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Room-temperature selective growth of dielectric films by liquid-phase deposition

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Abstract. In multilevel interconnection processes, because thermal stress affects device characteristics and wiring reliability, low-temperature deposition has been required for interlayer dielectrics (SiO_2). This research investigated high growth rate and selective growth conditions of room-temperature interlayer dielectrics formed using the liquid-phase deposition method. The dependence of deposition rate on growth temperature and H_3BO_3 concentration is confirmed, and a concentration of 3.8 mol l^{-1} of H_2SiF_6 is used to achieve a high deposition rate of 1250 Å h^{-1}. The degree of supersaturation of silica of the immersing solution is found to define three ranges of growth conditions: the non-deposition range, selective deposition range, and conformal deposition range. A selective deposition model is proposed to clarify the mechanism of room-temperature selective SiO_2 growth.

1. Introduction

Interlayer dielectric film formation technology is essential for the fabrication of multilevel interconnections in ULSI. Low-temperature deposition has been required for multilevel interconnection interlayer dielectrics because thermal stress affects device characteristics and wiring reliability. This problem is likely to become more serious in future deep-submicrometre interconnections. Low-temperature deposition techniques using organic sources such as TEOS–ozone APVCD, H_2O–TEOS PECVD, and biased ECR CVD have been investigated for use in fabricating multilevel interconnections [1–4]. However, all of these techniques share a fatal drawback: it is impossible to reduce the temperature significantly, because a substrate temperature above 300 °C is required for polymerization and dehydration. Therefore deposition at a lower temperature without residual OH has been difficult to achieve. Recently, researchers have attempted to develop room-temperature interlayer dielectric deposition technology for deep-submicrometre multilevel interconnections [5]. In particular, techniques providing selective growth capability for complete planarization by using the liquid-phase deposition (LPD) method [6, 7] have attracted much attention. This type of method is simple, and the equipment required is very inexpensive. However, to date the deposition rates achieved have been so low that this type of method remains impractical for industrial use. Thus the critical issue at this juncture is whether or not a technology can be developed to supply a high growth rate and selective growth. In addition, room-temperature selective growth will become suitable for a wider range of applications, if the range of growth conditions and the growth mechanism can be clarified. This research investigated room-temperature high growth rate and the range of selective growth conditions using the LPD method.

2. Experiment

The apparatus used in this research is illustrated in the schematic diagram in figure 1. The room-temperature control bath was adjusted to the desired reaction temperature (RT) RT ± 0.01 °C. The immersing solution was prepared by dissolving highly purified silica particles (SiO_2) in H_2SiF_6 at 23 °C to obtain a saturated solution

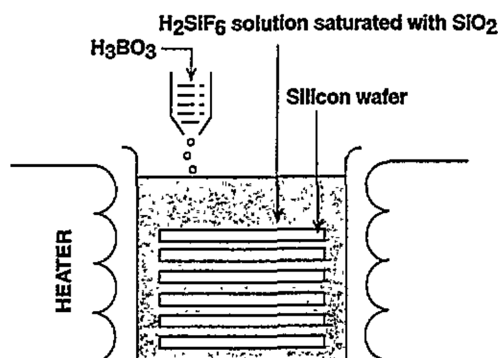

Figure 1. A schematic diagram of the apparatus used for liquid-phase deposition of dioxide.

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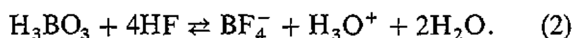
of 4.0 mol l^{-1} with silica, followed by filtering to remove undissolved silica. To obtain a supersaturated state with SiO_2 in the immersing solution, a boric acid solution (0.1 mol l^{-1}) was added and the solution was stirred for 20 min. The SiO_2 film was then prepared by immersing Si wafers in the solution. The film thickness was adjusted by controlling the immersion time. The chemical reaction for SiO_2 growth can be represented by the following two equilibrium processes in the treatment solution. The one process is in the hydrofluosilicic acid as shown in equilibrium (1):

$$H_2SiF_6 + 2H_2O \rightleftarrows 6HF + SiO_2. \quad (1)$$

In this equilibrium, the addition of SiO_2 will lead the shift from right to left. Therefore the treatment solution comprising hydrofluosilicic acid saturated with silica may include hydrofluoric acid which was minimized in equilibrium (1). However, this equilibrium may be changed by the addition of boric acid to the treatment solution. Normally boric acid easily reacts with hydrofluoric acid as shown by equilibrium (2):



$$H_3BO_3 + 4HF \rightleftarrows BF_4^- + H_3O^+ + 2H_2O. \quad (2)$$

Accordingly, the addition of boric acid to the treatment solution leads to the consumption of the minimized hydrofluoric acid and brings about a transient state supersaturated with SiO_2 in equilibrium (1). Such supersaturation of SiO_2 shifts the equilibrium process (1) from left to right following a silica deposition mainly on the substrate.

The concentration of H_2SiF_6 and boric acid (H_3BO_3) and the temperature can influence the degree of supersaturation and the rate of SiO_2 growth. For an H_2SiF_6 concentration of 2.0 mol l^{-1}, the deposition rate has been reported to be about 80–300 Å h^{-1}, depending on temperature [7]. According to our investigations, however, at this concentration LPD SiO_2 can hardly be produced at all. Consequently, in this study a concentration of 3.8 mol l^{-1} of H_2SiF_6 was used to enable us to investigate high growth rate and selective growth capability.

Growth of SiO_2 films was performed mainly on Si wafers at constant RT. First, to study the dependence of the growth rate on temperature, various RT (35, 40 and 45 °C) were selected, and an H_3BO_3 concentration of 1.46×10^{-2} mol l^{-1} was adopted. Next, to study the dependence of the deposition rate on H_3BO_3 concentration, the quantity of H_3BO_3 was varied in the range of $(1.46–2.55) \times 10^{-2}$ mol l^{-1}, while the bath temperature was fixed at 35 °C. Ellipsometry, a sensitive tool for monitoring the film thickness (t) and refractive index (N) of a dielectric film, was used. To examine the effect of deposition conditions on chemical stability, the P-etch rate using the solution (48% HF: 70% HNO_3: H_2O = 3:2:60 in volume) at room temperature was also evaluated. To investigate the conformability and the property of selective growth, the LPD SiO_2 growth profiles, which were formed on the double-layer structure of tungsten interconnection lines covered with positive photoresist, were inspected using scanning electron microscopy (SEM).

3. Results and discussion

3.1. Growth temperature dependence

We investigated the growth of LPD SiO_2 film at 35 °C in a solution with 3.8 mol l^{-1} of H_2SiF_6 and 1.46×10^{-2} mol l^{-1} of H_3BO_3. Fourier transform infrared spectroscopy (FTIR) of an as-deposited LPD SiO_2 film indicates intensive peaks around 1092.5 cm^{-1} and 927.3 cm^{-1} due to the stretching vibration of Si–O–Si bonds and Si–F bonds respectively. This obviously shows that the LPD SiO_2 film is rich in Si–O–Si bonds and has an orderly silica network and consequently good chemical stability. The refractive index of the LPD SiO_2 is shown to be 1.43. These chemical properties reveal that the LPD SiO_2 film is similar to the film grown in 2.0 mol l^{-1} reported in [10]. The growth of SiO_2 is linearly dependent on the immersion time, and the deposition rate (DR) can be easily obtained. We also found that, as shown in figure 2, the DR decreased slightly with immersion time owing to the consumption of boric acid with increased immersion time. Because the chemical reaction for LPD SiO_2 growth is dependent on temperature, as shown in equilibrium processes (1) and (2), it is possible that the DR can be controlled by changing the solution temperature. As shown in figures 2 and 3, the deposition rate indeed increases with temperature. Comparing our results with the deposition rates reported in [7], we find that the new condition of 3.8 mol l^{-1} of H_2SiF_6 and 1.46×10^{-2} mol l^{-1} of H_3BO_3 adopted in this research apparently enhanced the rate of growth of LPD SiO_2 film.

From FTIR evaluation, we have confirmed that an increase of growth temperature had no effect on the chemical composition of the LPD SiO_2 films. However, as depicted in figure 4, the refractive index of the dielectric films increases linearly with the growth temperature. This result indicates there must be a slight difference in the structure of films grown at different temperatures. In fact, the chemical stability in terms of the P-etch rate was evaluated for all the LPD SiO_2 films. As shown in figure 4, the film grown at higher temperature has a higher P-etch rate and thus seems to be less dense. However, for LPD SiO_2, a low P-etch rate (24 Å s^{-1}) may also be due to its superior chemical stability.

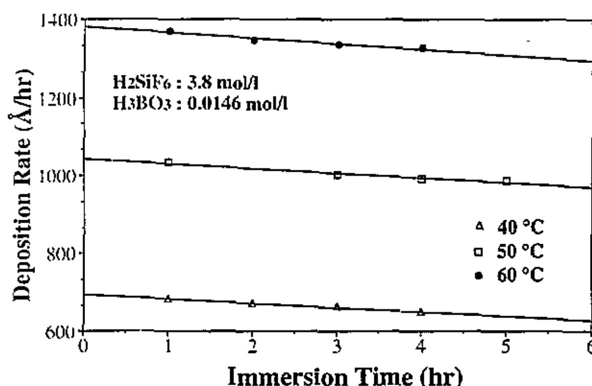


Figure 2. Dependence of deposition rates on immersion time at different temperatures for the solution with 3.8 mol l^{-1} of H_2SiF_6 and 0.0146 mol l^{-1} of H_3BO_3.

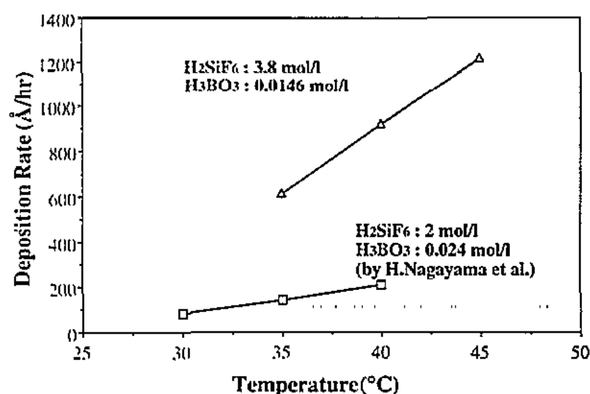


Figure 3. Dependence of deposition rate on solution temperature for the solution with 3.8 mol l^{-1} of H_2SiF_6 and 0.0146 mol l^{-1} of H_3BO_3. For comparison, the deposition rate obtained by Nagayama *et al* [7] for the solution with 2 mol l^{-1} of H_2SiF_6 and 0.024 mol l^{-1} of H_3BO_3 is also shown.

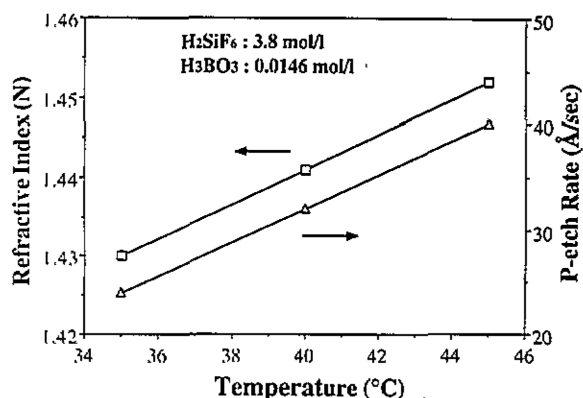


Figure 4. Relationship of the refractive index and the P-etch rate to the growth temperature for dielectric films prepared in the solution with 3.8 mol l^{-1} of H_2SiF_6 and 0.0146 mol l^{-1} of H_3BO_3.

3.2. H_3BO_3 dependence

Besides using a high concentration (3.8 mol l^{-1}) of H_2SiF_6 solution, an alternative method of achieving a high DR is to increase the concentration of H_3BO_3, thereby increasing the supersaturated degree of silica. As depicted in figure 5, the deposition rate is greater than 600 Å h^{-1} when the concentration of H_3BO_3 is over

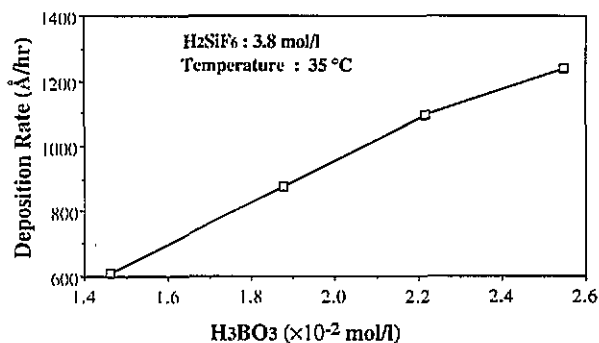


Figure 5. Relationship of deposition rate to H_3BO_3 concentration at 35 °C for the solution with 3.8 mol l^{-1} of H_2SiF_6.

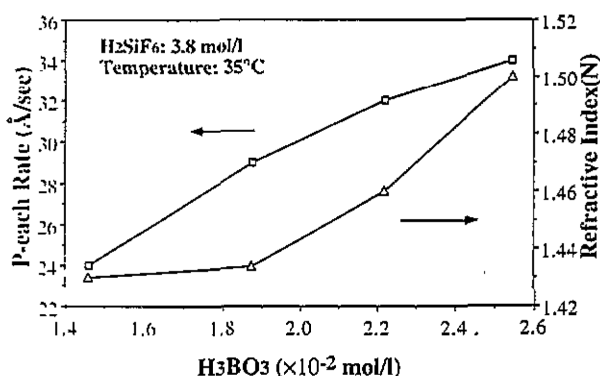


Figure 6. Relationship of the refractive index and the P-etch rate to H_3BO_3 concentration at 35 °C for the solution with 3.8 mol l^{-1} of H_2SiF_6.

1.46×10^{-2} mol l^{-1}, and it increases to 1250 Å h^{-1} at a concentration of 2.548×10^{-2} mol l^{-1}. In this high-DR region, we again confirmed from FTIR evaluation that no compositional alterations occurred in the as-grown films. However, as depicted in figure 6, the refractive index (N) of the dielectric films shows an increasing dependence on the concentration of H_3BO_3. This result also implies that there must be a difference in the structure of the LPD SiO_2 films grown in solutions with various degrees of supersaturation. This can be corroborated by P-etch testing for these films. As depicted in figure 6, the film grown in a more supersaturated solution appears less dense, because of its increased P-etch rate.

3.3. Selective growth

In a previous experiment [11], we found that the conformal deposition could be easily carried out with 2.0 mol l^{-1} H_2SiF_6 solution. However, we failed to achieve selective growth with a solution of this concentration. After the concentration of the solution was increased to 3.8 mol l^{-1}, experiments with both temperature and H_3BO_3 concentration as parameters revealed that there exist a range of degrees of supersaturation in which selective growth of LPD SiO_2 can be carried out. As shown by the two curves in figure 7, in which the x axis represents the growth temperature and the y axis represents the concentrations of H_3BO_3, there are three ranges: the non-deposition range, the selective deposition range and the conformal deposition range. These ranges were determined by SEM cross-sectional inspection of all the LPD SiO_2 growth profiles on the double-layer structure of photoresist/tungsten lines (figure 8(*a*)). Conformal deposition means that the deposition occurs all over the surface, including photoresist as illustrated in figure 8(*b*), while selective deposition (figure 8(*c*)) means that the deposition occurs only on the substrate (in this case, SiO_2). In the selective deposition profiles, there is a rounded shape at both edges of every space line. This will be explained below using a selective growth model. As for non-deposition, LPD SiO_2 is not grown; in some cases the original SiO_2 substrate or the side-walls of tungsten interconnection have been etched (figure 8(*d*)).

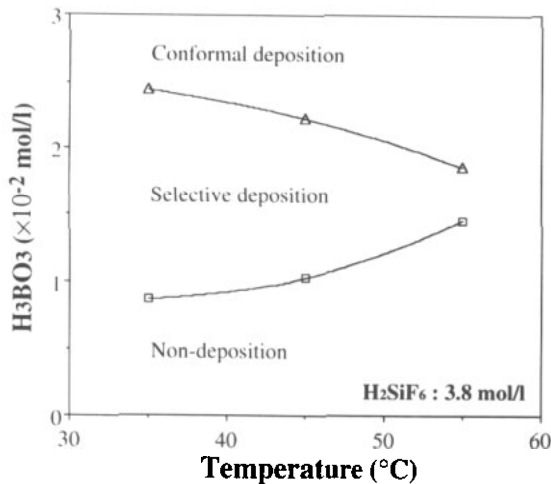


Figure 7. Three condition ranges, including (i) conformal deposition, (ii) selective deposition, and (iii) non-deposition, defined by the two deposition key factors of growth temperature and H_3BO_3 concentration.

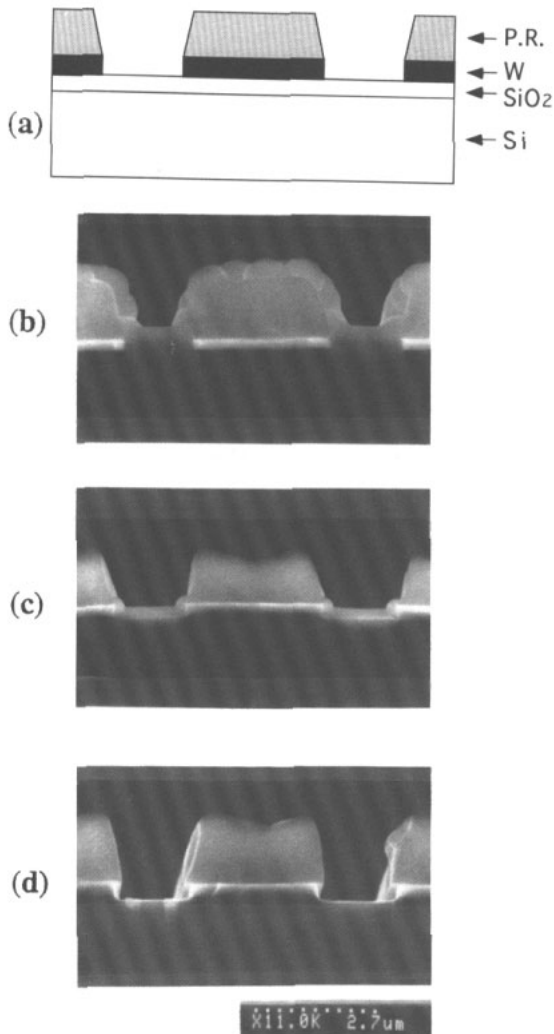


Figure 8. SEM cross-section views of LPD SiO_2 profiles prepared on the double-layer structure of photoresist/tungsten line. (*a*) Typical representative view, (*b*) conformal deposition, (*c*) selective deposition and (*d*) non-deposition. (*b*), (*c*) and (*d*) correspond to the three condition ranges illustrated in figure 7.

At higher H_3BO_3 concentration, because the reaction rate of reaction (2) increases with temperature, the supersaturated degree of silica also increases with temperature. Thus a lower concentration of H_3BO_3 is required to achieve conformal deposition at higher temperatures. In the conformal deposition range shown in figure 7, the supersaturated degree of silica is sufficiently high for both photoresist and substrate, hence the LPD SiO_2 grows easily all over both surfaces conformally. At a lower H_3BO_3 concentration ($<0.868 \times 10^{-2}$ mol l^{-1}) in the non-deposition range, the supersaturated degree of silica is too low to deposit silica. While the saturated H_2SiF_6 solution evaporates at room temperature, the concentration of the solution will decrease. In this case, the higher the temperature is, the lower the H_2SiF_6 solution concentration will be, so the degree of supersaturation is too low to form silica. Occasionally the reverse reaction to (1) occurs and the oxide substrate is etched. Thus, it is essential to add more boric acid to increase the degree of supersaturation at high temperatures. In the selective deposition range, owing to the sufficiently high degree of supersaturation, which is adequate for LPD SiO_2 growth on the substrate rather than on the photoresist, selective growth of LPD SiO_2 on the substrate against the photoresist was achieved.

3.4. Selective growth model

Why selective growth of LPD SiO_2 occurs under the conditions in the selective deposition range is an important question. Before we attempt to formulate a model to explain our findings, two facts have to be emphasized. One is that the main difference between the three deposition ranges depicted in figure 7 lies in the degree of supersaturation of the immersing solution. The other fact is that whether or not LPD SiO_2 growth occurs on a surface is determined by the chemical structure of the surface, such as the organic polymer of the photoresist or the inorganic silicon dioxide. On the basis of these two facts, we suggest that a surface composed of a different material requires a solution with a different degree of supersaturation of SiO_2 for LPD SiO_2 deposition.

If an immersing solution is sufficiently supersaturated with SiO_2, silica will first be segregated throughout the solution; then it may react with the surface and be deposited on the surface by stabilized bonds. If the reaction energy owing to the surface chemical structure is not high enough to overcome the activation energy, segregated silica will migrate. If deposition occurs, owing to the lack of strong bonds the chemical structure of the film will be essentially different from that of film with strong bonds. As an example of this difference in chemical structure of the surface, the cross-sectional view in figure 8(*b*) clearly indicates that the structures of as-deposited film on photoresist and substrate dioxides are different from each other. Accordingly, a selective deposition model can be proposed. In the selective deposition range, segregated silica can easily bond with substrate dioxide

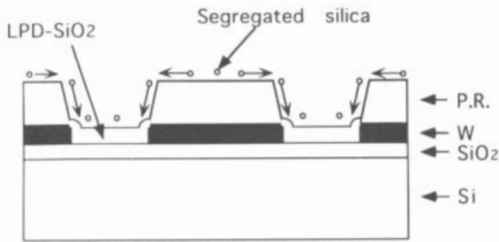


Figure 9. A model for selective LPD SiO_2 growth.

and deposition with uniform structure occurs, while silica hardly bonds with the polymer surface at all but, as illustrated in figure 9, surface migration will occur. Thus the deposition rate at both edges of each space-line is high, and a rounded deposition shape occurs.

4. Conclusion

This study has investigated the room-temperature selective growth conditions of LPD SiO_2. The dependence of deposition rate on growth temperature and H_3BO_3 concentration indicates that a high deposition rate can easily be obtained using a 3.8 mol l^{-1} H_2SiF_6 immersing solution. We have shown that both growth temperature and H_3BO_3 concentration have an important effect on the chemical properties of the LPD SiO_2 deposited. The degree of supersaturation of silica of the immersing solution has been found to determine three ranges of deposition behaviour: the non-deposition range, selective deposition range, and conformal deposition range. Our results should be instructive in attempts to achieve room-temperature formation of planarized interlayer dielectrics for multilevel interconnections. The selective deposition model proposed here should also help to clarify the mechanism of room-temperature selective deposition.

Acknowledgments

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