L. I. Maissel
R. E. Jones
C. L. Standley

Re-emission of Sputtered SiO_2 During Growth and Its Relation to Film Quality

Abstract: An improved technique for measuring re-emission coefficients is described and data on the effect of temperature are presented. These are discussed in the light of a physical model of film growth during sputtering wherein constant re-emission of material throughout deposition occurs. Evidence is then presented that such re-emission is essential if films of high quality are to be obtained. To help assess "quality" in a quantitative fashion use has been made of the PBUT (pin-hole breakup thickness) phenomenon, which is described in some detail. The influence on PBUT of several system parameters such as sputtering pressure and impurity content is discussed and related to the re-emission coefficient.

Introduction

In a previous paper[1] the re-emission coefficients of SiO_2 films deposited through rf sputtering were measured and values as high as 0.85 were reported. It was also noted in passing that material that had been deposited on the underside of the substrate, and thus presumably subjected to little or no re-emission during its growth, was invariably of very poor quality. With the development of new understanding of the causes of re-emission[2,3] there was thus considerable incentive to seek correlations between the re-emission coefficient and film quality. This, in turn, required more quantitative measurements of both quantities.

Measurement of re-emission coefficient

In the earlier work[1] the coefficient was measured by forming a "sandwich" of two silicon wafers separated by a thin spacer about 8 mils thick. Material re-emitted from the lower wafer surface was collected on the under-side of the top wafer and the assumption was made that no material made a second bounce, i.e., that no additional re-emission was occurring from the underside. If this were not true, then the measured re-emission coefficients would be too low. In particular, any re-emission due to temperature alone would not be correctly measured since both surfaces would be equally affected. Accordingly, rather than trying to measure re-emission per se a technique previously developed by Devienne[4] for measuring impingement rates was modified to suit our needs. The principle is similar to that used in building a "black body" and is illustrated in Fig. 1(a). The collector is a hollow can with a small hole of known area at the top. Any material entering the can must do so through this hole and the chance of any material subsequently escaping as a result of re-emission is very small. The impingement rate I can be measured by weighing the can before and after a run. The accumulation (or deposition) rate A is measured by either weighing the protective shield (before and after) or, if the density of the film is known, directly from the thickness. The re-emission coefficient is then given by

$$\rho = (I - A)/I. \tag{1}$$

The disadvantage of the configuration shown in Fig. 1(a) is that the experimental error was fairly large since the absolute amount of material collected was small. Typical figures were 17 micrograms ± 1 micrograms for

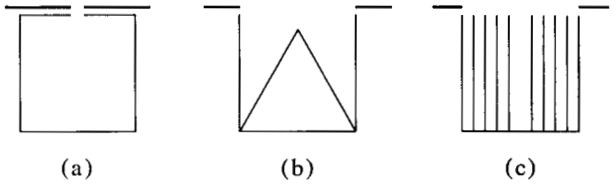


Figure 1 Film collecting devices with zero re-emission.

L. I. Maissel is located at the IBM Components Division Laboratory, E. Fishkill, New York 12533; R. E. Jones, at the IBM Systems Development Division Laboratory, San Jose, California 95114; and C. L. Standley, at the Components Division Laboratory, Poughkeepsie, New York 12601.

an SiO_2 film thickness of 1 micron. Although the electrostatic balance that was used for weighing had the required sensitivity, problems associated with varying amounts of condensed moisture on the can, etc., created numerous difficulties. To overcome this, the designs shown in Figs. 1(b) and 1(c) were developed. In design (b), material re-emitted from the surface of the cone still tended to collect on the cylindrical inner wall, while in design (c) material re-emitted from the flat bottom surface recondensed on one of the cylindrical surfaces. A typical figure for the amount of material collected would be 200 micrograms $\pm$ 5 micrograms. Both designs have been experimentally proven by direct comparison with design (a) and measurements from all three types have always agreed within the experimental error. In practice, design (b) weighed somewhat less but design (c) was easier to construct and tended therefore to be preferred.

Effect of temperature

The dependence of the re-emission coefficient on deposition temperature could now be measured with some confidence and the results (for SiO_2) are shown in Fig. 2.

Provided that the impingement rate I does not depend on temperature, a relationship between the re-emission coefficient ρ and the deposition rate A is readily deduced by differentiating Eq. (1):

$$-\frac{1}{A}\frac{dA}{dT} = \frac{1}{(1-\rho)}\frac{d\rho}{dT}. \tag{2}$$

The data in Fig. 2 show that $d\rho/dT$ is a constant. Hence, as is seen after substituting for ρ from Eq. (1), $(1/I)dA/dT$ is also constant. This is consistent with previously published data on the "temperature coefficient of deposition rate."[5]

The linear increase of the re-emission coefficient with temperature shown in Fig. 2 demonstrates that there is a contribution to the re-emission from the surface that occurs as a result of temperature alone. If it is supposed that molecules are initially bound to the surface with an energy spectrum of the type shown schematically in Fig. 3 (curve A), then at some temperature T_1 only molecules from the higher energy portion of this spectrum (curve B) will remain and become incorporated into the film, the lower-energy, more loosely bound molecules having been thermally re-emitted. At still higher temperature T_2 the curve will shift to progressively higher energies (curve C), as shown.

A quantitative theory for the re-emission coefficient can be developed by considering the mean times required by surface molecules for (1) re-emission or (2) incorporation into the film. According to Frenkel[6] the mean time to thermal re-emission is

$$\tau_r = \tau_0 \exp(E_i/kT), \tag{3}$$

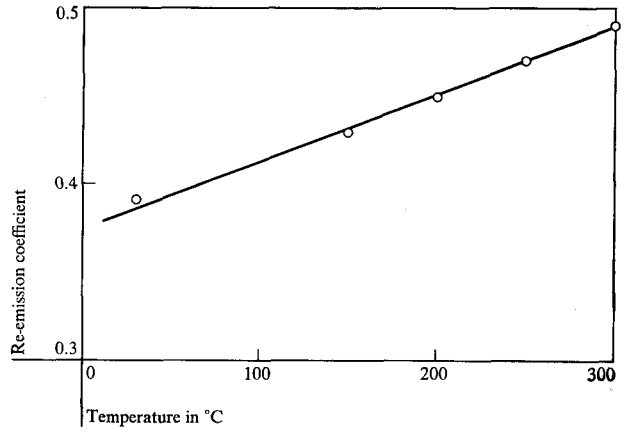


Figure 2 Re-emission coefficient for SiO_2 films as a function of substrate temperature.

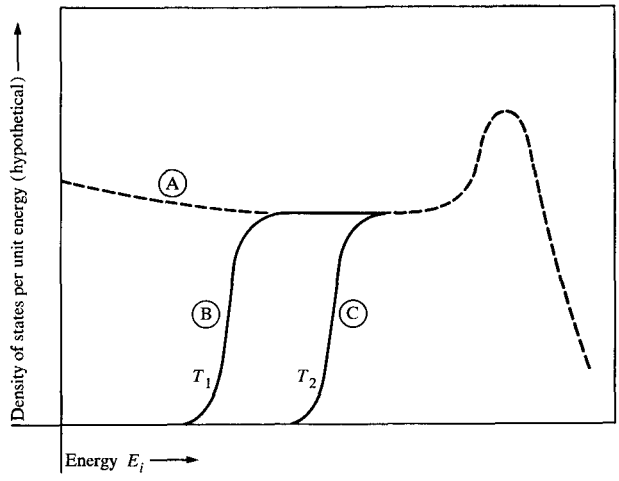


Figure 3 Hypothetical curve showing distribution of binding energies for SiO_2 molecules at the surface of a growing film.

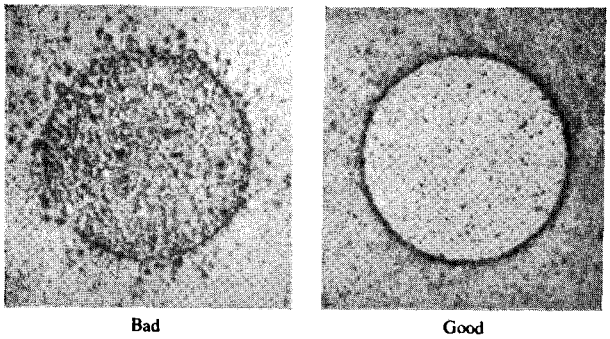
where τ_0 is 10^{-13} seconds and E_i is the binding energy to the surface. In a competing process, molecules become buried in the film during a mean time τ_b which is inversely proportional to the deposition rate:

$$\tau_b = 1/\sigma A, \tag{4}$$

where σ is the effective area of a molecule of the film. By analogy with Eq. (1), the expression for the re-emission coefficient of molecules bound with energy E_i can be written:

$$\rho(E_i) = \tau_r^{-1}/(\tau_r^{-1} + \tau_b^{-1}). \tag{5}$$

Integration of Eq. (5) over a spectrum of binding energies (such as curve A in Fig. 3) will then give the observed re-emission coefficient, ρ.



Bad Good

Figure 4 Holes in SiO_2 films obtained by etching; their appearance is compared for materials of different quality.

Experimental data defining the exact form of Fig. 3 are not available, but it was found that the integration yielded a linear decrease of the re-emission coefficient with temperature (as in Fig. 2) if a flat spectrum was arbitrarily chosen. This is shown schematically in Fig. 3 between curves B and C.

This picture of film growth has important implications regarding the properties of the deposited film since, for a higher re-emission coefficient, less of the loosely bound material will be incorporated into the film and film properties such as etch rate and density will more nearly approach ideal values. We will now discuss some of the experimental data confirming this.

Influence of re-emission on etch behavior (PBUT phenomenon)

Earlier work[5] on the effect of deposition temperature on the quality of SiO_2 films had shown a dependence of the P-etch rate[7] on deposition temperature. However, little or no change in P-etch rate was seen for deposition temperatures in excess of about 250°C, whereas Fig. 2 shows that the re-emission coefficient continues to increase in this temperature range. This, and other observations, suggested that any improvements in SiO_2 film quality associated with a re-emission coefficient greater than about 0.4 would not be detected by a change in P-etch rate.

A more sensitive measure of SiO_2 film quality was provided by the PBUT phenomenon, which will now be described.

When etching holes in SiO_2 films as part of the fabrication of multilayer integrated circuits, it is common practice to use an etchant of known characteristics such as buffered HF* so that (for a known film thickness) etching may be terminated at just the right depth. In the course of such work it was discovered that holes often etched through much faster than would have been expected from etch rate measurements made over larger areas. In addition, microscopic examination revealed that etching had occurred very unevenly, the bottom and sides of the etched hole being covered with a large number of fine etch pits. Examples of holes etched in "normal" as well as "bad" SiO_2 films are shown in Fig. 4. In order to allow for more quantitative comparison between SiO_2 films with respect to this type of behavior, the following approach was taken.

If the substrate is a conductor, pin-holes in thin insulating films can be revealed through the copper decoration technique. In this method, one attempts to copper plate the insulating film, using a dc plating voltage along with some superimposed ac ripple for dispersion of bubbles. In regions where pin-holes exist in the film, copper will plate out in the form of tiny spheres, revealing (very graphically) the location of the defects.

The plating solution used in our experiments consisted of

Cu CN	4.1 gm
Na CN	4.8 gm
Na_2CO_3	3.0 gm
$KNaC_4H_4O_6 \cdot 4H_2O$	6.0 gm
H_2O	100 cm^3

and the plating was performed at an applied voltage of 6 volts with a superimposed 60 cycle ripple of $\pm$ 4 volts. The current was kept below 20 mA and was passed for about 20 seconds. The region on the substrate which was to be decorated was roughly delineated by using black wax and measured approximately 200 by 200 mils. Copper balls at the decorated sites were 2 to 5 mils in diameter.

Attempts to decorate the as-deposited films invariably revealed very few pin-holes, irrespective of any subsequent etching behavior of the films. If, however, a film was repeatedly etched in buffered HF and, after each etch step, an attempt was made to decorate, it was found that the density of decorated sites increased quite suddenly from near zero to a substantial quantity. This sudden increase in decorated-site density occurred between etch steps differing in thickness by only 1,000 Å. The thickness, measured from the inner surface, at which this heavy decoration by copper first begins, is called the pin-hole breakup thickness (hereafter to be referred to as PBUT).

Not unexpectedly, a close correlation was found between PBUT and the quality of etched holes as determined from photographs such as those of Fig. 4. It was also found that the PBUT varied with thickness, showing that it was not a phenomenon associated with only the lower surface of the SiO_2 film. A curve illustrating the variation of PBUT with thickness for a set of films formed under similar deposition conditions is shown in Fig. 5.

A more general figure of merit for SiO_2 film quality is thus the ratio of the PBUT to the total film thickness,

* 300 gm NH_4F, 60 cm^3 conc. HF, 450 cm^3 H_2O

a quantity which we will call the "PBUT ratio" (0.6 in Fig. 5). Note that a smaller PBUT ratio indicates better film quality.

Variation of PBUT ratio with deposition conditions

It had already been reported[1] that the re-emission coefficient varied over a wide range as a function of sputtering pressure. It was therefore not surprising that a strong dependence of PBUT ratio on pressure was also found, as shown in Table 1.

PBUT ratios of less than about 0.1 were found to be difficult to measure because the presence of pin-holes, surface defects, etc., tended to mask the sharp change in pin-hole density needed to define a PBUT value. In fact, in general, higher values of the PBUT ratio were always measured for films deposited onto anything but the cleanest and smoothest of substrates (the latter being, in our case, vapor etched silicon wafers). For films deposited at pressures in excess of about 30 millitorr the PBUT ratio approached unity and was again difficult to measure with any degree of precision as the film was so porous that the occurrence of PBUT was obscured.

In the early stages of this work it was thought that the PBUT phenomenon might be associated with the presence of some impurity gas in the sputtering ambient. The effect of various additives was therefore studied. These included hydrogen, helium, oxygen, nitrogen, carbon dioxide, and carbon monoxide.

The most noticeable effect of some of these gases was to bring about a marked reduction in the deposition rate of the SiO_2 films. The influence of hydrogen on the deposition rate of sputtered films has already been reported by Stern and Caswell[8] and is a consequence of the fact that hydrogen (because of its high mobility) carries more than its proportionate share of the discharge current but, because of its low mass, produces little or no sputtering. The same explanation holds for helium. The influence of oxygen on the deposition rate of SiO_2 films has also been previously reported[9] and is associated with the replacement out of the gas of oxygen atoms on the target surface removed through sputtering. The influence of CO_2 is believed to come from oxygen generated as a result of partial cracking. CO and N_2 had very little influence on deposition rate.

The addition of certain gases had a pronounced effect on the PBUT ratio. For H_2, O_2 and He, it improved quite significantly while nitrogen and CO did not appear to influence it. Typical data, for a 1% concentration of added impurity, are summarized below in Table 2.

CO_2 was unique among the gases studied, in that it increased the PBUT ratio. Even this, however, was only over a narrow concentration range, as illustrated in Fig. 6. It is suspected that the reduced values seen for the higher CO_2 concentrations are a result of partial cracking into

Table 1 Dependence of PBUT ratio on sputtering pressure.

*Pressure in millitorr**	*PBUT ratio*	*Re-emission coeffiicient†*
5	0.13	0.55
15	0.38	0.44
20	0.72	0.40

* Substrate temperature 250°C.
† Measured under similar deposition conditions as PBUT ratio but in different runs.

Figure 5 Variation of the pin-hole breakup thickness with initial thickness.

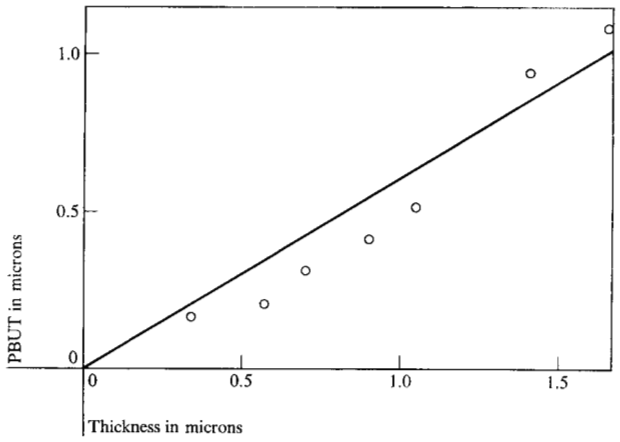
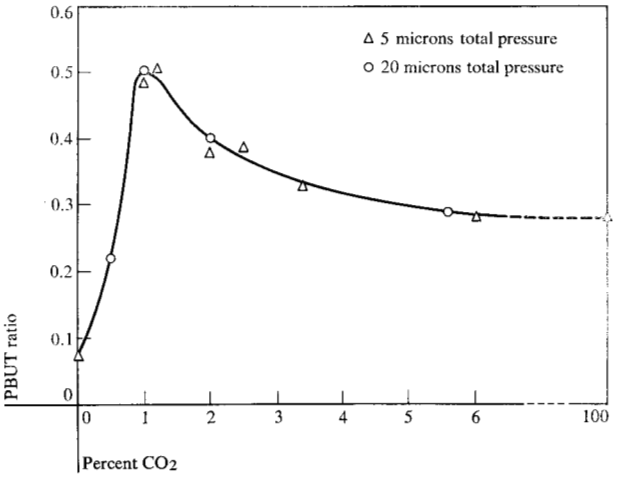


Figure 6 PBUT ratio of SiO_2 films as a function of carbon dioxide concentration in the sputtering ambient.



CO and O. The former does not influence the PBUT ratio, whereas the latter more than overcomes the effect of the uncracked fraction of CO_2. Limited solubility of CO_2 in SiO_2 could not be invoked as an explanation as it was demonstrated[10] that the amount of CO_2 trapped in the films increased with increasing CO_2 concentration in the sputtering ambient.

Unfortunately, systematic measurements of the direct influence of these impurities on the re-emission coefficient have not yet been made. However, the marked decrease in PBUT ratio associated with the presence of either hydrogen or helium is understandable in the light of some results published by Sinha.[11]

Using tungsten as his target material, Sinha showed that, *at low bombarding energies*, the order of the relative sputtering yields for the inert gases as a function of mass is reversed. Thus, at energies above 180 volts the yields go in the order Xe > Kr > Ar > Ne whereas below 80 volts this is reversed. He explains this as a consequence of the amount of gas trapped in the target surface. This amount is larger for the lighter gases. For example, at 80 volts the saturation density for imbedded neon is 1500 times greater than for argon. This ratio is even greater at lower ion energies. Sinha speculates that trapped gas at the surface causes an increase in sputtering yield by straining the bonds between surface atoms in such a way as to reduce the energy required to eject them.

Thus, at relatively low substrate potentials (in our case typically less than 60 volts for re-emission coefficients less than 0.5), hydrogen or helium would actually give sputtering yields greater than that of argon. Relatively small amounts would then be quite effective since, as already noted, their high mobility causes them to carry more than their proportionate share of the current. Furthermore, the presence of small amounts of these gases in the surface would, presumably, greatly increase the sputtering efficiency of the argon atoms as well.

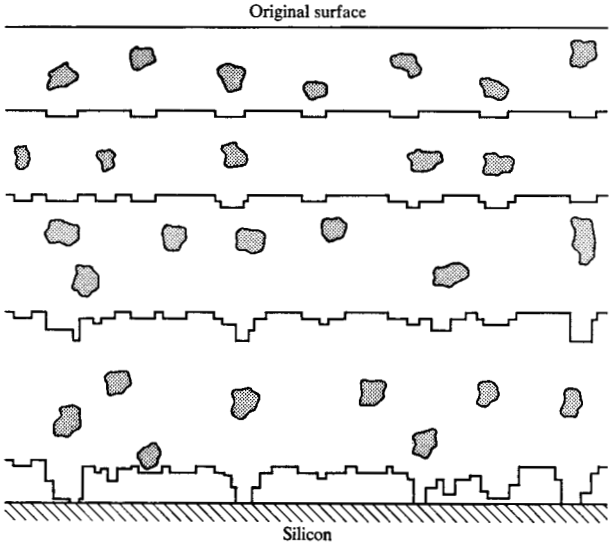
The relatively small decrease in the PBUT ratio associated with the presence of oxygen probably results from the decrease in deposition rate that is obtained while power and pressure remain the same. In view of the latter, the amount of resputtering does not change when oxygen is added to the system but the sharp decrease in deposition rate causes an increase in the ratio of resputtered to impinging atoms. The effects of nitrogen and carbon monoxide are not considered significant within experimental error, while the effect of CO_2 is not understood at this time.

Table 2 Influence of added gases on the PBUT ratio.

*Added gas**	*Deposition rate in Å per min.*	*PBUT ratio*
none	260	0.41
nitrogen	250	0.38
carbon monoxide	280	0.38
oxygen	150	0.28
helium	218	0.22
hydrogen	230	0.18
carbon dioxide	160	0.50

* Impurity concentration 1%.

Figure 7 Model for the PBUT phenomenon showing how PBUT would be proportional to initial thickness.



Physical model for the PBUT phenomenon

Since the presence of a significant PBUT ratio implies that the film has etched much faster in some regions than in others, it might be assumed that pipe-like regions of the film (extending from surface to surface) have a higher etch rate than "regular" SiO_2, the PBUT ratio being therefore a measure of the relative etch rates of the two types of region. An alternative explanation would be that relatively large regions of extremely high etch rate material are uniformly dispersed throughout the film. Pin-holes would then appear in an advancing etch front wherever these regions happen to line up, as illustrated in Fig. 7, where successive etch fronts are shown for a single film. We have tended to prefer the latter model but can offer no real support for this except, perhaps, for the electrical properties discussed in the next section.

In a number of experiments, deposition conditions were changed in the middle of a run so that both a "good" and a "bad" layer of SiO_2 were deposited. The same PBUT value was measured irrespective of the relative positions of the "good" and "bad" layers. This indicated that nucleation effects do not play a significant role in determining PBUT ratio.

Table 3 Dielectric strength of SiO_2 films deposited through rf sputtering, as a function of quality.

Qualitative description	*Re-emission coefficient*	*PBUT ratio*	*Initial yield in percent*	*Recovery yield in percent*	*Dielectric strength* Median 10^6 V/cm	*Dielectric strength* Spread 10^6 V/cm
very good	0.6	0.1	95-100	95-100	5	1-20
fair	0.5	0.3	75	95	2	0.8-20
poor	0.35	0.8	20	40	1	0.7-20
very poor	0.3	≈1	0	20	0.8	0.3-20

Correlation between PBUT ratio and electrical properties

The electrical properties of sputtered SiO_2 films of varying PBUT ratio were examined. No clear systematic dependence of either dielectric constant or loss tangent on PBUT ratio was seen. The dielectric strength, however, did correlate with PBUT ratio in a rather interesting manner:

Films to be tested were deposited directly onto silicon wafers whose surfaces had been vapor polished. SiO_2 film thicknesses were in the range 2500 to 4000 Å. Aluminum dot electrodes about 1 micron thick and 60 mils in diameter were then deposited through a mask to give approximately 110 dots per wafer.

When a field of about 3×10^5 V/cm was applied between a given dot and the underlying silicon, the leakage current measured was either insignificant (less than 10^{-8} amp) or so large as to constitute a short. In this manner an "initial yield" of good capacitors could be measured. The applied voltage across the good units was then increased until breakdown occurred. In other experiments, the applied test voltage was increased very gradually from zero. This allowed self-healing of the capacitors to occur since the breakdown of individual weak spots under a given dot electrode caused local removal (by melting or vaporization) of the portion of the metal electrode immediately above them. After the applied field had been raised above about 10^5 V/cm, very little further change took place and a "recovery yield" of capacitors (also at 3×10^5 V/cm) could be measured. These results are shown in Table 3.

The most interesting feature of these results is that all films, irrespective of quality, contained a few areas that were able to withstand the maximum field of 2×10^7 V/cm. This, and the fact that the median dielectric strength increased with decreasing PBUT ratio, would appear to support a physical model for sputtered SiO_2 of the type shown in Fig. 7, the dielectric strength of the shaded regions being very low.

Conclusions

Both theoretical and experimental considerations show that re-emission of sputtered material during growth (at least for SiO_2) is essential for obtaining films of good quality. This is believed to be a consequence of the fact that many molecules that would otherwise be trapped in non-optimum positions are returned to the vapor phase (and probably to the target) leaving behind material of higher quality. A good index of the latter is the PBUT ratio, whose value should be less than about 0.15. At deposition temperatures of around 250°C this is achieved by using a re-emission coefficient greater than about 0.55.

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