Si-N films made at 350, 300, 250, 200, 150, and 100 W rf power. As shown in Figs. 4—6, the $\ln I$-vs-T^{-1} plots for films made at 350, 300, and 250 W also show significant deviations from linearity and, hence, from the Frenkel-Poole model. Table I summarizes the results on ϵ_d, $\mathcal{E}_a$, and φ_B. The φ_B values were calculated for 80 °C, and taking into account the variations in $\mathcal{E}_a$ and ϵ_d, the tabulated φ_B values should be valid within ± 10% over the temperature range 25—150 °C. Figure 7 shows the $\ln I$-vs-T^{-1} data for a CVD Si_3N_4 film. This film has a larger barrier height ($\varphi_B\sim1.7$ V) and a higher thermal activation energy for leakage ($\mathcal{E}_a\sim0.5$ eV) as compared to the present RPD films for which $\varphi_B\sim1.3$ V and $\mathcal{E}_a\sim0.3$ eV.

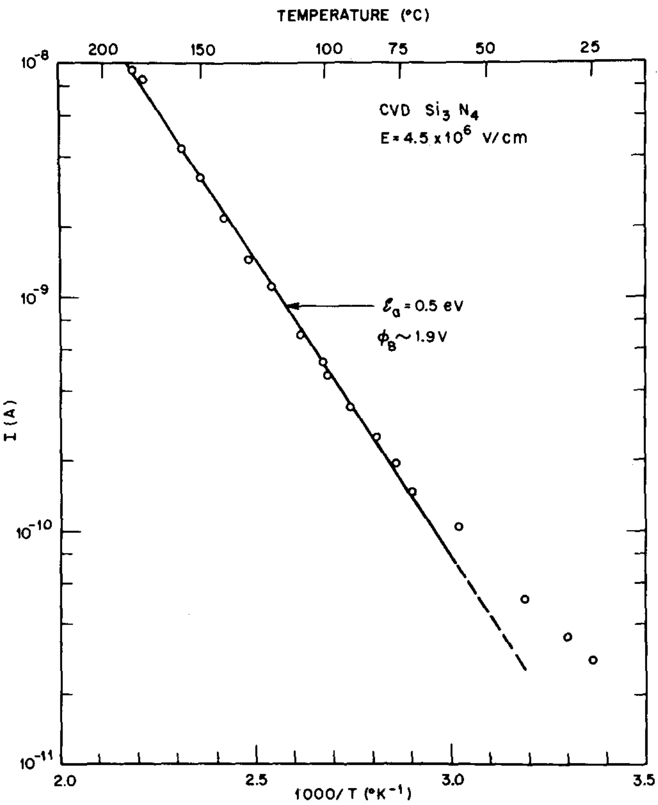

FIG. 7. Arrhenius plot of leakage current at 4.5×10^6 V/cm for a CVD Si_3N_4 film.

B. Resistivity

Figure 8 shows the resistivity, at a constant arbitrary field of 2×10^6 V/cm, as a function of composition of various Si-N films. The resistivities span a remarkable range of about 17 orders of magnitude. The resistivity increases logarithmically from 10^4 to 10^{15} Ω cm with decreasing Si-N ratio from 1.9 to 0.8, obtained by changing the rf power from 100 to 300 W. Upon further increasing the power to 350 and 400 W, the composition levels off at the stoichiometric value. However, the resistivity increases very rapidly in this composition range, reaching 5×10^{19} Ω cm for the film made at 400 W. The value for CVD film is yet one order of magnitude higher.

It would seem that for near-stoichiometric films ($0.75 \le Si/N \le 0.8$) some kind of profound structure changes are taking place. These may be related to film density which is 2.8 g cm^{-3} for the film made at 350 W and is expected to be ~3.2 g cm^{-3} for the CVD Si_3N_4.[4] There is evidence from infrared spectra that RPD Si-N films contain appreciable amounts of hydrogen bonded mainly to Si atoms.[8] As the composition changes from Si rich to stoichiometric, the amount of hydrogen may be expected to rapidly decrease. It may then be speculated that Si-H or Si-Si bonds might contribute to the higher conductivity observed for RPD films as compared to CVD Si_3N_4. Nothing is known about the details of short-range order in these amorphous films—this may be another important factor affecting the electronic transport properties.

C. Dielectric strength

The dielectric strength or breakdown field of Si-N films is difficult to determine because of large conductance at high field. In a majority of cases, for $0.75 \le Si/N \le 1.0$, catastrophic breakdown occurred at currents of 2—5 μA. It is convenient to define, here, dielectric strength as the field corresponding to a current of 4 μA. The dielectric strengths listed in Table I range from 0.8×10^6 V/cm for a RPD film deposited at 100 W (Si/N = 1.9) to 8×10^6 V/cm for a film deposited at 400 W (Si/N = 0.75).

IV. *C-V* MEASUREMENTS

A. Dielectric constant

The "static" dielectric constant ϵ_s of the films discussed in Sec. III C was obtained by measuring the capacitance at 1 MHz under conditions of strong accumulation. The results are shown in Fig. 9. For RPD films, there seems to be a weak overall tendency for increase in ϵ_s (from ~6 to ~8) as the films become Si rich. On the other hand, the dynamic dielectric constant ϵ_d decreases slightly as the Si/N ratio increases. This is difficult to understand since, in the simplest model, ϵ_d would be approximately equal to the square of the refractive index,[9] which increases with increasing Si/N ratio. In the case of CVD Si_3N_4, both its static and dynamic dielectric constants do not fit with the plot for RPD films, again suggesting some real structural differences between the CVD and the RPD material with Si/N = 0.75.

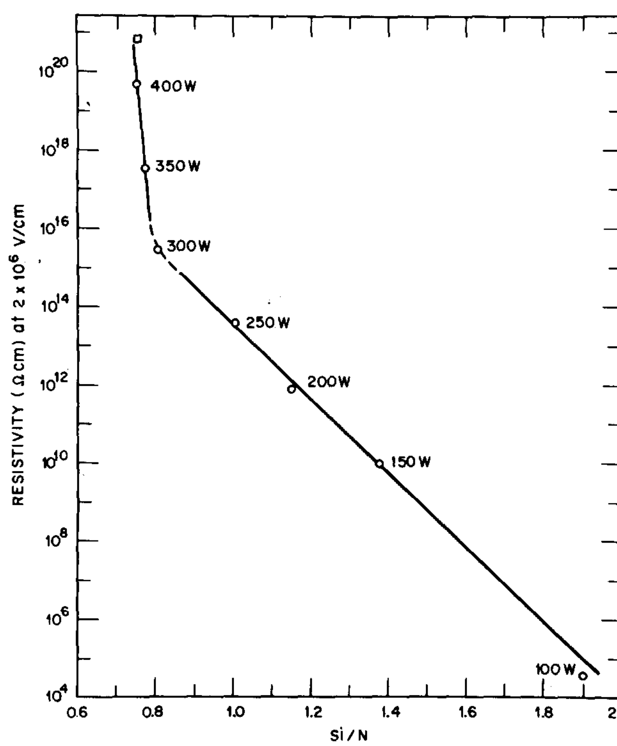

FIG. 8. Variation of Si-N film resistivity at 2×10^6 V/cm with composition. ○—RPD Si-N films deposited at various rf powers; □—CVD Si_3N_4 film.

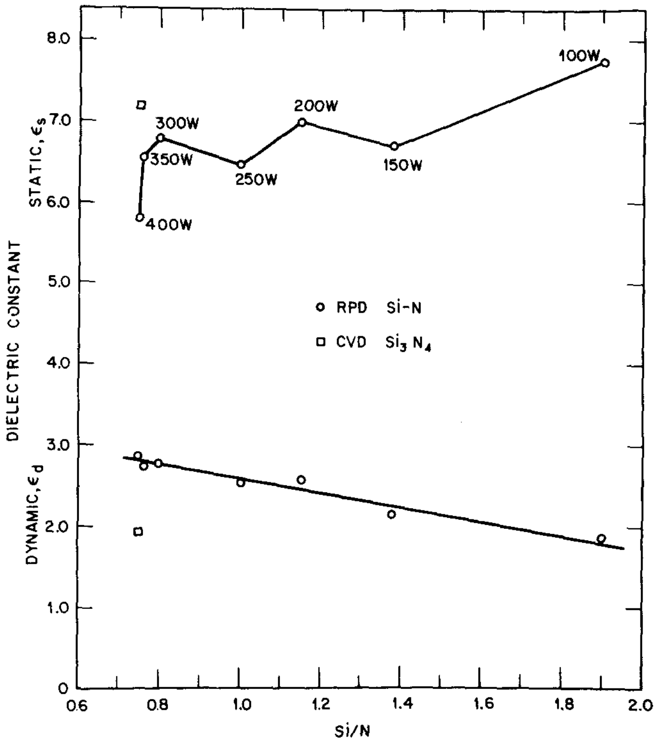

FIG. 9. Static (1 MHz) and dynamic dielectric constant of Si-N films of various compositions.

B. Surface charge

The C-V curves for RPD as well as CVD nitrides showed large hysteresis. Under such conditions, the surface charge becomes a somewhat ambiguous quantity. Using the flatband voltage for the case where the MIS capacitor was being swept from inversion into accumulation, the upper range of Q_{ss} is estimated as $(1-2)\times 10^{12}$ cm^{-2}.

C. Trapping

In agreement with the electronic conduction model, the C-V measurements show much evidence of charge trapping.[10,11] This was manifested upon bias-temperature aging by a shift of C-V curves in the negative direction upon negative bias aging and in a positive direction upon positive bias aging. Typical trapping shifts for RPD Si-N were 5 V at room temperature (under bias of 3×10^6 V/cm) and 10 V after 250 °C, 15 min (bias $\simeq 1\times 10^6$ V/cm) aging. Both positive and negative values of bias were applied, and trapping was always found to dominate over any polarization effects. The latter results in a shift opposite to that by trapping and was earlier observed by Deal *et al.* for CVD Si_3N_4 (Ref. 4) and phosphosilicate glass[12] under conditions of high temperature and low to moderate bias.

V. SUMMARY AND CONCLUSIONS

Electrical properties of various RPD Si-N films ($0.75 \le Si/N \le 1.9$) have been compared with those of CVD Si_3N_4.

(1) The dominant conduction mode appears to be Frenkel-Poole (F-P) emission. This is consistent with a linear I-$V^{1/2}$ relationship, a relatively small dynamic dielectric constant (~3.0), and a temperature-dependent conductivity with activation energy of ~0.3 eV. The barrier height is ~1.3 V.

(2) The film resistivity (at 2×10^6 V/cm) and dielectric strengths are a sensitive function of composition in the range $0.8 \le Si/N \le 1.9$. For near-stoichiometric films, both quantities increase rapidly with rf power during deposition, nearly reaching the values for CVD Si_3N_4 (for 400 W deposition).

(3) The static dielectric constant (1 MHz) ranges from 6 to 8. The surface-charge density is $>10^{12}$ cm^{-2}, and there is evidence for much interface trapping even at room temperature.

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