Photoassisted Liquid-Phase Deposition of Silicon Dioxide

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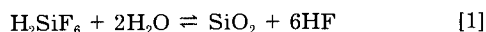
ABSTRACT

The deposition rate of SiO_2 by liquid-phase deposition (LPD) in a H_2SiF_6 solution is significantly increased by 254 nm ultraviolet (UV) illumination. The photoenhancement effect is much stronger at 3.09 *M* H_2SiF_6 than at 1.34 *M* H_2SiF_6 concentration. At a constant boric acid concentration the deposition rate of SiO_2 is found to increase linearly with UV light intensity. The photoassisted effect is much stronger at higher boric acid concentration. However, within the UV intensity range studied, the photoeffect on the oxide growth rate is not as strong as other parameters such as H_2SiF_6 concentration and boric acid addition. The UV spectrophotometric results show that the strong UV absorption of the growth solution is associated with SiF_6^{2-} but not with H_2O, H_3BO_3, or BF_4^- species in the solution. The observed photoenhancement effect is discussed in the light of the existing LPD models.

The growth of SiO_2 films by liquid-phase deposition has received increased attention recently because of its advantages of low temperature processing, reduced capital cost, high throughput, and excellent selectivity over the traditional techniques such as chemical vapor deposition (CVD), radio frequency (RF) reactive sputtering, E-gun deposition, thermal oxidation, etc.[1] The growth of liquid-phase deposited SiO_2 (LPD-SiO_2) is typically conducted in a supersaturated hydrofluosilicic acid (H_2SiF_6) solution at a temperature between 25 and 50°C.[2-14] A simplified mechanism of LPD growth was originally proposed by Nagayama *et al.*[2] based on the reaction of H_2SiF_6 with water to form hydrofluoric acid and solid SiO_2



$$H_2SiF_6 + 2H_2O \rightleftharpoons SiO_2 + 6HF \quad [1]$$

This model has been fairly successful in explaining the increased supersaturation and hence the increased deposition of SiO_2 by the addition of boric acid (H_3BO_3), [2,3] or aluminum,[4] or water[5] to the growth solution. In the first two cases, either boric acid or aluminum would react with HF to form BF_4^- [15] or AlF_3,[16] 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_2 is formed. According to reaction 1 the addition of water to the growth solution also drives the reaction to the right favoring the SiO_2 deposition, and this fact has been utilized by several groups in LPD growth.[5-8] Although evidence supporting this simplified model has been reported by Raman spectroscopy data,[9] it cannot explain the selective deposition of LPD-SiO_2 and the incorporation of fluorine atoms in the grown films as reported by many investigators.[4,6,8-12] For example, LPD-SiO_2 film deposition has been reported to occur on the surface of thermal-SiO_2, CVD-SiO_2, and native oxide on silicon or polysilicon but not on the surface of photoresist, sputtered-tungsten, or bared silicon.[13,14] Two sophisticated models have recently been advanced to explain the selective deposition and the fluorine incorporation.[6,13] 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.[6,13] The deposition of LPD-SiO_2 is brought about by the reaction of the intermediate species with Si-OH bonds on the substrate surface. Two different intermediate species, $SiF_m(OH)_{4-m}$ ($m < 4$) [13,17] and $[SiF_6 \cdot SiF_4]^{2-}$, [6,18] have been suggested. Although the correctness of these models remains to be proved, recent report of Chou and Lee[8] on the significant difference (about ten times) in deposition rate for two growth solutions with the same H_2SiF_6 concentration (2 *M*) but prepared by two different routes does support the notion of the existence of active intermediate species in LPD reaction. Since exactly the same growth conditions were employed for the two growth solutions in their growth runs, the observed variation was attributed to the difference in the concentration of the intermediate species resulting from the different processes.

One of the major disadvantages of LPD is the low deposition rate which limits its use.[14] It is, therefore, very desirable to develop a technique which can increase the deposition rate of LPD-SiO_2. It is well known that many reactions can be enhanced by means of UV light illumination. Examples can be found in photoCVD[19,20] and photoassisted sol-gel processing.[21] The common aspect of these processes is that the reacting molecules absorb ultraviolet spectra of a light source and are activated so that the chemical reaction is greatly enhanced. Generally the light source used in photoassisted processes can be laser, deuterium lamp, or mercury lamp, depending on the UV absorption spectra of the reacting molecules. In this paper, we propose a new photoassisted liquid-phase deposition (photoLPD) method. The results confirm that UV irradiation has a small but significant effect on the rate of LPD-SiO_2.

Experimental

The substrates used in this experiment were n-type (100) Si wafers. The native oxides on the Si wafers were not removed to ensure the growth of LPD-SiO_2. After ultrasonically cleaning in acetone twice for 20 min and rinsing in DI water for 10 min, they were immersed into the growth solution with stirring for SiO_2 deposition. The starting solution is a commercial (Riedel-de Haën, Germany) 34 weight percent (w/o) hydrofluosilicic acid (H_2SiF_6) solution from which saturated growth solutions with two different H_2SiF_6 concentrations, 3.09 and 1.34 *M*, were prepared. Excess silicic acid powders ($SiO_2 \cdot xH_2O$) were added to the solutions and thoroughly mixed by stirring for 6 h to ensure saturation at 25°C. After saturation, the undissolved silicic acid powders were filtered out using a 0.2 μm Teflon filter. Oxidized Si dummy samples were used to check the saturation level of the filtered H_2SiF_6 solutions; by immersing them into the solutions at 25°C for 4 days, we measured the oxide thickness and found no difference before and after immersion. This shows that the filtered H_2SiF_6 solutions was indeed saturated. Before immersing the substrates for deposition, various quantities of boric acid (0.1 *M*) and DI water were added all at one time to the solution so that the concentration of boric acid in the growth solution was varied from 0 to 0.0177 *M*. The volume of the growth solution was kept constant at 90 ml for each growth run. The supersaturated solutions were stirred for 1 h in a constant temperature water bath at 40°C to ensure that boric acid had completely reacted with hydrofluoric acid and that solution temperature had been stabilized. The growth runs were conducted in the dark either with or without UV illumination with the solution always in circulation by stirring. For photoLPD-SiO_2 deposition, mercury lamps of 254 nm wavelength were used to illuminate the solution from the top at a distance of 4 cm. Two different light intensities, 4.6 and 9.6 mW/cm², were used. The UV intensity was measured by a radiometer at a distance of 4 cm. The growth solution was constantly stirred during growth in a constant temperature bath. The temperature

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fluctuation due to UV light illumination was monitored and found to be less than 0.8°C. Generally, fresh growth solution was used for each growth run of one specimen at a time. The total deposition time for each run was varied from 2 to 6 h depending on the deposition rate so that a total oxide thickness of at least several hundred angstrom can be formed for subsequent measurement. The thicknesses and refractive indexes of the deposited films were measured by ellipsometry. The effective growth rate was calculated by dividing the total oxide thickness by the total deposition time. The UV transmission spectra of solutions were measured on a UV spectrophotometer (Model DU-7400, Beckman Co., USA) using standard low absorption quartz cell with an optical path length of 1 cm.

Results and Discussion

Figure 1 shows the variation of the oxide film thickness as a function of deposition time. The boric acid addition was kept constant at 0.013 *M* for the three cases but 3.09 *M* H_2SiF_6 solutions were used for cases A and B while 1.34 *M* H_2SiF_6 solution was used for case C. Cases B and C were conventional LPD runs in the dark without UV illumination while case A was a photoLPD run with UV illumination at an intensity level of 9.6 mW/cm^2. The thicknesses of the SiO_2 films in all cases depend linearly on deposition time indicating constant deposition rates of 69, 54, and 17 nm/h for curves A, B, and C, respectively. Clearly a higher H_2SiF_6 concentration results in a higher deposition rate and UV illumination further enhances the deposition rate. Intuitively one would not expect the deposition rate to remain constant indefinitely because the supersaturation decreases as more and more SiO_2 is removed from the growth solution. However, it is reasonable to claim, based on Fig. 1, that a constant deposition rate was maintained throughout each of the growth runs which were typically limited to within 6 h.

Figures 2 and 3 show the combined effect of boric acid addition and UV illumination on the deposition rate of SiO_2 for 1.34 *M* H_2SiF_6 and 3.09 M H_2SiF_6 growth solutions, respectively. The deposition rate increases roughly quadratically with boric acid concentration, a result consistent with other investigators[7] and has been successfully explained by Nagayama's model[2] that boric acid reacts with HF to form BF_4^- thus reducing the HF concentration in the growth solution. This would drive reaction 1 to the right leading to increased SiO_2 deposition. The deposition rate is also enhanced by UV illumination in both figures although it is evident by comparing Fig. 2 and 3 that UV illumination has a more prominent effect on the deposition rate of the 3.09 *M* H_2SiF_6 solution than that of the 1.34 *M* H_2SiF_6 solution. Figures 4 and 5 show the dependence of deposition rate as a function of UV intensity at various boric addition levels for the 1.34 and 3.09 *M* solutions, respectively. At a constant boric acid concentration the effect of UV intensity on deposition is found to be linear within the intensity range studied. The photochemical effect appears to be dependent on the boric acid concentration. This is clearly revealed by the increased slope with increasing boric acid concentration as shown in Fig. 4 and 5.

The growth solutions used in the present study are found to absorb UV light strongly. Figure 6 shows the UV transmission spectra of two growth solutions with the compositions of 20 ml 1.34 *M* H_2SiF_6 + 3 ml 0.1 *M* H_3BO_3 (curve A)

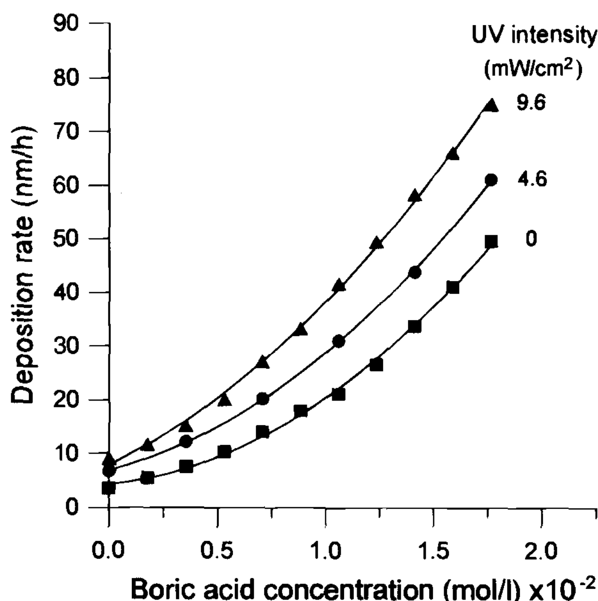

Fig. 2. The effect of boric acid concentration on the deposition rate of SiO_2 at three different UV intensity levels. The H_2SiF_6 concentration of the growth solution is 1.34 *M* and the growth temperature is 40°C.

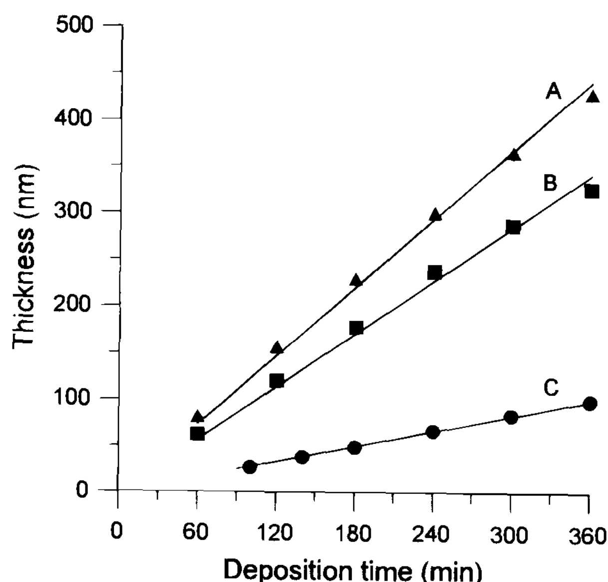

Fig. 1. Dependence of deposition rate of SiO_2 on deposition time. Curve A: 3.09 *M* H_2SiF_6 with 9.6 mW/cm^2 UV illumination; curve B: 3.09 *M* H_2SiF_6 without UV illumination; and curve C: 1.34 *M* H_2SiF_6 without UV illumination.

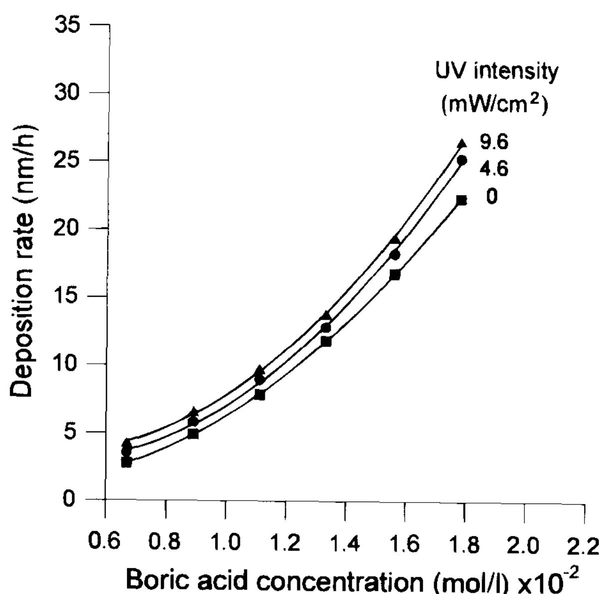

Fig. 3. The effect of boric acid concentration on the deposition rate of SiO_2 at three different UV intensity levels. The H_2SiF_6 concentration of the growth solution is 3.09 *M* and the growth temperature is 40°C.

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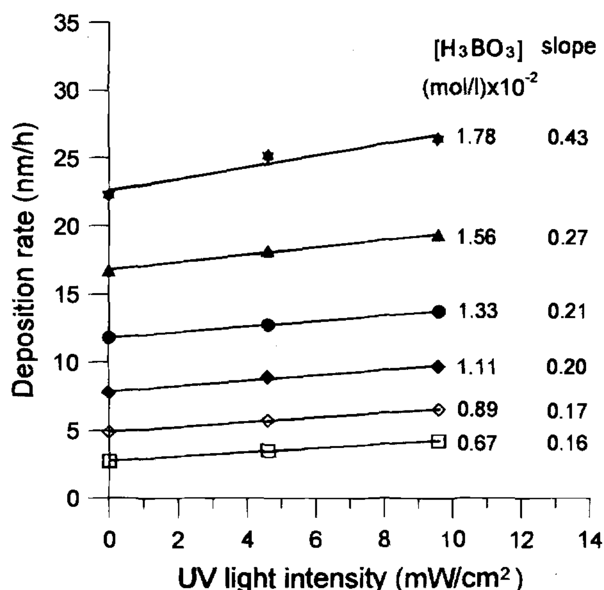

Fig. 4. The effect of UV intensity on the deposition rate of SiO_2 at different boric acid concentrations. The H_2SiF_6 concentration of the growth solution is 1.34 *M* and the growth temperature is 40°C.

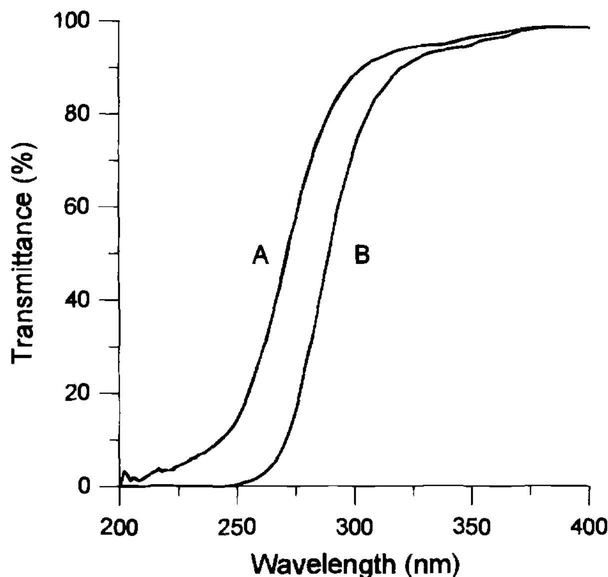

Fig. 6. UV transmission spectra of two growth solutions. Curve A: 20 ml H_2SiF_6 (1.34 *M*) + 3 ml H_3BO_3 (0.1 *M*). Curve B: 20 ml H_2SiF_6 (3.09 *M*) + 3 ml H_3BO_3 (0.1 *M*).

and 20 ml 3.09 *M* H_2SiF_6 + 3 ml 0.1 *M* H_3BO_3 (curve B), measured by using a standard UV quartz cell of 1 cm optical path length. It indicates that UV light with a wavelength shorter than about 300 nm is strongly absorbed by the solutions supersaturated with SiO_2. It is also evident in Fig. 6 that the higher the H_2SiF_6 concentration the greater the UV absorption.

There are four major chemical species, H_2O, H_3BO_3, BF_4^-, and SiF_6^{2-}, in a growth solution according to Nagayama's LPD model.[2] To identify the species responsible for the UV absorption, the UV transmission spectra of pure H_2O, pure H_3BO_3 solution (0.1 *M*), and pure H_2SiF_6 solutions (1.34 and 3.09 *M*) were measured under the same conditions as those employed for Fig. 6. Figure 7 shows the UV transmission spectra of pure H_2O and pure H_3BO_3. It should be pointed out that curve B only shows the net effect of boric acid absorption because the contribution of H_2O (namely, curve A) has been subtracted out. Curve A in this figure shows clearly that, except for the small (<5%) absorption between 400 to 500 nm, H_2O is practically not absorbing UV light from 200 to 700 nm. Similarly, the transmittance of H_3BO_3 is typically greater than 90% from 200 to 700 nm as revealed by curve B. These results imply that the UV absorption observed in the growth solutions is not caused by H_2O or H_3BO_3. The transmission spectra of pure 1.34 and 3.09 *M* H_2SiF_6 solutions (with the absorption of H_2O subtracted out) are shown in Fig. 8 as curve A and B, respectively. It shows that H_2SiF_6 solutions strongly absorb UV light. Note that the UV transmission spectra of the pure H_2SiF_6 solutions shown in Fig. 8 are very similar to those of the growth solutions shown in Fig. 6. By way of subtraction the absorption effect of BF_4^- must be negligibly small. From the forgoing discussion, we may conclude that the UV absorption observed in Fig. 6 is definitely related to SiF_6^{2-} species in the growth solutions. Much remains to be done to clarify the mechanism of the photochemical effect in the LPD process. In the light of the existing LPD

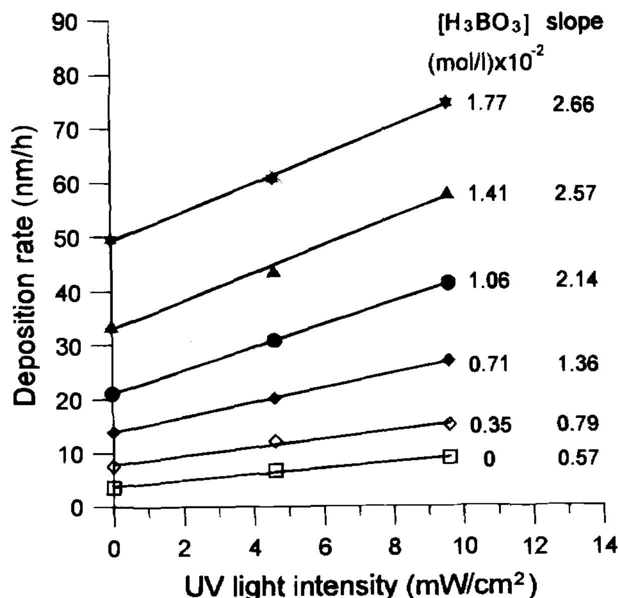

Fig. 5. The effect of UV intensity on the deposition rate of SiO_2 at different boric acid concentrations. The H_2SiF_6 concentration of the growth solution is 3.09 *M* and the growth temperature is 40°C.

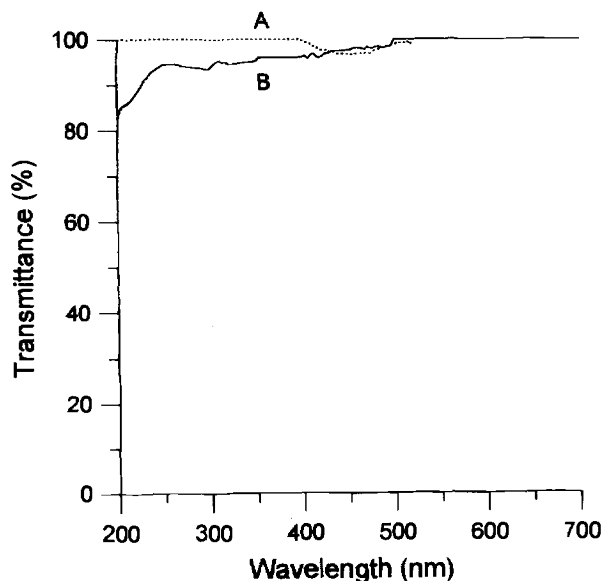

Fig. 7. UV transmission spectra of H_2O (curve A) and 0.1 *M* H_3BO_3 (curve B).

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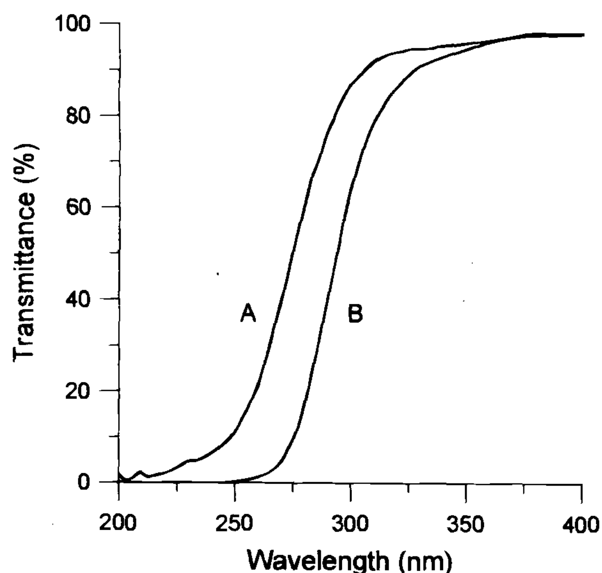

Fig. 8. UV transmission spectra of 1.34 *M* (curve A) and 3.09 *M* (curve B) H_2SiF_6 solutions.

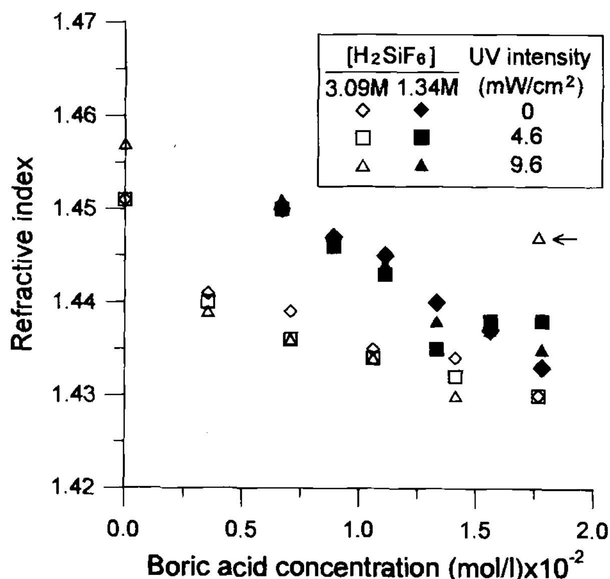

Fig. 9. Dependance of refractive index on boric acid concentration for SiO_2 films grown from two different concentrations of H_2SiF_6 solution under different UV illumination.

model, the strong absorbing ability of SiF_6^{2-} species probably results in a significant increase in the concentration of the important intermediate species $SiF_m(OH)_{4-m}$ ($m < 4$)[13,17] leading to the observed increase in the deposition rate.

Figure 9 shows the refractive index of all the films grown in the present study. The data in this figure are divided into two groups. The open symbols are for films grown in 3.09 *M* H_2SiF_6 solutions while the closed symbols are for films grown in 1.34 *M* H_2SiF_6 solutions. Three observations can be made from this figure: (*i*) except for one outlier (arrowed point in Fig. 9), the refractive index is generally decreased slightly with increasing boric acid concentration in both groups; (*ii*) films formed in 1.34 *M* H_2SiF_6 solutions have slightly higher refractive index than those formed in 3.09 *M* H_2SiF_6 solutions; and (*iii*) UV intensity has a small effect on refractive index but the effect does not seem to follow any particular trend.

It has been shown previously in Fig. 2 and 4 that at a constant H_2SiF_6 concentration the film is deposited at a higher rate at higher boric acid concentration. Also, SiO_2 film is grown at a faster rate in a 3.09 *M* H_2SiF_6 solution than in a 1.34 *M* H_2SiF_6 solution. Therefore, the first two observations are equivalent to that an LPD-SiO_2 film grown at a higher rate has a lower refractive index. This observation has been reported previously by other investigators.[3,14] Using etch rate as an indicator of film density (*i.e.*, lower etch rate corresponding to higher density), Yeh *et al.*[14] claimed that a film deposited at a lower rate has a higher refractive index because of denser structure. However, Kawahara *et al.*[3] have pointed out the inconsistency of using etch rate as density indicator for LPD-SiO_2, and instead he was able to correlate the decrease of refractive index of LPD-SiO_2 with increasing fluorine content incorporated into the film. In the light of Kawahara's result the second observation may be attributed to the difference in fluorine content in the film. It is expected that boron may also be incorporated into the oxide film during LPD growth, but the extent of this incorporation and its effect on refractive index are yet to be determined. Within the UV intensity level investigated in the present study the effect of UV illumination on SiO_2 deposition rate is not as big as that of the boric acid concentration as evidenced in Fig. 2 and 4, therefore its effect on refractive index is less significant. The outlier in Fig. 9 is obtained from the sample deposited at the highest rate, and the film appears cloudy which may have affected its refractive index measurement.

Conclusions

The growth of SiO_2 by photoassisted liquid-phase deposition (photoLPD) in silica-saturated H_2SiF_6 solution was studied. PhotoLPD by 254 nm UV illumination enhances SiO_2 deposition rate over the conventional LPD process and the photoenhancement becomes more prominent when the H_2SiF_6 concentration of the growth solution is increased from 1.34 to 3.09 *M*. At a constant boric acid concentration the deposition rate of SiO_2 increases linearly with the UV light intensity and the higher the boric acid concentration the stronger the UV intensity effect. The deposition rate of SiO_2 increases with the boric acid concentration with or without UV illumination. The observed strong UV absorption of the growth solution is mainly related to the SiF_6^{2-} species but not to the H_2O, H_3BO_3, or BF_4^- species in the solution. The increased SiO_2 deposition rate of photoLPD may be attributed to the increased concentration of intermediate species due to the activation of SiF_6^{2-} species by UV illumination. Within the UV intensity range studied, the photoeffect on the oxide growth rate is not as strong as other parameters such as H_2SiF_6 concentration and boric acid addition. However, since the growth rate is linearly dependent on UV intensity, a dramatic increase in growth rate may be expected with extremely high intensity UV source like excimer laser.

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Electrochemically Reduced Polycrystalline Tin Oxide Thin Films

Surface Analysis and Electroplated Copper Adhesion

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ABSTRACT

In previously reported work, a conductivity enhancement effect in polycrystalline tin oxide thin films, which are widely used for the front electrodes in flat panel displays, has been achieved by electroplating copper onto the 300 nm high sidewalls of the electrode. Recent experiments show that if an electrolytic reduction is introduced as a surface modification process just before electroplating then excellent adhesion between copper and tin oxide can be achieved. In this paper, the chemical, physical and surface morphological changes of tin oxide electrodes have been characterized by using atomic force microscopy, x-ray diffraction, x-ray photoelectron spectroscopy, and surface sheet resistance measurements by a four-point probe method. The electrolytic reduction was found to result in an increase in the intensity of the x-ray reflection from the (110) planes of tin oxide, and compositional nonuniformity of the tin oxide surface layers, where metallic tin is trapped at the surface, and oxygen is enriched in the subsurface region. These results, taken together, suggest that the observed adhesion improvement may be due to a combination of tin oxide surface roughening due to preferential etching and the increased (110) orientation, *in situ* cleaning, and chemical bonding introduced by surface chemical changes.

Introduction

Tin oxide (TO, SnO_2) and indium tin oxide (ITO, $InSnO_2$) are widely used materials for the front electrodes in flat panel displays including liquid crystal (LC), dc or ac electroluminescent (EL), and plasma displays (PD). Response time, brightness, uniformity, and power consumption depend critically on electrode line resistance, especially for large area displays. The conduction mechanism in tin oxide and indium tin oxide limits their intrinsic conductivity to approximately $2.5 \times 10^6\ \Omega^{-1}\ m^{-1}$. [1] To achieve higher conductivity of the transparent electrodes, a combined electrode scheme using a thin aluminum metal stripe in contact with indium tin oxide, thus forming a hybrid electrode was proposed by Hope *et al.*[2] Since then, there have been several systems based on this idea.[3,4] However, it is reported[5] that the combination suffers severe corrosion when the combined conductor is cleaned in weak alkaline solutions, thereby causing disconnection and device failures. Furthermore, the contact resistance between aluminum and tin oxide or indium tin oxide is quite high; typically 80 Ω for a contact area of 1.6×10^3 μm. At temperatures above 200°C which may be encountered in the fabrication of subsequent layers such as ZnS:Mn or during the device operation, the tin oxide or indium tin oxide is readily reduced by the aluminum via the formation of the more stable oxide, Al_2O_3. Compared to aluminum, copper is an attractive alternative because its bulk resistivity is lower than that of aluminum and copper is also expected to be resistant to electromigration.[5] In addition, for the hybrid electrode of aluminum stripe and tin oxide, the aluminum film was prepared by vacuum methods.[2-4] By comparison, the copper electroplating process is cheap, easy to operate, and especially suitable for large area display and industrial production.

In our previous work,[6] a similar hybrid electrode was prepared by electroplating copper onto the sidewall of the tin oxide. By doing so, a one-order of magnitude improvement in electrode conductivity with minimal loss of transmission was obtained.[5] However, copper is less adhesive to the commonly used substrate than aluminum because of its lower activity. This is a frequently encountered problem for physical and chemical copper deposition[7] and the same problem was encountered in our experiments. In a wide range of both solution concentration (from 250 g/liter $CuSO_4 \cdot 5H_2O$ and 110 g/liter H_2SO_4 to 160 g/liter $CuSO_4 \cdot 5H_2O$ and 75 g/liter H_2SO_4) and electroplating current density (from 5 to 100 mA/cm^2), the deposited copper layers varied from powdery to dense; none of which had sufficiently good adhesion to the tin oxide thin film substrate. However, it was shown that if surface modification by electrolytic reduction was introduced just before electroplating, excellent adhesion between copper and tin oxide could be achieved with a fixed concentration (0.1 *M*) of H_2SO_4 acid and a reduction time of a few seconds to a few minutes at a current density between 5 to 25 mA/cm^2.[2] In this earlier work adhesion was assessed qualitatively by ultrasonic agitation, annealing to 150°C, rubbing, and peel tests. More recent measurements using a Sebastian Five *z*-axis load application unit has identified a 100 kg/cm^2

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