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Argon Content of SiO_2 Films Deposited by RF Sputtering in Argon

Abstract: When SiO_2 is deposited by sputtering in an argon rf glow discharge, the films so produced contain considerable amounts of trapped argon, as determined by x-ray fluorescence analysis. This argon content was measured as a function of various sputtering parameters: argon pressure, rf power, electrode spacing, substrate temperature, and magnetic field, the latter two being most influential. A simple theoretical model for the capture and release of argon is presented which explains an observed linear decrease of the argon concentration in SiO_2 with increasing temperature. Incorporation of argon into the sputtered SiO_2 film does not seem to impair the film's ability to act as a good passivating and insulating layer.

Introduction

Since rf-sputtered films are exposed to the glow discharge during deposition and it is well known that energetic rare gas atoms or ions can be embedded in SiO_2 surfaces under these circumstances, there has been speculation about the amount of argon actually trapped during sputtering, and how such argon affects the properties of the films thus deposited. The first measurements of argon content in sputtered SiO_2 films were made recently by Hoffmeister and Zuegel,[1] who showed that some films contain large amounts of argon. (Under some sputtering conditions the molar ratio of argon to SiO_2 can exceed 0.1.) The work reported in this paper extends the measurements of Hoffmeister and Zuegel to a wider range of sputtering conditions and also addresses the problem of the relationship between argon content and film properties.

Theoretical

There is considerable information describing the mechanism of the capture and subsequent release of rare gases by glass surfaces, the most recent survey of which is a review article by Grant and Carter.[2] It is generally agreed that the gas sorption is largely due to positive ion bombardment; however, there is the evidence of Winters and Kay[3] that energetic neutral atoms may also be involved. It is believed that the gas initially is held at or just below the glass surface and that some immediate desorption occurs due to a combination of bombardment-induced and thermally-induced re-emission. In the experiments to be described, there is an additional process to be considered: the simultaneous deposition of SiO_2. The impinging SiO_2 continuously buries sorbed argon, providing a fresh surface for further gas sorption.

By using an argon-free glass surface, the rate of argon capture has been found to be proportional to the bombardment rate of argon ions.[4] The capture process can be visualized: an incoming energetic argon ion or atom can strike the surface, either at an empty site where it will stick, or at an occupied site where it will be reflected. The net rate of argon capture can be written as:

$$\text{Rate (capture)} = I\sigma_C(n_0 - n), \tag{1}$$

where I is the flux of energetic argon, σ_C is a proportionality constant or capture cross section, n_0 is the number of potential capture sites, and n is the number of filled sites.

The release of sorbed gas by ion bombardment has been demonstrated clearly in experiments where one inert gas is used to recover another gas that had been previously sorbed.[5] During the recovery process, the second gas is itself sorbed on the surface. Thus, the rate of sputtering re-emission can be given as

$$\text{Rate (sputtering)} = I\sigma_S n, \tag{2}$$

where σ_S is the cross section for sputtering. Thus, while reflection of argon from filled sites, Eq. (1), and bombardment-induced re-emission, Eq. (2), are introduced as separate processes, their effects are indistinguishable.

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It has been reported[5] that if argon was initially sorbed and krypton subsequently used to remove it, the amount of krypton sorbed was closely equivalent to the amount that would have been sorbed had no argon been present. Thus, the incident species which cause the sputtering can be regarded as having the same probability of becoming embedded in the surface as any other incident species.

The mechanism of the bombardment-release process has been discussed by several authors, and two alternatives have been considered: direct gas sputtering and sputtering of the glass with simultaneous gas release. The most extensive work has been done by James and Carter,[6] who conclude that the predominant mechanism in their system is direct gas sputtering. However, it is known that SiO_2 is resputtered during deposition by rf sputtering,[7] so that in this instance the glass sputtering mechanism for releasing argon may also be important.

The initial rate of pumping and the maximum quantity of gas sorbed decrease with increasing surface temperature. Thermally induced re-emission, therefore, must be included as a release mechanism. The rate of thermal re-emission from sites to which the argon is bound with a binding energy E has been assumed to obey a relationship:

$$\text{Rate (thermal re-emission)} = n/\tau, \tag{3}$$

where

$$\tau = \tau_0 \exp (E/kT), \tag{4}$$

and τ_0 is the mean time during which a sorbed argon atom stays on the surface at very high temperatures or in sites of zero binding energy (the commonly accepted value of τ_0 is 10^{-13} seconds).[8]

Carter and Leck[9] have concluded from their study of thermal desorption of rare gases in glass ionization gauges that, since desorption occurs over a very wide temperature range, E cannot be single-valued. The simplest energy distribution that can be assumed is one that is uniform between zero and some limit $E_{\max}$. In this case the number of states in the energy interval E to $E + dE$ will equal $N(E)dE$, where $N(E)$ has the form

$$N(E) = N_0/E_{\max} \text{ for } 0 \leq E \leq E_{\max}, \tag{5a}$$

and

$$N(E) = 0 \text{ for } E > E_{\max}, \tag{5b}$$

with N_0 as the total number of sites on the surface.

As SiO_2 is accumulated on the surface, the argon held in surface sites will be covered by incident SiO_2 molecules. This will create a fresh SiO_2 surface, and the argon thus buried will, in effect, be removed from sites on the surface. If A is the accumulation rate of SiO_2, then

$$\text{Rate (burial)} = A\sigma_B n, \tag{6}$$

where σ_B is the cross section for burial.

The assumption will be made that once the argon is buried it cannot be released. Therefore, the amount of argon embedded in the deposited SiO_2 layer is given by:

$$\frac{\text{moles Ar}}{\text{moles } SiO_2} = \frac{A\sigma_B n}{A} = \sigma_B n. \tag{7}$$

Since σ_B is a geometrical factor (the effective area of an SiO_2 molecule), the molar ratio of argon to SiO_2 will depend only on n, the number of surface sites filled with argon. When a steady state is reached at the surface, the rates of capture and release are equal. For a given energy state E_i, therefore,

$$I\sigma_C(n_{0i} - n_i) = I\sigma_S n_i + A\sigma_B n_i + \tau_i^{-1} n_i, \tag{8}$$

or

$$n_i = I\sigma_C n_{0i}/[I(\sigma_C + \sigma_S) + A\sigma_B + \tau_i^{-1}]. \tag{9}$$

Since the energy distribution given by Eq. (5) has been assumed, to find the total number of filled sites for all possible energy states, we substitute $N(E)dE$ for n_{0i} and integrate over the distribution:

$$\begin{aligned} n &= I\sigma_C \frac{N_0}{E_{\max}} \int_0^{E_{\max}} \frac{dE}{G + \tau_0^{-1} \exp(-E_{\max}/kT)} \\ &= \frac{I\sigma_C N_0}{G} \\ &\quad \times \left\{1 - \frac{kT}{E_{\max}} \ln \left[\frac{G + \tau_0^{-1}}{G + \tau_0^{-1} \exp(-E_{\max}/kT)}\right]\right\}, \end{aligned} \tag{10}$$

where, for convenience,

$$G \equiv I(\sigma_C + \sigma_S) + A\,\sigma_B.$$

Because of the artificial energy distribution which has been assumed, Eq. (10) is at best a first approximation to the real dependence. Equation (10) can be simplified if we consider the magnitudes of τ_0 (the mean time of residence at a site having no binding energy), and $\tau_{\max} = \tau_0 \exp (E_{\max}/kT)$ (the mean time of residence at a site having the maximum binding energy). As stated before, τ_0 is assumed to be very small (10^{-13} sec). Since rare gases embedded in the walls of an ionization gauge will not desorb for many hours or days at room temperature, $\tau_{\max}$ must be very large. It will be shown later that both $I(\sigma_C + \sigma_S)$ and $A\sigma_B$ are probably of the order of 1 to 10 $\sec^{-1}$. Therefore, $\tau_0^{-1} \gg G$; and, at room temperature,

$$\tau_0^{-1} \exp(-E_{\max}/kT) \ll G.$$

Therefore, near room temperature, Eq. (10) becomes

$$n = \frac{I\sigma_c N_0}{G}\left[1 - \frac{kT}{E_{\max}}(\ln \tau_0^{-1} - \ln G)\right]\cdot \tag{11}$$

This equation predicts a linear decrease in the molar ratio of argon to SiO_2 with increasing temperature in the temperature range for which the approximation $G \gg \tau_{\max}^{-1}$ is valid. In the limit of very high temperature, $n \rightarrow 0$; but as the limit is approached, n will no longer be linearly dependent on T since, for higher temperatures where $\tau_{\max}^{-1} \gg G$, the equation for n becomes

$$n \approx \left(\frac{kT}{E_{\max}}\right) \frac{I\sigma_c N_0}{\tau_0^{-1} \exp\left(-E_{\max}/kT\right)}. \tag{12}$$

The dependence of the argon concentration in the sputtered film on power, pressure, electrode-to-substrate spacing, and magnetic field, is not apparent from Eq. (11), since only the accumulation rate A is known as a function of these parameters. We cannot measure the argon ion flux because the SiO_2 film is an insulator; we cannot measure the flux of energetic neutrals; and there is no independent source of information regarding the cross sections.

Described in the following section are the method of determining the argon content, its measurement as a function of the various sputtering parameters, and finally, the relationship between the argon content and the film properties.

Experimental

All experiments were performed with a diode-type rf sputtering system, described elsewhere.[10] The back side of each wafer was coated with gallium to ensure good thermal contact with the substrate holder. Because the diffusion of argon through SiO_2 at the temperatures studied is extremely slow, it has been assumed that the argon content of the film did not change significantly once the rf glow discharge was turned off and sputtering had ceased.

• *Determining the argon content*

The argon content of the films was measured by x-ray fluorescence analysis, a technique first used by Hoffmeister and Zuegel,[1] and many of the results reported here are simply a confirmation of their data. Argon concentration is reported as the molar ratio of argon to SiO_2. X-ray fluorescence measurements were made using a Siemens SRS-1 vacuum spectrograph equipped with a chromium target x-ray tube, PET analyzing crystal, and a thin-window (2-micron Makrofol*) flow-proportional counter with P-10 flow gas. Aluminum sample holders with 23 mm circular openings were used for most samples, and measurements were made at the center of each wafer. For special samples, where uniformity of argon content over the sample area was being checked, similar holders with 8-mm circular openings were used. Samples were rotated (at 10 rpm) during x-ray measurements to minimize errors caused by diffraction of the primary x-ray beam by the single-crystal silicon wafers used as substrates. The first-order Ar K_α x-ray peak was measured and a background measurement was made at an off-peak location on each sample. For some samples in which the argon content was very low, the x-ray emission intensity of the uncoated substrate was measured and subtracted from the net argon count. Argon intensities of 1,650 counts per minute (net count) per microgram of argon were typical. Two methods were used to calibrate the x-ray emission measurement: a KCl technique and a weight loss measurement.

The KCl technique was a procedure analogous to that carried out by Hoffmeister and Zuegel.[1] For this purpose, a KCl film (1600 ± 100 Å thick) was deposited on a substrate similar to that used for SiO_2. The x-ray net count rates were then measured for the K_α lines of K and Cl under the same conditions as used for Ar-K_α measurements. Since K and Cl bracket Ar in the atomic table, it was assumed that the x-ray intensity per unit mass of Ar would be approximately equal to the average of the intensities per unit mass measured for K and Cl.

In the weight-loss technique, measurements were made of Ar count rates on several SiO_2 films which were then baked until the Ar count was reduced essentially to zero. Weight losses of 50–165 μgm (measured to ± 5 μgm using a Mettler Micro-Balance, Type M5), depending on the sample, were assumed to be due entirely to argon.

The calibrations obtained by these two methods are in excellent agreement. The values obtained by the weight-loss method have been used throughout this report since they differ by only 2% from those obtained by the KCl calibration. The results obtained are also in good agreement with the results reported by Hoffmeister and Zuegel.[1] Since no absolute standard is available, the accuracy of the calibration is uncertain, but we believe the absolute argon values obtained to be accurate to at least 25%.

The apparent values of argon content (μgm Ar/cm^2) found by these methods were corrected for absorption of the x-rays by SiO_2 using the formula

$$[\mathrm{Ar}]_{\mathrm{corrected}} = [\mathrm{Ar}]_{\mathrm{apparent}}[I_{\mathrm{no\,abs}}/I_{\mathrm{meas}}], \tag{13}$$

where I_{meas} is the measured fluorescence intensity for a film of thickness x(cm), and $I_{\mathrm{no\,abs}}$ is the hypothetical intensity for a film exhibiting no absorption. An approximate expression[12] was used to take absorption into account:

$$I_{\mathrm{meas}}/I_{\mathrm{no\,abs}} = (1 - e^{-Kx})/Kx. \tag{14}$$

The factor $K(\approx 3300\ \mathrm{cm}^{-1})$ occurring in this expression was calculated, taking into account the angle of incidence (45°), the angle of emission (45°), the absorption of the incident and emitted x-rays (by silicon and oxygen), and the density of SiO_2 (2.2 gm/cm^3).

If the absorption correction is valid, and there are no other thickness effects (as might be produced by diffusion, for example), the corrected argon content should be independent of SiO_2 thickness. This is discussed below.

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* Frabenfabriken Bayer Ag, Leverkusen, Germany

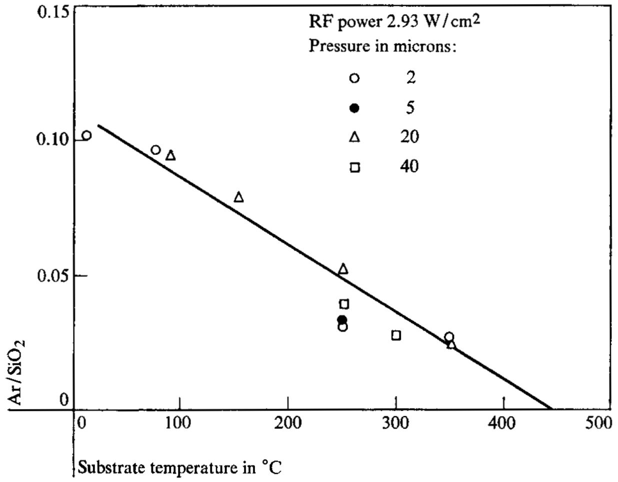

Figure 1 Argon concentration as a function of substrate temperature; with magnets, close (1.125 in.) spacing.

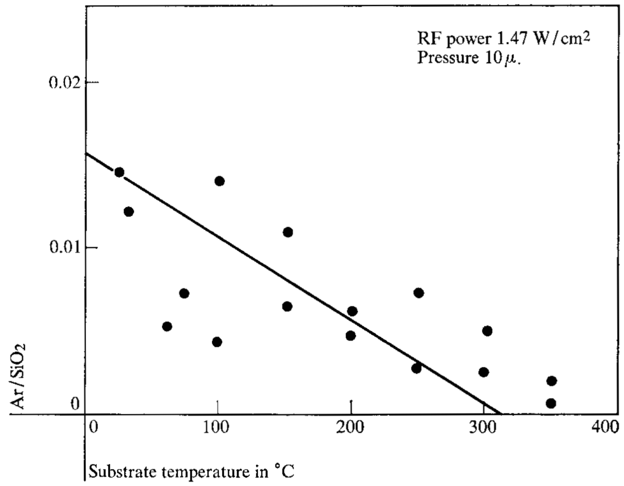

Figure 2 Argon concentration as a function of substrate temperature; without magnets, wide (1.625 in.) spacing.

• *Dependence of argon content on sputtering parameters*

Magnetic field and target-to-substrate spacing

Two modes of sputtering were used: with and without a magnetic field. When permanent magnets were used (giving fields of 50 to 100 gauss) they were positioned under the substrate holder.[10] The usual electrode-to-substrate spacing was 1.125 in., but when the magnets were removed this spacing was increased to 1.625 in., which was needed to maintain a self-sustained discharge. To separate the effects of the wider (1.625 in.) spacing and the magnetic field, an experiment was performed with the magnets in position by using the wider spacing. The results are given in Table 1. Increasing the spacing decreased the argon concentration about 35%, while removing the magnets and keeping the spacing constant reduced the argon concentration to about a third of its original value. For other sputtering conditions, the effect of a magnetic field was even more pronounced; for example, at 2.93 W-cm^{-2}, 40 microns pressure, and 250°C, the argon concentration with the magnetic field was about twenty times that obtained without magnets.

There is evidence[13] that as an increasing magnetic field is applied to the rf glow discharge, the floating (i.e., zero-current) potential of the substrate becomes increasingly more negative. This suggests that when magnets are used the argon ions impinge on the film surface with greater energy and thus have a higher probability of becoming embedded. When magnets are not present the floating potential is lower and the probability of ion capture is considerably less. In the latter case, energetic neutrals (which are believed to originate near the rf electrode surface) may be playing the principal role in determining the argon content of the films.

Table 1 Effect of magnetic field and spacing.[a]

Argon pressure, μ	*Magnets*	*Spacing in inches*	*Ar/SiO$_2$ ratio* ($\times 10^{-2}$)
5	In	1⅛	3.861
5	In	1⅝	3.346
10	In	1⅛	3.038
10	In	1⅝	2.760
10	Out	1⅝	0.873

[a] Power density: 2.93 watt cm^{-2}; substrate temperature: 300°C.

Temperature

Temperature was independently controlled, since the wafers were in direct contact with a temperature-controlled holder through the gallium backing. The argon concentration of SiO$_2$ films decreases linearly with increasing temperature for both sputtering models. Data are given in Fig. 1 for sputtering in a magnetic field performed at 2.93 W-cm^{-2} and at various pressures; while the results obtained without magnets, shown in Fig. 2, were obtained at 1.47 W-cm^{-2} and 10 microns pressure. The scatter of the experimental points in Fig. 2 is very pronounced. This is not surprising since the amount of argon in these films is very low and, at the lower levels, the background count (sometimes more than half the total) is impossible to determine accurately because of variable scattering of the primary x-ray beam from the single-crystal wafers.

The observed linear decrease of argon concentration with increasing temperature is as predicted by Eq. (11). For sputtering with a magnetic field, the decrease is approximately a factor of six between room temperature and 350°C, and apparently extrapolates to zero at a temperature $T^* \approx 450$°C.

Without magnets, however, the extrapolated value $T^* \approx 310$°C; this difference may merely reflect the wide

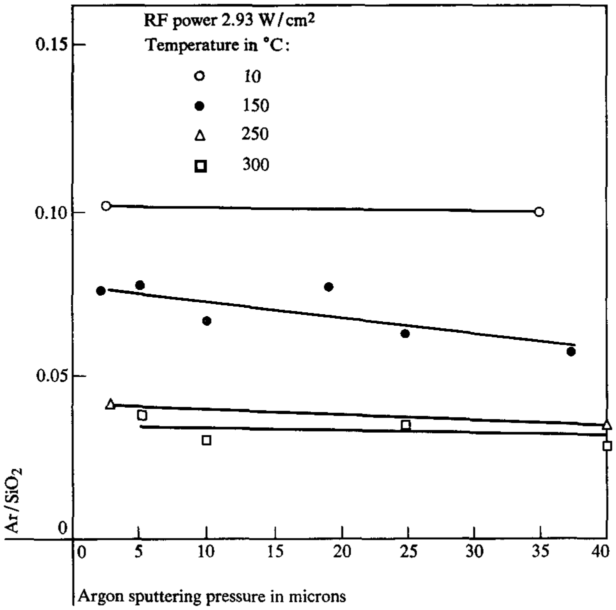

Figure 3 Argon concentration as a function of sputtering pressure; with magnets, close (1.125 in.) spacing.

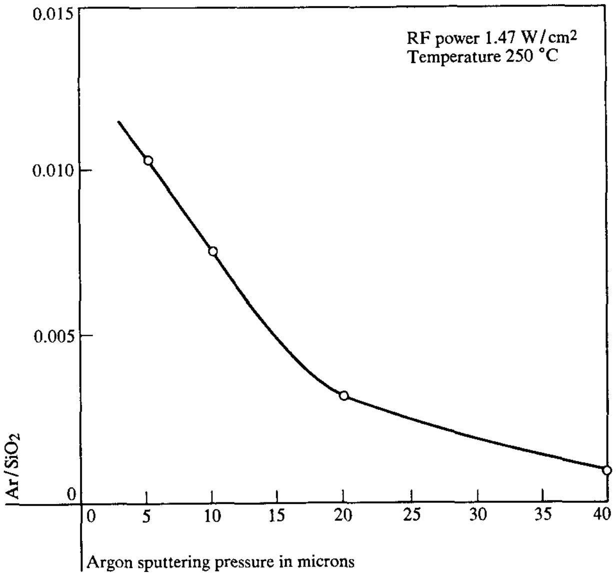

Figure 4 Argon concentration as a function of sputtering pressure; without magnets, wide (1.625 in.) spacing.

scatter of the data, or it may be real, indicating more loosely bound argon in this case.

At the temperature T^* at which the argon concentration apparently extrapolates to zero, Eq. (11) becomes

$$E_{\max} = kT^*\{\ln \tau_0^{-1} - \ln [I(\sigma_C + \sigma_S) + A\sigma_B]\}. \quad (15)$$

One can estimate $E_{\max}$ if reasonable values can be assigned to the argon flux and the cross sections. Measurements made during rf sputtering of silicon, rather than SiO_2, have been used to estimate ion flux. Table 2 shows data reflecting the with-magnets mode.

At 2.42 W-cm^{-2}, the ion flux is about 4.2×10^{15} ions cm^{-2} sec^{-1}. This is probably a low estimate for the total energetic argon flux (I) since it does not include the contribution of energetic neutrals. Using a density of 2.2 gm/cm^3 for sputtered SiO_2, the effective area of an SiO_2 molecule was calculated to be 13 Å^2, and this value was used for σ_C, σ_S and σ_B. The accumulation rate of 500 Å/min then corresponds to $A = 1.8 \times 10^{15}$ molecules cm^{-2} sec^{-1}. We will then have $I(\sigma_C + \sigma_S) \approx 11$ sec^{-1} and $A\sigma_B \approx 2.3$ sec^{-1}. Since τ_0^{-1} had previously been estimated as 10^{13} sec^{-1} and T^* found experimentally to be ≈450°C ($kT^* = 0.066$ eV), $E_{\max}$ has the approximate value of 1.8 eV. The value calculated for $E_{\max}$ is fairly insensitive to the values assumed for the cross sections. For example, if the cross section for sputtering σ_S is several times that for capture and burial, as suggested by the results of Kornelsen,[14] the value of $E_{\max}$ would not be changed significantly since it has a logarithmic dependence on all of the cross sections in Eq. (15).

Table 2 RF sputtering of silicon[a]

RF power in watt cm^{-2}	*Argon pressure in microns*	*Estimated ion flux,[b] I^+, in mA cm^{-2}*	*V (i = 0)[c] in volts*	*Rate of SiO_2 accumulation[d] in Å min^{-1}*
0.60	5	0.20	−23	125
1.21	5	0.43	−45	250
2.42	5	0.67	−50	500
2.42	10	0.77	−42	550
2.42	20	0.98	−14	460

[a] These trends in potential as a function of pressure and rf power have also been observed for SiO_2 in a private communication by J. S. Logan, IBM Components Division, East Fishkill, N. Y.

[b] Measured with no dc return to ground.

[c] Estimated from dc Langmuir probe measurements at the wafer position.

[d] From SiO_2 runs performed under identical conditions.

Since the bond energies of an SiO_2 molecule are about 5 eV, $E_{\max} = 1.8$ eV is not an implausible value as it represents a situation for which a considerable fraction of the SiO_2 bond energy must be provided before the argon can escape. The value of 1.8 eV for $E_{\max}$ is also in reasonable agreement with the results of Cobic, Carter and Leck,[4] who conclude from their studies on ion pumping that for argon sorption there are no sites having an energy of binding greater than 50 kcal/mole (2.17 eV).

Pressure

Whether or not a magnetic field is used, there is a decrease in argon concentration with increasing sputtering pressure; however, the dependence is much stronger without a magnetic field. The results for sputtering in the presence

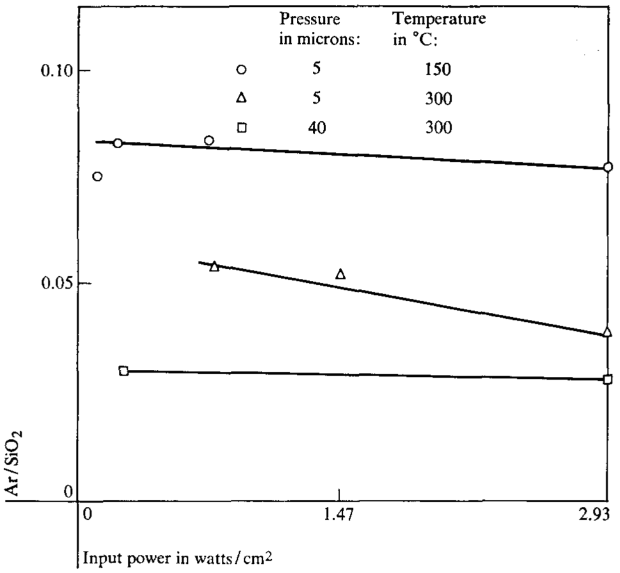

Figure 5 Argon concentration as a function of input power; with magnets, close (1.125 in.) spacing.

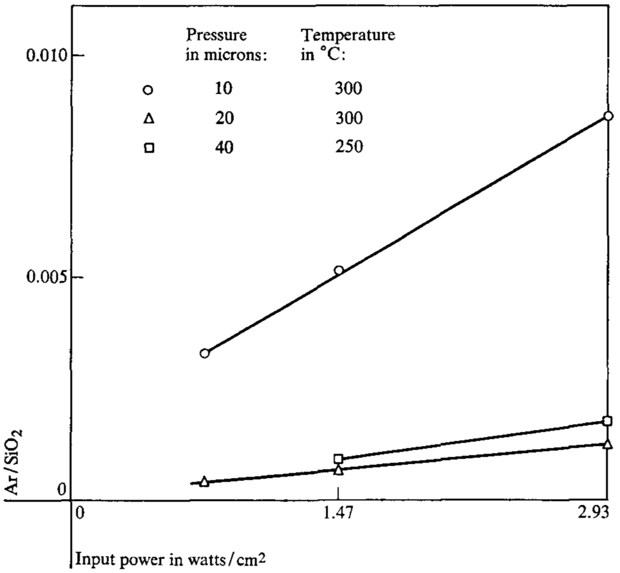

Figure 6 Argon concentration as a function of input power; without magnets, wide (1.625 in.) spacing.

of a magnetic field, given in Fig. 3, indicate only a slight decrease in argon concentration with increasing argon pressure. For sputtering without magnets (Fig. 4), the argon concentration drops by a factor of 10 as the pressure increases from 5 microns to 40 microns.

In the with-magnets mode, the negative floating potential draws the argon ions into the SiO$_2$ surface. From Table 2 it is seen that the voltage on the surface decreases with increasing pressure in this mode; therefore, the argon ions are impelled into the surface with less kinetic energy, with a resulting decrease in argon concentration.

When magnets are not used, energetic neutrals are probably the principal species being embedded, the floating potential being too small in this case to cause ions to be embedded. The more frequent the collisions as the pressure is increased, the lower will be the average kinetic energy of these neutrals reaching the substrate; this will also result in a decrease in argon concentration.

Winters and Kay[3] report that the pressure dependence of the argon concentration of sputtered nickel films depends on the substrate bias voltage. For films deposited at zero bias there was a rapid decrease in the argon concentration with increasing pressure, while for films deposited at -300 V bias voltage, there was a slight increase with increasing pressure. As described above, our results are in qualitative agreement with the findings of Winters and Kay.[3]

Power

The dependence of the argon concentration on power when a magnetic field was used contrasted sharply with the data taken without magnets. In the first mode there was a small decrease of argon concentration with increasing rf input power, while for the second mode the argon concentration increased by a factor of from two to four for a four-fold increase in power (see Figs. 5 and 6).

Wafer position

The argon concentration depended to some extent on the wafer's position under the rf electrode. For sputtering performed in a magnetic field the argon concentration was generally larger for wafers mounted near the rim of the electrode than for those mounted on the axis. The opposite was true for films made in the absence of a field. The argon concentration was also found to vary slightly with position over a single wafer, decreasing near the edge in the one case for which it was measured. The causes of these various non-uniformities are not understood at this time.

Effect of SiO$_2$ thickness

Figures 7–9 present four sets of corrected argon content data for series of films made under common deposition techniques. The data plotted in Fig. 7 are for films deposited at 2.93 W-cm^{-2} rf power, 5 microns argon pressure, 150°C substrate temperature, and with a magnetic field; the thickness was varied by increasing the run time in a series of sputtering runs. Figure 8 represents a single run at 0.78 W-cm^{-2}, 5 microns, 350°C, and with a magnetic field; the thickness variation was achieved by etching the wafer for progressively increasing periods of time. The curves in Fig. 9 were obtained for two modes of deposition

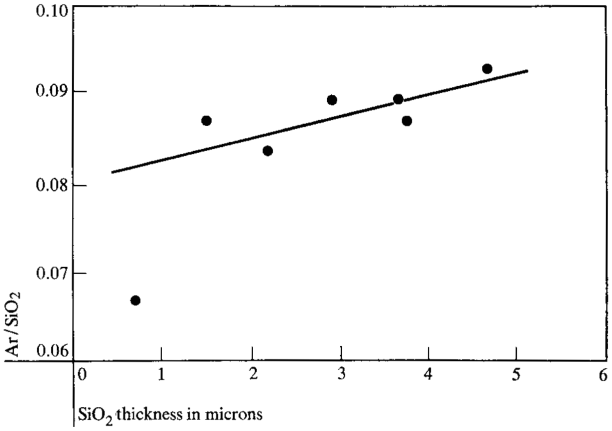

Figure 7 Argon concentration as a function of SiO_2 thickness; with magnets, close (1.125 in.) spacing, 2.93 W-cm^{-2}, 5 microns pressure, 350°C, increasing etch times.

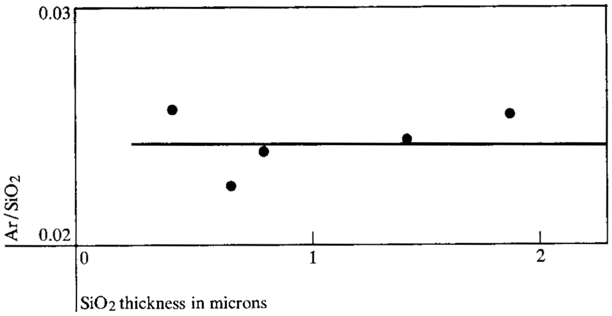

Figure 8 Argon concentration as a function of SiO_2 thickness; with magnets, close (1.125 in.) spacing, 0.78 W-cm^{-2}, 5 microns pressure, 350°C, increasing etch times.

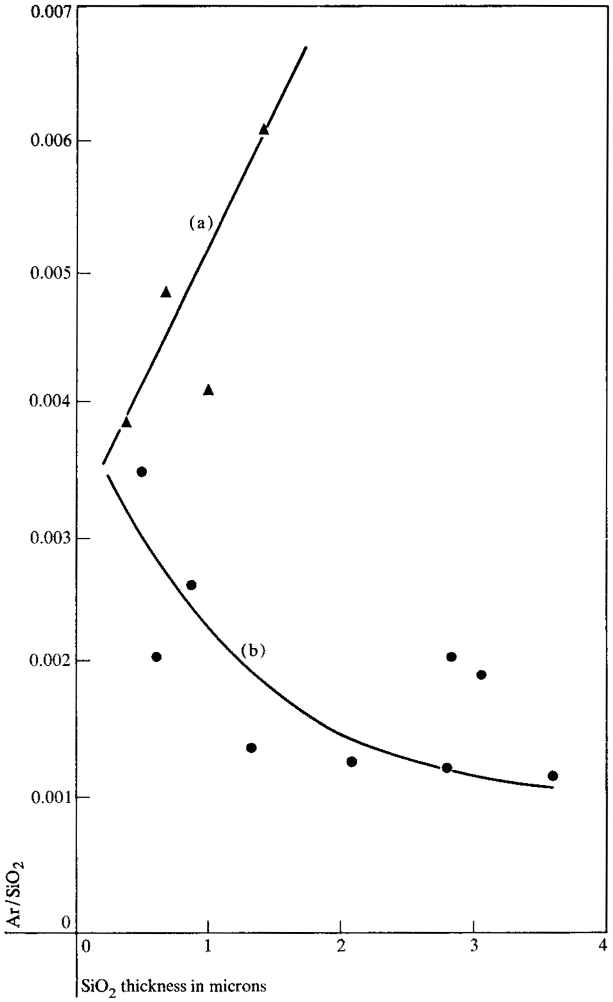

Figure 9 Argon concentration as a function of SiO_2 thickness; without magnets, wide (1.625 in.) spacing; (a) 2.93 W-cm^{-2} 10 microns pressure, 300°C, increasing run times, (b) 2.93 W-cm^{-2}, 40 microns pressure, 150°C, increasing run times.

Table 3 Comparison of SiO_2 properties.

Property	*Thermally grown SiO_2*	*Sputtered SiO_2* A *(2.93 W-cm^{-2} rf power; 10 microns pressure; 300°C; with magnets)*	B *(2.93 W-cm^{-2} rf power; 10 microns pressure; 300°C; with magnets)*	C *(2.93 W-cm^{-2} rf power; 40 microns pressure; 300°C; without magnets)*
Ar/SiO_2	—	0.03	0.009	0.001
P etch rate,[15] Å/min	120 at 25°C	325 at 24°C	280 at 22°C	3800
Density[a]	2.20	2.28	2.16	1.98
Refractive Index (at λ = 5461)	1.461_8	1.47		1.465[b]

[a] C. L. Standley, unpublished work, IBM Components Division, Poughkeepsie, N. Y.

[b] After heating in vacuo at 500°C for 1 hr., the refractive index dropped to 1.447. After several weeks at room temperature and humidity, the refractive index increased to 1.479.

without magnets. The reasons for the inconsistent relationship between SiO_2 thickness and argon concentration are not understood at this time. For some modes of deposition, however, this inconsistency may be the result of different SiO_2 densities or of argon diffusion (see Table 3). Fortunately the thickness correction was small and did not significantly influence the general conclusions regarding argon content.

Argon concentration and film properties

We shall now consider the relationship between the argon concentration in a sputtered SiO_2 film and the properties of that film. There are many properties that characterize an SiO_2 film, among which are etch rate, density, refractive index, and infrared spectra. Thermally grown SiO_2, which is vitreous quartz in its purest thin-film form, is the standard with which other SiO_2 films are compared. It must be remembered that many of the properties are interrelated[16] and that no attempt is being made to discuss this question thoroughly.

In Table 3, several properties of SiO_2 films sputtered in three different modes are compared to thermally grown standard SiO_2. Comparing films B and C to thermally grown SiO_2, we see that a film containing a high concentration of argon (B) can have properties (notably the P-etch rate[15]) closer to thermal oxide than one with a low argon content (C). Film C has the lowest argon content of the three, yet it has the fastest etch rate and the lowest refractive index; electron micrographs of such films show what can be interpreted as a porous structure, which is not seen in films such as A and B. However, this surprising correlation does not always hold; Films A and B have comparable etch rates, even though one (A) has three times the argon content of the other (B). We can only conclude that the effect of argon on the properties of sputtered SiO_2 is small compared to the effect of other processes occurring during deposition, such as thermal annealing and bombardment "annealing".

This conclusion—the negligible effect of argon on SiO_2—is reinforced by examining the dependence of etch rates on the sputtering pressures used (see Fig. 10). When a magnetic field is used (a), the etch rate increases almost imperceptibly for films sputtered at increasing pressures, thereby paralleling the very slight decrease in argon concentration. However, for sputtering without magnets (b), the etch rate increases dramatically for films sputtered at pressures above 20 microns, while the argon concentration decreases very rapidly until it reaches a pressure of about 20 microns, diminishing more gradually thereafter.

For both sputtering modes, decreasing the substrate temperature increases both argon concentration and etch rate. However, decreasing substrate temperature has been shown previously to give films that are somewhat less dense, have more bond straining, and contain more hydrogen-bonded silanol groups.[15] It may indeed be these latter factors, rather than the argon content, that cause the etch rate to increase.

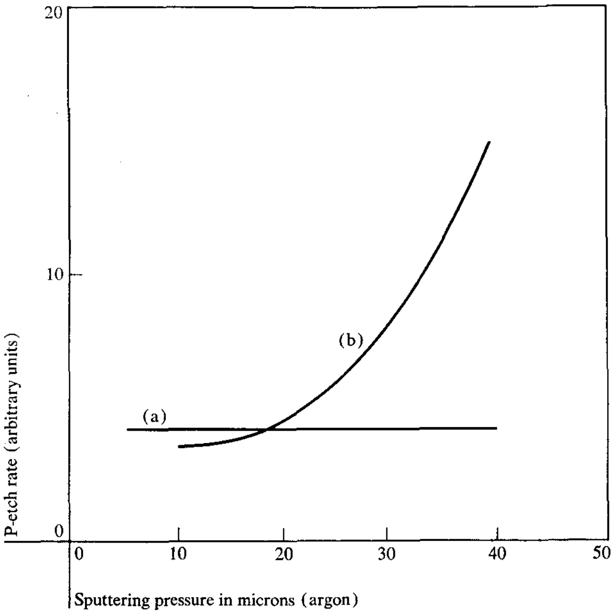

Figure 10 P etch rate as a function of sputtering pressure; (a) with magnets, close (1.125 in.) spacing; (b) without magnets, wide (1.625 in.) spacing.

Summary

SiO_2 films deposited by rf sputtering in argon have been found to contain significant quantities of argon. The argon concentration has been determined by using x-ray fluorescence analysis with a suitable calibration scheme and a correction for the absorption of x-rays by SiO_2.

The argon in the films is a result of the embedding of energetic argon ions and neutrals. During deposition, embedded argon is partially removed from the film surface as a result of bombardment-induced re-emission and thermal release mechanisms; this argon is covered by incident SiO_2 molecules and thus, in effect, removed from sites on the surface.

The argon concentration has been found to be dependent on the operating parameters of the rf discharge, principally the substrate temperature and the presence of a magnetic field during deposition. Without a magnetic field the argon content was generally low and considerably dependent on the rf power and argon pressure used. With a magnetic field, however, the argon content was less dependent on power and pressure. This is believed to be due to the increased negative voltage on the film surface during its growth in the presence of a magnetic field. From the observed dependence on substrate temperature it was deduced that the embedded argon is bound to the film surface by energies ranging from 0 to 1.8 eV.

The presence of argon in the film does not appear to have an adverse effect on the insulating properties of the SiO_2. In fact, films containing large amounts of argon generally have properties more closely approaching those of thermally grown SiO_2 than do films with a low argon content.

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