

# On Liquid-Phase Deposition of Silicon Dioxide by Boric Acid Addition

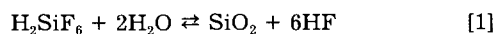
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## ABSTRACT

The current status of liquid-phase deposition (LPD) of SiO<sub>2</sub> by adding boric acid (H<sub>3</sub>BO<sub>3</sub>) to a hydrofluosilicic acid (H<sub>2</sub>SiF<sub>6</sub>) is reviewed and compared with some new results from the authors' laboratory. Large discrepancies exist in the literature concerning the effects of various processing parameters on deposition rate. We have shown that much confusion arises from the misconception of using on SiO<sub>2</sub> additive to "saturate" and using water to "dilute" the growth solution. In this paper the role of H<sub>2</sub>O as a reagent and the detrimental effect of an SiO<sub>2</sub> additive as seeds for depleting the nutrient in the growth solution if added after the H<sub>2</sub>O addition are emphasized. Despite the variations between different investigators, the following characteristics of the LPD process are in general agreement: (i) the deposition process is surface controlled, (ii) the deposition rate depends approximately linearly on temperature, (iii) the deposition rate is constant (independent of time) over a wide range of experimental conditions, and (iv) the deposition rate increases with increasing boric acid concentration.

The recently developed liquid-phase deposition (LPD) process allows the selective growth of thin SiO<sub>2</sub> films on suitable substrates at very low temperatures (20 to 50°C).<sup>1-21</sup> The growth is typically conducted in a supersaturated hydrofluosilicic acid (H<sub>2</sub>SiF<sub>6</sub>) solution. A simplified model due to Nagayama *et al.*<sup>1</sup> shows that the deposition is the result of the reaction between H<sub>2</sub>SiF<sub>6</sub> and water



According to this reaction, more SiO<sub>2</sub> may be formed if the concentration of H<sub>2</sub>SiF<sub>6</sub> or H<sub>2</sub>O is increased, or the concentration of HF is reduced. Experimentally, three different techniques have been successfully developed based on the above reaction to bring about the SiO<sub>2</sub> deposition from an H<sub>2</sub>SiF<sub>6</sub> solution simply by adding either boric acid (H<sub>3</sub>BO<sub>3</sub>)<sup>1-15</sup> or Al<sup>18-21</sup>, or water<sup>14-17</sup> to the growth solution. In the first two cases, boric acid or aluminum reacts with HF to form BF<sub>4</sub><sup>-</sup><sup>22</sup> or AlF<sub>3</sub>,<sup>23</sup> respectively. These reactions consume hydrofluoric acid in the growth solution thus promoting reaction 1 to the right according to Le Chatelier's principle so that more SiO<sub>2</sub> is formed. The addition of water to the growth solution also drives reaction 1 to the right thus favoring the SiO<sub>2</sub> deposition.

By far, the addition of boric acid to the H<sub>2</sub>SiF<sub>6</sub> solution is the most popular technique in LPD-SiO<sub>2</sub> deposition. However, in an attempt to compare the results obtained by different groups of the SiO<sub>2</sub> deposition rate as a function of boric acid addition, a very large variation is noted as revealed in Fig. 1. The disagreement is so large that under certain conditions it exceeds two orders of magnitude (for instance in Fig. 1 at the boric acid concentration of 2 × 10<sup>-2</sup> mol/liter the deposition rate varies from 0. to 260 nm). In one case (the Homma results, the (▲) curve in Fig. 1] the addition of boric acid below 2.5 × 10<sup>-2</sup> mol/liter even resulted in the etching (negative deposition rate) instead of deposition of SiO<sub>2</sub>. Table I summarizes the relevant experimental conditions used by each investigator whose data are included in Fig. 1. It shows that significant variation exists in the details of LPD processing employed by different groups. In this paper the current status of the LPD

process is reviewed, some of the most recent results from the authors' laboratory are presented to clarify some of the confusing issues and to explain the large discrepancy revealed in Fig. 1. The emphasis of the paper is on the technique of growing SiO<sub>2</sub> by the addition of boric acid to H<sub>2</sub>SiF<sub>6</sub> solution, but most of the discussions are equally applicable to other techniques of the LPD process. The organization of the following discussion is such that the important LPD processing parameters are reviewed sequentially and individually with special reference to Fig. 1 and Table I.

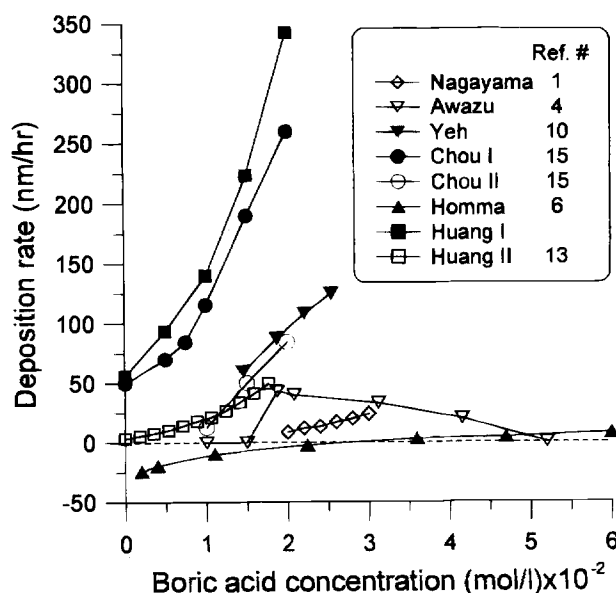


Fig. 1. The effect of boric acid concentration on the deposition rate of SiO<sub>2</sub> as reported by various investigators.

Table I. Experimental conditions employed by various investigators.

1	2	3	4	5	6	7	8	9	10	11	12	13
Investigator	Starting $H_2SiF_6$ conc. (M)	$SiO_2$ additive	Stirring time (h)	Temp. for dissolving $SiO_2$ additive (°C)	$H_2SiF_6$ Conc. in growth solution (M)	Growth solution preparation route	Stock boric acid conc. (M)	$H_3BO_3$ conc. in growth solution (M)	Substrate	Deposition temperature (°C)	Deposition rate (nm/h)	Ref. No.
Nagayama Homma	2.0 3.5	Silica gel Silica	16 —	35 35	— —	II II	— 0.1	0.02 ~ 0.03 0 ~ 0.2	Glass Si with CVD $SiO_2$	35 35	8.4 ~ 23.8 -24 ~ 20	1 6
Awazu	2.5	Silica gel	—	35	—	II	0.518	0.02 ~ 0.052	(100) bare Si	35	0 ~ 43	4
Yeh Chou	4.0 3.09	Silica Silicic acid	17 3	23 30	3.8 2.0	II I	0.1 0.1	0.0146 ~ 0.0255 0 ~ 0.02	Si with $SiO_2$ Si with native oxide	35 50	60 ~ 125 50 ~ 260	10 15
Huang I	3.09	Silicic acid	6	25	2.0	I	0.1	0 ~ 0.02	Si with native oxide	50	56 ~ 343	13
Huang II	3.09	Silicic acid	6	25	2.54	I	0.1	0 ~ 0.0178	Si with native oxide	40	4 ~ 50	13
Huang III	3.09	Silicic acid	6	25	2.0	I	0.1	0 ~ 0.02	Si with native oxide	40	31 ~ 190	13
Huang IV	3.09	Silicic acid	6	25	1.5	I	0.1	0 ~ 0.015	Si with native oxide	40	43 ~ 175	13

### The Starting $H_2SiF_6$ Solution

Except for Awazu *et al.*,<sup>4</sup> who prepared his own  $H_2SiF_6$  solution by dissolving silica gel in an HF solution, other investigators used commercial grade  $H_2SiF_6$  solutions. As shown in column 2 of Table I, the concentration of  $H_2SiF_6$  in the starting solution varies from 2 to 4 M. An  $SiO_2$  additive was used by every group to react with the free HF in the starting solution in order to “saturate” the solution. The choice of the additive may be either silica gel or silicic acid (column 3), the stirring time for the dissolution of  $SiO_2$  additives varies from 3 to 17 h (column 4), and the dissolution temperature differs from 23 to 35°C (column 5). Generally silicic acid dissolves much faster than silica gel. The difference in the dissolution rate compounded with the variation in dissolution temperature and in stirring time could lead to significant variation in the actual concentration of  $H_2SiF_6$  even if the same concentration is reported, thus rendering scattered results on the reported deposition rate even under the same growth conditions. Kawahara *et al.*<sup>16</sup> has shown that a very low low dissolution temperature (-3°C) coupled with a high growth temperature (60°C) may be utilized to effect a very high growth rate. This result is consistent with the fact that the dissolution of  $SiO_2$  in HF is an exothermic reaction<sup>24</sup> so that the dissolution of  $SiO_2$  additives is enhanced at a lower temperature. A large supersaturation is induced when the solution saturated at a lower temperature is brought up to 60°C for growth, therefore a high growth rate results.

The erratic behavior of Awazu's data in comparison with others in Fig. 1 casts serious doubt on the reported  $H_2SiF_6$  concentration of his self-made solution. Since this set of data is so different from others, it is considered rather unreliable and will be excluded from further discussion.

### The Growth Solution

The growth solution for LPD- $SiO_2$  deposition is usually prepared from the starting solution by further modifying its chemical content. One of the most important parameters concerning the growth solution is its  $H_2SiF_6$  concentration. Experimentally two different routes may be chosen depending on the sequence of adding an  $SiO_2$  additive and water. Some investigators added the  $SiO_2$  additive prior to diluting with water (route I) while others “diluted” their  $H_2SiF_6$  solution with water prior to the addition of an  $SiO_2$  additive (route II). The reported molar concentration of  $H_2SiF_6$  in the growth solution is generally calculated from the volume change due to the water addition, and in so doing the calculated  $H_2SiF_6$  concentration is always the same irrespective of the sequence of  $SiO_2$  and water addition. Interestingly, the deposition rate has been found to vary dramatically with the sequence of additions and in a controlled experiment Chou and Lee<sup>15</sup> have shown that the deposition rate for growth solutions prepared by route I (Chou I in Fig. 1) is much greater than those prepared by route II (Chou II in Fig. 1). A model was proposed by Chou *et al.*<sup>15</sup> for explaining the variation of deposition rate in terms of the difference in the amount of intermediate species formed by the two different routes. However, it is also possible to interpret the results in a different way as follows: it should be emphasized that according to reaction 1 water is a reagent and not simply a solvent, and when added to the starting solution it is expected to react with  $H_2SiF_6$  to form  $SiO_2$  and HF. In this context it is very misleading to call the addition of water to  $H_2SiF_6$  solution “dilution” as in diluting salty water with  $H_2O$ . It casts doubt on the conventional way of calculating the  $H_2SiF_6$  concentration by the volume change due to water addition because the reaction between the two species,  $H_2SiF_6$  and  $H_2O$ , is totally ignored. Although reaction 1 indicates that adding  $H_2O$  to  $H_2SiF_6$  would cause  $SiO_2$  to form, usually this does not happen spontaneously unless a proper substrate (typically one with  $SiO_2$  surface) is immersed in the solution and then the deposition occurs on the  $SiO_2$  surface only. It appears therefore that the  $SiO_2$  surface lowers

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the activation barrier for SiO<sub>2</sub> precipitation from an LPD growth solution. Now consider route II as described earlier, when H<sub>2</sub>O is added first to the H<sub>2</sub>SiF<sub>6</sub> solution, a reaction between the two species is about to occur, but without a proper substrate the solution is maintained at a metastable state without deposition. The subsequently added SiO<sub>2</sub> additives actually serve as the needed substrates that provide an enormously large SiO<sub>2</sub> surface for SiO<sub>2</sub> to deposit from the solution. In this regard the growth solution is in reality being depleted of SiO<sub>2</sub> instead of being saturated as previously mistakenly suggested by most investigators. On the other hand, when route I is followed, the first SiO<sub>2</sub> additive would react with any free HF in the starting solution to bring the H<sub>2</sub>SiF<sub>6</sub> concentration to its saturation level. The H<sub>2</sub>O added subsequently tends to react with H<sub>2</sub>SiF<sub>6</sub>, but without a proper substrate the solution is in a metastable condition with its ability to deposit SiO<sub>2</sub> completely preserved. Later in the actual growth run a much higher deposition rate is observed with solutions prepared by route I than route II. It is worth noting that in Fig. 1 the Nagayama *et al.* and Homma *et al.* solutions were prepared by route II and their observed deposition rates are much lower than the others', as expected from the forgoing argument. It is also highly probable that the solution in Homma's study was so depleted with the SiO<sub>2</sub> nutrient such that etching of the substrate resulted.

The concentration of H<sub>2</sub>SiF<sub>6</sub> in the growth solution is bound to affect the deposition rate. According to reaction 1 a larger deposition rate is expected of a solution with a higher starting H<sub>2</sub>SiF<sub>6</sub> concentration if other parameters remain constant, but the exact dependence is yet to be established.

### The Boric Acid Addition

Despite the large variation in the deposition rate observed by various groups, all the curves in Fig. 1 (except Awazu *et al.*) show a positive dependence of deposition rate on boric acid concentration, although the magnitude of the dependence differs significantly due to the variation in other experimental parameters. The data of Chou I [(●) curve] and Huang I [(■) curve] in Fig. 1 show the largest dependence on boric acid concentration. These two studies have at least several experimental parameters common to the other studies, except for the deposition temperature of 50°C which is not only unique to them but also higher than the temperature employed by others. It is therefore likely that dependence of the deposition rate on boric acid concentration is enhanced by increasing temperature. It is worth noting that the only difference in the experimental conditions between Chou I and Huang I is in the temperature for dissolving an SiO<sub>2</sub> additive (column 5 of Table I), the former used 30°C while the latter used 25°C. As discussed earlier since a lower dissolution temperature gives rise to higher H<sub>2</sub>SiF<sub>6</sub> concentration in the saturation solution, it is therefore not too surprising to see that these two sets of data agree reasonably well and that Huang I shows a slightly higher deposition rate than Chou I. The high deposition rate observed for these two cases can be attributed to two factors: high deposition temperature and preparing the growth solution by route 1.

Two issues are of primary concern considering the addition of boric acid, namely, its quantity and concentration when added to the growth solution. Commercial boric acid is generally in powder form, for LPD application it is always used in the form of an aqueous solution. Column 8 of Table I lists the stock boric acid concentration used by each investigator. As can be seen, most investigators used 0.1 M boric acid stock solution; a notable exception is Awazu *et al.*<sup>4</sup> who used a 0.518 M solution. The actual boric acid concentration in the growth solution is, however, different from the concentration of the stock solution because it must be corrected for the volume of the H<sub>2</sub>SiF<sub>6</sub> solution into which the boric acid solution is added. The corrected boric acid concentrations for each investigator are listed in column 9 of Table I. Reciprocally, the H<sub>2</sub>SiF<sub>6</sub>

concentration in the growth solution is also affected by the boric acid addition because the total volume is changed. This point, which has been overlooked before by almost every group, causes a large uncertainty in the reported H<sub>2</sub>SiF<sub>6</sub> concentrations especially when using stock boric acid solutions of different concentrations. Under such circumstances the water content in the added boric acid solution is varied such that the actual H<sub>2</sub>SiF<sub>6</sub> concentration varies accordingly.

Another important observation is that SiO<sub>2</sub> deposition does not happen spontaneously after the addition of boric acid if its concentration is below a certain level; a proper substrate is required for activating the deposition process. This phenomenon is quite similar to the effect of water addition described earlier. On the other hand, it is also observed that spontaneous SiO<sub>2</sub> deposition in the form of feathery powders suspended in the growth solution could occur with no need of a substrate if a larger amount of boric acid is added to the H<sub>2</sub>SiF<sub>6</sub> solution. At the present time the cutoff boric acid concentration where spontaneous deposition sets in is yet to be determined, but our experience shows that it is greater than 0.02 mol/liter in the solution used in our earlier study.<sup>13</sup> Nevertheless once a proper substrate is introduced, a growth solution with boric acid addition always has a higher deposition rate than without the boric acid addition.<sup>15</sup>

Other minor issues such as the mixing time after boric acid addition and the way of adding boric acid (batch or continuous) are also at variance among different groups. In our view, however, these points are only of secondary importance.

### Growth Temperature

The deposition rate of LPD-SiO<sub>2</sub> is affected by the temperature, and Fig. 2 compares the literature data with some of our unpublished results. The comparison between different curves in this figure is not straightforward because other experimental conditions were not kept constant, but even so the trend in Fig. 2 demonstrates clearly that for each and every curve the deposition rate is increased with increasing temperature. The difference among the curves is evidently due to other parameters such as the concentrations of hydrofluosilicic acid and boric acid, substrates, etc. The divergence of the curves in Fig. 2 decreases rapidly as the temperature is decreased indicating that the effects of other processing factors become less significant at lower temperatures. Figure 2 also shows that the temperature dependence of the deposition rate is fairly linear between 30 to 50°C. A higher growth temperature is advantageous for faster SiO<sub>2</sub> deposition but the increased variability in deposition rate is a concern from the process point of view. Another drawback of higher temperature growth is the significant loss of growth solution due to evaporation which is usually insignificant below 30°C but becomes evident at 50°C. It is not clear exactly what is being evaporated as yet, but the fact that the condensation of the evaporating vapor on the top of the reactor always results in the formation of powdery SiO<sub>2</sub> implying a rather complex vapor chemistry. The evaporation loss certainly changes the concentration of the growth solution thus affecting the deposition rate. For this reason the higher temperature data in Fig. 1 and 2 should be viewed with some caution. Nonetheless, the large variation observed in Fig. 1 cannot be totally ascribed to the temperature effect because, by comparing Yeh *et al.* and Homma *et al.* data in Fig. 1, one may see that even at the same temperature (35°C) the deposition rate still varies by about two orders of magnitude, which is much greater than that would be expected from the temperature effect depicted in Fig. 2.

### Substrate

LPD is highly selective; SiO<sub>2</sub> deposition occurs on the surface of thermal SiO<sub>2</sub>, chemically vapor deposited (CVD) SiO<sub>2</sub>, native oxide on silicon, or polysilicon, but not on the surface of photoresist and sputtered tungsten.<sup>7,10</sup> The



results on bare silicon are somewhat controversial, Chou<sup>15</sup> reported a small amount of growth but the overwhelming majority of published results reported no deposition.<sup>7</sup> The deposition of LPD-SiO<sub>2</sub> on plastic is also possible if the substrate surface is pretreated by a silane coupling agent with an amino functional group such as  $\gamma$ -aminopropyltriethoxysilane.<sup>19</sup> The growth rate is not affected by the physical arrangement of the substrate in the growth solution, it may be either faceup, facedown, or face sideways. As pointed out earlier that a proper substrate is absolutely essential to the growth of LPD-SiO<sub>2</sub>, so a surface-controlled growth mechanism is implied. Two models have recently been proposed for explaining the selective deposition of LPD.<sup>7,17</sup> The common features of these models are the necessity of Si-OH bonds on the substrate surface and the formation of intermediate species in the growth solution; the deposition of LPD-SiO<sub>2</sub> is brought about by the reaction of the intermediate species with Si-OH bonds on the substrate surface. Two different intermediate species, SiF<sub>m</sub>(OH)<sub>4-m</sub> ( $m < 4$ )<sup>7</sup> and [SiF<sub>6</sub> · SiF<sub>4</sub>]<sup>2-</sup>,<sup>17</sup> have been suggested but confirmation of this is yet to come. We have performed the following simple experiment to confirm the surface-controlled characteristics of LPD process: LPD-SiO<sub>2</sub> deposition was conducted at 40°C on oxidized Si substrates with the dimension of 4.5 × 1.7 cm (sample A) and 4.5 × 3.4 cm (sample B) in a 1 M H<sub>2</sub>SiF<sub>6</sub> solution diluted from a 3.09 M H<sub>2</sub>SiF<sub>6</sub> solution by water addition. Separate batch but equal volume (92.7 cm<sup>3</sup>) of growth solutions were employed for the two samples and the growth rate was found to be 41.1 and 42.7 nm/h, respectively, for sample A and B. Using a third sample (sample C) of the same size as sample A to grow SiO<sub>2</sub> under the same condition but with a solution of twice the volume (185.4 cm<sup>3</sup>), the

growth rate was found to be 43.7 nm/h. The difference in the growth rate among these three samples is within 5% and thus is considered insignificant experimentally, so these results indicate that the deposition rate is practically independent of the volume of the growth solution and of the surface area of the substrate. It is reasonable to expect that the absolute quantity of SiO<sub>2</sub> available for growth in a growth solution is doubled when the solution volume is doubled. If the growth were due to a volume-controlled mechanism, the growth rate of sample C would have been twice that of sample A because of the doubling in solution volume. On the other hand, if the growth of LPD-SiO<sub>2</sub> requires Si-OH bonds on the substrate surface then a constant growth rate is expected irrespective of the volume of the growth solution, as indeed observed experimentally. Additionally, it may be pointed out in comparing samples A and B, the SiO<sub>2</sub> content available for deposition in the growth solution is the same because growth solutions of equal volume were used, the fact that sample B though having twice the surface area but showing the same growth rate as sample A indicates that twice the amount of SiO<sub>2</sub> is deposited on sample B than sample A. This is only possible if the deposition process is dictated by the surface of the substrate; the number of Si-OH bonds per unit area is constant independent of the substrate surface area, so a growth rate expressed in terms of the increase in thickness per unit time is expected to be constant if the growth is surface controlled.

### Reactor Design

The primary concern of the reactor design for LPD-SiO<sub>2</sub> deposition is the ease of handling. The reactor must also be able to withstand the attack of HF acid under moderate temperature. Evaporation loss is an important issue in designing a new reactor and the key point is to keep the exposed surface of the growth solution to a minimum. Part of the scattering shown in Fig. 1 may come from the variation in evaporation loss due to the difference in reactor design. Mechanical or magnetic stirring devices are often used in LPD reactors to improve mixing thus enhancing the uniformity of deposition. Some investigators<sup>9,12,20</sup> circulated the growth solution through a filtering device in order to remove any SiO<sub>2</sub> precipitates suspended in the solution. Our experience shows that the suspended SiO<sub>2</sub> precipitates form spontaneously only when the boric acid concentration is higher than a certain level (about 20 × 10<sup>-2</sup> mol/liter for the present study, depending on temperature and H<sub>2</sub>SiF<sub>6</sub> concentration),<sup>13</sup> below which the growth solution always remains clear indefinitely. The filtering out of the SiO<sub>2</sub> precipitates inevitably causes a shift in the equilibrium of the chemical species in reaction 1 resulting in significant change in the subsequent deposition kinetics relative to an unfiltered growth solution. In view of the foregoing discussions, the results in Fig. 1 corresponding to the higher boric acid concentration should be viewed and compared with greater caution. It is recommended that the boric acid addition should be kept below 2.0 × 10<sup>-2</sup> mol/liter for future fundamental studies of the LPD kinetics in order to avoid the SiO<sub>2</sub> precipitation in the growth solution.

### Growth Rate

The reported growth rate is typically calculated by dividing measured film thickness by the growth time, so it represents a global average growth rate instead of the (instantaneous) true growth rate. However, it is found experimentally that in most cases the grown SiO<sub>2</sub> film thickness varies linearly with deposition time, as clearly demonstrated in Fig. 3. Because of the variations in other processing parameters, the data in Fig. 3 show very large scattering, but the linear dependence is generally followed. A small negative deviation from a linear dependence is observed in one case [(♦) data in Fig. 3]; this deviation is not unexpected because, in principle, the growth rate can never be sustained at the same rate as the deposition is prolonged and the nutrient in the growth solution is

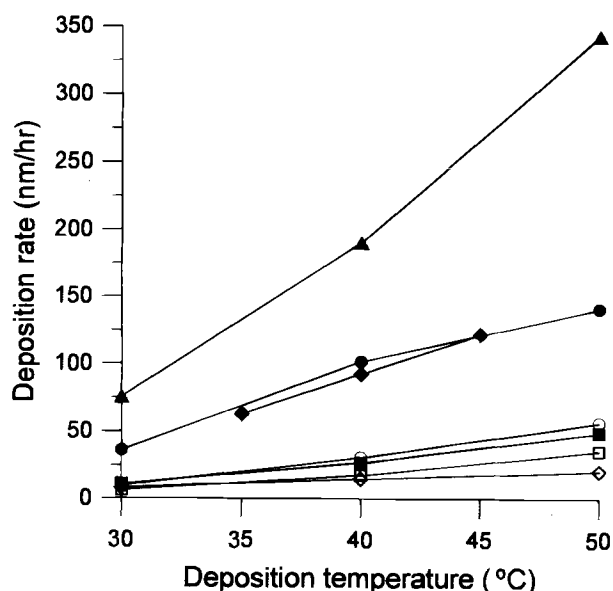
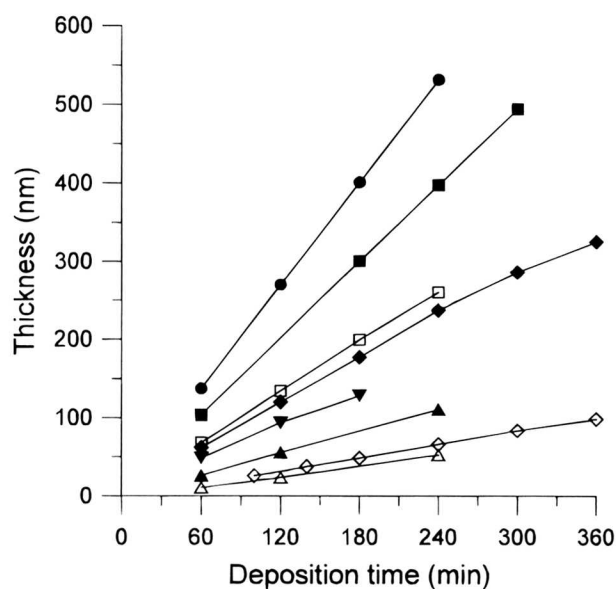


Fig. 2. The effect of growth temperature on the deposition rate of SiO<sub>2</sub> as reported by various investigators.

Author	[H <sub>3</sub> BO <sub>3</sub> ] (mol/l)	[H <sub>2</sub> SiF <sub>6</sub> ] (mol/l)	Substrate	Ref. #
◇ Nagayama	0.024	2.0	glass	1
◆ Yeh	0.0146	3.8	Si	10
□ Chou A	0	2.0	bared Si	15
■ Chou B	0	2.0	Si	15
○ Huang A	0	2.0	Si	
● Huang B	0.01	2.0	Si	
▲ Huang C	0.02	2.0	Si	



		Temp. (°C)	[H <sub>3</sub> BO <sub>3</sub> ] (mol/l)	[H <sub>2</sub> SiF <sub>6</sub> ] (mol/l)	Ref. #
◇	Huang	40	0.013	1.04	13
◆	Huang	40	0.013	2.54	13
□	Yeh	40	0.0146	3.8	10
■	Yeh	50	0.0146	3.8	10
●	Yeh	60	0.0146	3.8	10
△	Chou	30	0	2.0	15
▲	Chou	40	0	2.0	15
▼	Chou	50	0	2.0	15

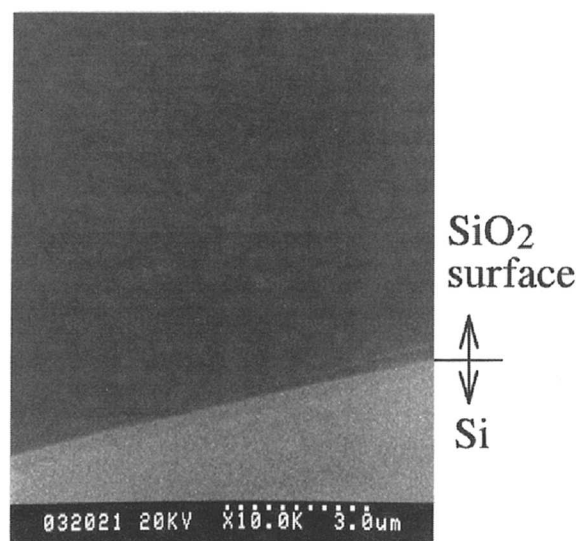
Fig. 3. The dependence of SiO<sub>2</sub> film thickness on the deposition time as reported by various investigators.

being depleted. For IC applications the required SiO<sub>2</sub> film thickness is such that the deposition time rarely exceeds several hours so that the growth is typically within the linear regime. Under such conditions the global growth rate is the same as the true growth rate.

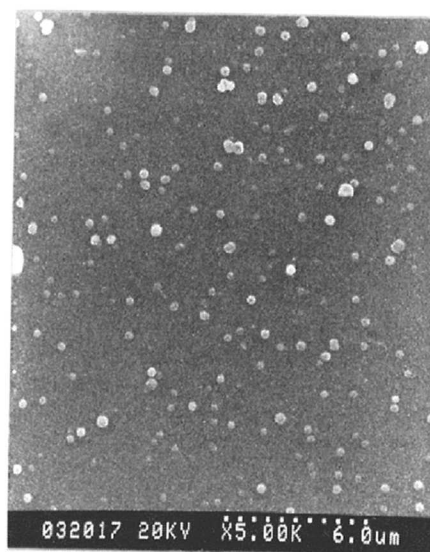
Another interesting observation of Fig. 3 is that, although not drawn, all the curves seem to converge reasonably well to the origin. This means that there is no delay of deposition once the substrate is immersed in the growth solution. On the other hand, Chou and Lee<sup>15</sup> have claimed that there is a delay of deposition and the delay time is decreased from 25.4 to 15.3 min as the deposition temperature is increased from 30 to 50°C. We feel that there is not enough data at the present time to make any meaningful evaluation of the growth behavior at the early stage of LPD-SiO<sub>2</sub> deposition (let alone interpret the physical significance of a negative delay time). More work is definitely needed to understand the initial stage of LPD-SiO<sub>2</sub> growth.

### Film Properties

Visual inspection shows that the surface quality of LPD-SiO<sub>2</sub> films, as shown in Fig. 4a, is comparable to the oxide films prepared by other techniques, such as thermal oxidation and CVD deposition. Only at high rate of deposition (for example, in a high temperature growth run with large amount of boric acid addition) do the films become cloudy, as shown in Fig. 4b, because of the presence of powdery SiO<sub>2</sub> precipitates in the growth solution. This problem may be alleviated by filtering out the suspended precipitates continuously as several investigators did in their studies.<sup>9,12,20</sup> The residual stress of an as-deposited film is tensile<sup>3,8</sup> and its magnitude increases somewhat upon annealing at 400°C due to the reduction of water components in the films,<sup>3</sup> but the residual stress is changed



(a)



(b)

Fig. 4. SEM microstructures of LPD-SiO<sub>2</sub> films on Si substrates. The boric acid concentration in the growth solution was (a) 0.01 and (b) 0.022 mol/liter at 40°C, respectively.

to the compressive state if the films are annealed at 900°C due to densification.<sup>8</sup> The refractive index of the as-deposited LPD-SiO<sub>2</sub> films is around 1.43,<sup>2,8,9,20</sup> and it decreases slightly with increasing deposition rate<sup>9,10,13</sup> or increasing postannealing temperature.<sup>17</sup> The planar etch rate in a buffered HF solution is found to be slightly higher for the as-deposited LPD-SiO<sub>2</sub> films than for the thermal or CVD oxides.<sup>1,3,18</sup> The etch rate increases with increasing deposition rate,<sup>9,12,17</sup> postannealing can result in a significant (>50%) decrease in the etch rate due to the densification of the film.<sup>1,2,8,17,20</sup> Table II summarizes the etch rate data from various studies. Despite the large variation in the deposition rate, the etch rate of LPD-SiO<sub>2</sub> generally falls within a much narrower range of 15 to 83 nm/min. The LPD-SiO<sub>2</sub> have better electrical properties than CVD-SiO<sub>2</sub> films,<sup>8,9</sup> the leakage current density is 14 nA/cm<sup>2</sup> at 5 MV/cm,<sup>11</sup> the dielectric breakdown strength is >6.3 MV/cm,<sup>6,8,9,11,14</sup> and the dielectric constant is <3.9 at 1 MHz.<sup>6,8,9,11</sup> Because of the use of fluorine-con-



Table II. Etching conditions employed by various investigators.

Investigator	Etchant solution	Etch temp. (°C)	LDP-SiO <sub>2</sub>	Etch rate (nm/min)	Ref. No.
Nagayama <i>et al.</i>	46% HF: 60% HNO <sub>3</sub> :H <sub>2</sub> O = 24:11:900 (in volume)	22	As-dep. (at 35°C) Annealed at 350°C Annealed at 500°C	30 19.7 10.2	1
Goda <i>et al.</i>	48% HF:70% HNO <sub>3</sub> :H <sub>2</sub> O = 3:2:60 (in volume)	—	As-dep. (at 35°C) Annealed at 500°C Annealed at 1000°C	78 ~ 90 52 10.4	2
Yoshitomi <i>et al.</i>	48% HF:70% HNO <sub>3</sub> :H <sub>2</sub> O = 3:2:60 (in volume)	—	As-dep. (at 35°C) Annealed at 200°C Annealed at 400°C Annealed at 600°C Annealed at 800°C Annealed at 1000°C	42 ~ 60 37.2 36 30 21 6	20
Hishinuma <i>et al.</i>	48% HF: 70% HNO <sub>3</sub> :H <sub>2</sub> O = 3:2:60 (in volume)	25	As-dep. (at 30 ~ 35°C)	108 ~ 126	18
Kawahara <i>et al.</i>	48% HF:60% HNO <sub>3</sub> :H <sub>2</sub> O = 3:2:60 (in volume)	22	As-dep. (at 35°C)	60 ~ 205	3
Yeh I	48% HF:70% HNO <sub>3</sub> :H <sub>2</sub> O = 3:2:120 (in volume)	25	As-dep. (at 35°C) Annealed at 250°C Annealed at 400°C Annealed at 600°C Annealed at 800°C	126 104 70 49.2 11.2	17
Yeh II	48% HF:70% HNO <sub>3</sub> :H <sub>2</sub> O = 3:2:60 (in volume)	25	As-dep. (at 35°C) As-dep. (at 40°C) As-dep. (at 45°C)	144 192 240	9
Homma <i>et al.</i>	Buffered HF	—	As-dep. (at 35°C) Annealed at 400°C Annealed at 900°C	83 70 50	8

taining H<sub>2</sub>SiF<sub>6</sub> in the deposition process, LPD-SiO<sub>2</sub> films are always fluorinated. The fluorine content is about 5 atom percent in the as-deposited film<sup>8</sup> but it increases with increasing H<sub>2</sub>SiF<sub>6</sub> concentration in the growth solution,<sup>3</sup> and decreases with increasing postannealing temperature.<sup>2,8</sup> The fluorinated characteristic makes the films more resistant to hot electron and radiation damage.<sup>21</sup> The refractive index of an LPD-SiO<sub>2</sub> film is found to decrease with increasing fluorine incorporation.<sup>3</sup> It is suspected that boron may also be incorporated into LPD-SiO<sub>2</sub> film formed by boric acid addition, but the extent of boron incorporation and its effect on film properties are yet to be determined.

### Conclusions

The advantages of this room temperature process and self-fluorinated characteristics make LPD-SiO<sub>2</sub> film a promising candidate for many advanced applications. After critically reviewing the data in the open literature the following characteristics of the LPD process may be stated with general agreement: (i) the deposition process is surface controlled, (ii) the deposition rate shows approximately a linear dependence on temperature, (iii) the deposition rate is roughly constant (independent of time) over a wide range of experiment conditions, and (iv) the deposition rate increases with increasing boric acid concentration.

On the other hand, this paper also shows that, despite its early successful development, there are still many fundamental questions unanswered. The large discrepancies in the literature on the effects of various processing parameters reflect their complex interdependence and highlight the urgent needs for more elaborate and systematic studies. Much confusion exists in the literature concerning the misconception of using an SiO<sub>2</sub> additive to saturate and using water to dilute the growth solution. We have emphasized the role of H<sub>2</sub>O as a reagent and the detrimental effect of an SiO<sub>2</sub> additive as a seed for depleting the nutrient in the growth solution if added after the H<sub>2</sub>O addition.

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### REFERENCES

- H. Nagayama, H. Honda, and H. Kawahara, *This Journal*, **135**, 2013 (1988).
- T. Goda, H. Nagayama, A. Hishinuma, and H. Kawahara, *Mater. Res. Soc. Symp. Proc.*, **105**, 283 (1988).
- H. Kawahara, T. Goda, H. Nagayama, H. Honda, and A. Hishinuma, *Proc. SPIE-Int. Soc. Opt. Eng.*, **1128**, 2 (1989).
- K. Awazu, H. Kawazoe, and K. Seki, *J. Non-Cryst. Solids*, **151**, 102 (1992).
- T. Homma, T. Katoh, Y. Yamada, J. Shimizu, and Y. Murao, in *Proceedings of IEEE/JSAP Symposium on VLSI Technology*, p. 3 (1990).
- T. Homma, T. Katoh, Y. Yamada, J. Shimizu, and Y. Murao, *NEC Res. Develop.*, **32**, 315 (1991).
- T. Homma, T. Katoh, Y. Yamada, and Y. Murao, *This Journal*, **140**, 2410 (1993).
- T. Homma and Y. Murao, *Thin Solid Films*, **249**, 15 (1994).
- C. F. Yeh, S. S. Lin, C. L. Chen, and Y. C. Yang, *IEEE Electron Device Lett.*, **EDL-14**, 403 (1993).
- C. F. Yeh and C. L. Chen, *Semicond. Sci. Technol.*, **9**, 1250 (1994).
- C. F. Yeh, C. L. Chen, Y. C. Yang, and S. S. Lin, *Jpn. J. Appl. Phys.*, **33**, 1798 (1994).
- C. F. Yeh, S. S. Lin, T. Z. Yang, C. L. Chen, and Y. C. Yang, *IEEE Trans. Electron Devices*, **41**, 173 (1994).
- C. T. Huang, P. H. Chang, and J. S. Shie, *This Journal*, **143**, 2044 (1996).
- J. S. Chou and S. C. Lee, *Appl. Phys. Lett.*, **64**, 1971 (1994).
- J. S. Chou and S. C. Lee, *This Journal*, **141**, 3214 (1994).
- H. Kawahara, Y. Sakai, T. Goda, A. Hishinuma, and K. Takemura, in *Proceedings of Glasses for Optoelectronics II*, **1513**, 198, SPIE (1991).
- C. F. Yeh, C. L. Chen, and G. H. Lin, *This Journal*, **141**, 3177 (1994).
- A. Hishinuma, T. Goda, M. Kitaoka, S. Hayashi, and H. Kawahara, *Appl. Surf. Sci.*, **48&49**, 405 (1991).
- M. Kitaoka, H. Honda, H. Yoshida, A. Takigawa, and H. Kawahara, in *Proceedings of International Conference on Thin Film Physics and Applications*, **1519**, 109, SPIE (1991).
- S. Yoshitomi, S. Tomioka, and N. Honeji, in *Proceedings of the 1992 International Electron Devices and Materials Symposium*, Taipei, Taiwan, p. 22 (1992).
- W. S. Lu and J. G. Hwu, *Appl. Phys. Lett.*, **66**, 3322 (1995).
- D. Scarpiello and W. Cooper, *J. Chem. Eng. Data*, **9**, 364 (1964).
- W. L. Jolly, *Modern Inorganic Chemistry*, p. 280, McGraw-Hill, New York (1984).
- S. M. Thomsen, *J. Am. Chem. Soc.*, **74**, 1690 (1952).