Deposition of thick silica–titania sol–gel films on Si substrates

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(Received 23 August 1993; revised manuscript received 18 January 1994)

Abstract

A process for production of thick (>10 μm) titania-doped silica films on Si substrates by repetitive spin-coating of sol–gel material and rapid thermal annealing for 10 s in the range 800–1200°C is described. The dependence of overall thickness and etch rate in buffered HF on annealing temperature is described, and it is shown that films annealed at low (<1175°C) temperatures have a relatively large thickness and etch rate. However, films having the properties of fully densified material (minimum thickness and etch rate) can be produced by subsequent consolidation. The film stress characteristics are similar to those of phosphosilicate glass formed by the same process: films annealed below a critical temperature (<1075°C) are under tensile stress at the annealing temperature, and crack before a thick film can be built up. Refractive index data are given; these show that only fully consolidated films have the refractive index expected from their SiO₂ and TiO₂ compositions. Finally, discrepancies in results for thicknesses of unconsolidated single-layer and multilayer films are explained using a simple model that accounts for the effect of cumulative densification.

1. Introduction

Thick films of silica and doped silica are deposited on silicon substrates by a number of methods, including thermal oxidation [1], sputtering [2], chemical vapour deposition [3], plasma-enhanced chemical vapour deposition [4] and flame hydrolysis [5]. All of these techniques have been used in silica-on-silicon integrated optics, where very thick films (20–50 μm) are mandatory [6]. There has also been interest in the use of sol–gel methods [7,8] in this application, due to their relative simplicity, safety and flexibility.

Sol–gel glass has been successful when used in thin planar layers [9]. It has also been used for a limited range of optical devices, including multilayer dielectric filters [10] and waveguides formed by laser densification of thin films [11,12]. However, wider application of sol–gel methods in the field of integrated optics has largely been precluded by the tendency of thick films to fail by cracking [10]. Recently, this limitation has been overcome, and a complete process for the fabrication of topographic guides in silica-on-silicon based on titania-doped silica sol–gel has been demonstrated. This process involves the deposition of thick films as multilayers, by repetitive spin-coating and rapid thermal annealing at high temperature [13]. Reactive ion etching, reflow and burial of features in such films have all been...
demonstrated [14]. The conditions needed for crack-free films have been found by applying the process to the production of a different material, commercial phosphosilicate spin-on glass [15].

In this paper, we describe other parameters of the process for production of thick TiO$_2$ : SiO$_2$ films on Si substrates. We first examine other important properties of thick films, including the dependence of the overall thickness and the etch rate in buffered HF on the annealing temperature. We show that predictable characteristics can be obtained if a simple consolidation step is used after deposition. We then show that the stress behaviour of this material is essentially similar to that of phosphosilicate glass, which indicates that the process may easily be applied to other doped glasses. Finally, we investigate the effect of cumulative densification, and show that the properties of single-layer and multilayer films can be explained by a simple model.

2. Experimental procedure

The sols used in this work were prepared following the method developed by Martina and Green [16]. Tetraethylorthosilicate (TEOS) and tetrapropylorthotitanate (TPOT) precursors were obtained commercially at 99.99+ % purity. Both were dissolved separately in ethanol, and the TEOS solution was partially hydrolysed by adding sufficient quantity of 0.1M hydrochloric acid (HCl) to take the mixture to a water: alkoxide ratio of unity and refluxing for 2 h at 70°C. Next, an appropriate quantity of TPOT solution was added to give the required TiO$_2$: SiO$_2$ ratio in the final film, further HCl was added to give a water: alkoxide ratio of 2 and the mixture was refluxed again. Finally, the sol was aged, typically for 24 h, and diluted in ethanol to yield the desired film thickness.

The sol was dispensed by hand from a syringe fitted with a 0.1 μm Gelman Acrodisc™ filter, spin-coated onto 3" diameter, 381 μm thick, (100) oriented Si wafers, and densified by rapid thermal annealing. Due to the relatively small thickness (60–600 nm) that could be deposited in one cycle without cracking, thick layers were built up by repetition of the following steps. In each cycle, the wafer was spin-coated at a fixed speed for 30 s, then annealed at a fixed temperature in the range 800–1200°C for 10 s, then cooled by convection. The cycle time was around 3 min using manual wafer handling.

In early experiments, the optical quality of the films was degraded by the inclusion of silica flakes, originating from material accumulating on the spinner bowl and on the rim of the wafer [13]. To alleviate this problem, we fitted the spinner with
a continual solvent flush, as shown in Fig. 1. This inhibited gelation on the bowl, and reduced the rate of solvent evaporation from the wafer so that more of the excess material was spun away. However, the thickness of each layer when the solvent flush was used was reduced compared with the value obtained without it.

Annealing was performed in an oxygen atmosphere, using a rapid thermal annealer (AG Associates Heatpulse 610). The wafer was supported inside the work chamber on a quartz tray, and an additional quartz plate was placed above the wafer to prevent material being deposited on the roof of the chamber (Fig. 2). This plate was removed regularly for cleaning, to minimise contamination by re-deposition. The extra thermal mass of the quartzware increased the cooling time to $\approx 30$ s, while the heating time was $\approx 4$ s. The substrate temperature was monitored throughout by an optical pyrometer.

A number of measurements were made. The curvatures of the wafers before and after film deposition were deduced to an accuracy of $\pm 1.25 \times 10^{-3}$ m$^{-1}$ from measurements of their parabolic surface profiles obtained using a surface profiler (Dektak IIa). Film thicknesses and etch rates in buffered HF were then found by measuring the step heights of features formed by patterning and wet etching. The accuracy of all thickness measurements was limited to $\pm 2.5$ nm by the presence of surface striations.

Total film stresses, $\sigma_f$, were then deduced from Stony's formula [17,18]:

$$\sigma_f = \left[ \frac{E_s t_s^2}{6(1 - \nu_s) t_f} \right] \left[ \frac{1}{r_f} - \frac{1}{r_s} \right],$$  

(1)

where $1/r_s$, $t_s$, $E_s$ and $\nu_s$ are, respectively, the curvature, thickness, Young's modulus and Poisson's ratio of the substrate, $1/r_f$ is the curvature of the wafer after deposition and $t_f$ is the film thickness. Values of $1.08 \times 10^{11}$ N/m$^2$ and 0.42 were assumed for $E_s$ and $\nu_s$, respectively.

The thermal contribution to stress caused by cooling from the annealing temperature, $T_A$, to the final (room) temperature, $T_0$, was then estimated by assuming constant thermal expansion coefficients for the film and substrate, as

$$\sigma_{th} = E_f (\alpha_s - \alpha_f) (T_0 - T_A)/(1 - \nu_f),$$  

(2)

where $E_f$, $\nu_f$ and $\alpha_f$ are, respectively, the Young's modulus, Poisson's ratio and thermal expansion coefficient of the film, and $\alpha_s$ is the expansion coefficient of the substrate. Here we assumed $E_f = 7.15 \times 10^{10}$ N/m$^2$, $\nu_f = 0.165$, $\alpha_f = 0.55 \times 10^{-6}$/°C and $\alpha_s = 2.6 \times 10^{-6}$/°C. Finally, intrinsic stresses, $\sigma_i$ (i.e., stresses at the $T_A$), were estimated as $\sigma_i = \sigma_f - \sigma_{th}$.

Optical refractive indices were measured at $\lambda = 0.633 \mu$m wavelength to an accuracy of one

![Fig. 3. Variation of layer thickness with spin speed for single-layer films of 6.25 mol% TiO$_2$:iO$_2$ diluted with different proportions of ethanol and annealed at 1075°C (some data from Ref. 80).](image-url)
part in $10^{-2}$, by two methods: an ellipsometer (Rudolf Research Auto EL) was used for single-layer films, and an Abbé refractometer (Bellingham and Stanley) was used for thick ($> 5\ \mu m$) multilayer films.

3. Results

3.1. Variation of film thickness with spin speed and sol composition

The sols used in most of our experiments were designed to give films with a doping level of 6.25 mol$\%$ titania (6.25 mol$\%$ TiO$_2$:SiO$_2$), because films with this composition were found to have the smallest surface striations [13]; however, we also investigated other dopant concentrations. Fig. 3 shows the variation of film thickness, $t_f$, with spin speed, $\omega$, for single-layer films diluted with different proportions of ethanol. Here, the composition ratio 3:1 refers to sol diluted with three volumes of ethanol, and so on. For a given dilution, the thickness was found to vary approximately as

$$t_f = k \omega^{-\gamma},$$

where $k$ and $\gamma$ are constants and $\gamma = 0.45$ in all cases. The same functional dependence has been observed in other spin-coating processes [19], although different values of $\gamma$ apply to other systems. As expected, the thickness at a given spin speed decreased as the sol was made more dilute. An annealing temperature of 1075$^\circ$C was used in all cases, for reasons which are explained below.

The maximum thickness obtained was 0.56 $\mu m$, for undiluted (0:1) sol-gel spin-coated at 1000 rpm. However, we have so far been unable to establish a reliable thick-film process based on such a large single-layer thickness, and the following results are for material diluted 1:1 with ethanol and spun at 1000 rpm. In this case, the single-layer thickness is 0.27 $\mu m$.

3.2. Variation of film thickness and density with annealing temperature

Fig. 4 shows the variation in thickness of five-layer films with annealing temperature, $T_A$. For $T_A < 925^\circ$C, the total thickness is constant at $\approx 1.5\ \mu m$, corresponding to $\approx 0.3\ \mu m$ per layer. However, above 925$^\circ$C the total thickness falls sharply, to 1.15 $\mu m$ at $T_A = 1175^\circ$C (0.23 $\mu m$ per layer). These results show that the thickness is strongly dependent on $T_A$, and that annealing at low temperature yields incompletely densified films. It should also be noted that, at $T_A = 1075^\circ$C, the total thickness was 1.26 $\mu m$. In this case, the average individual layer thickness ($\approx 0.25\ \mu m$ per layer) is less than the value given in the previous

![Graph showing film thickness versus rapid thermal annealing temperature.](image-url)
Fig. 5. Etch rate in buffered HF versus rapid thermal annealing temperature, $T_A$, for five-layer films of 6.25 mol% TiO$_2$:SiO$_2$ spin-coated at 1000 rpm, measured after deposition and consolidation.

section for single-layer films (0.27 μm), implying that iterative processing causes additional densification. This effect, which is discussed in Section 4, is important because it means that the thickness after $N$ process cycles is not simply $N$ times the thickness of a single layer.

After deposition, the films were consolidated in a tube furnace by heating at 1260°C for 10 min. These parameters were chosen to correspond to the conditions we commonly use when reflowing TiO$_2$:SiO$_2$ channel waveguides to remove sidewall roughness [14]. The thicknesses of five-layer films obtained after reflow are superimposed on Fig. 4. Although there is some variation, the final thicknesses are all around 1.1 μm, and are roughly independent of the initial annealing temperature. This result suggests that a simple consolidation step can be used to densify multilayer films completely. The final thickness per layer is $\approx$ 0.22 μm, so that fully consolidated 10 μm thick films may be constructed from approximately 45 individual layers (in about 135 min, using our current process).

An estimate of the degree of densification may

Fig. 6. Curvature difference, $1/r_t - 1/r_s$ versus number of layers for films of 6.25 mol% TiO$_2$:SiO$_2$ spin-coated at 1000 rpm, annealed at different temperatures, measured after deposition. Points are experimental data; lines represent the best linear fit to the data.
be obtained by measuring wet etch rates, which increase rapidly for porous films. Fig. 5 shows the variation of the surface etch rate in buffered HF for the same films as in Fig. 4. For material that has simply been spin-coated and rapidly annealed, the etch rate increases rapidly as $T_A$ decreases. For example, for $T_A = 875^\circ C$, the etch rate is 7.14 $\mu m/min$, approximately 100 times larger than for films annealed at $1175^\circ C (75$ $nm/min)$. However, films consolidated as described above all have etch rates between 67 and 75 $nm/min$.

Fig. 7. Curvature difference, $1/r_1 - 1/r_4$, versus rapid thermal annealing temperature, $T_A$, for five-layer films of 6.25 mol% $TiO_2 - SiO_2$ spin-coated at 1000 rpm, after deposition and consolidation.

Fig. 8. Appearance of a failed sol-gel film.
3.3. Variation of film stress with annealing temperature

The deposited films are stressed, leading to bowing of the wafer. Fig. 6 shows the variation of the curvature difference, $1/r_f - 1/r_s$, with number of layers, for multilayer films annealed at different temperatures. In each case, the variation is approximately linear, and a least-squares fit of the data to a linear function yields a line passing almost, but not quite, through the origin [10]. From Eq. (1), we would deduce that the film stress, $\sigma_f$, is constant (although this assumption is only an approximation, as we show below). For films annealed at 875 and 975°C, the slope of the linear function is negative, showing that the film stress was tensile and that film surface became increasingly concave as the deposition progressed. For films annealed at 1075 and 1175°C, the stress was compressive and the surface shape was convex.

This trend is illustrated in more detail in Fig. 7, where the curvature difference $1/r_f - 1/r_s$ is plotted against annealing temperature, $T_A$, for the same set of five-layer films as before. The curvature difference increases with $T_A$, being negative below $T_A \approx 1000°C$ and positive above this temperature. However, after consolidation, the curvature difference of all films was positive, and approximately independent of the temperature originally used for rapid thermal annealing.

A major problem with the deposition of multilayer sol–gel films on Si is that films annealed at relatively low temperatures tend to fail by cracking after a relatively small number of layers. However, this tendency decreases as the annealing temperature is increased. For example, in our experiments, films annealed at 825°C failed after only five layers, whereas those annealed at 975°C survived to seven or eight layers. However, five-layer films that survived deposition and rapid thermal annealing at temperatures below 975°C cracked during the consolidation process previously described.

Fig. 8 shows the appearance of a typical failed film. In most regions, cracks are oriented at 45° to the intersection of the (111) planes with the wafer surface (at 45° to the edges of the photograph) [8,10]. However, the cracks tend to follow radial directions in the vicinity of small particulate inclusions, as seen near the centre of the figure.

Cracks are caused by the existence of tensile stresses in the film. Since the curvature difference in Fig. 7 is zero at $T_A \approx 1000°C$, we might expect to be able to deposit stress-free films using this annealing temperature, and hence build up thick (> 10 μm) multilayers. In fact, even films

![Fig. 9. Total, intrinsic and thermal stress versus rapid thermal annealing temperature, $T_A$, for five-layer films of 6.25 mol% TiO<sub>2</sub>:SiO<sub>2</sub> spin-coated at 1000 rpm, measured after deposition.](image-url)
annealed at 1045°C failed after only 15 layers ($t_f = 3.5$ μm). The explanation is provided by Fig. 9, which shows the variation of the film stress, $\sigma_f$, the thermal stress, $\sigma_{th}$, and the intrinsic stress, $\sigma_i$, with $T_a$, as found from Eqs. (1) and (2) using the data of Figs. 4 and 7. While $\sigma_f$ is indeed zero at a critical annealing temperature, $T_{AC} \approx 1000°C$, $\sigma_i$ is not: it is large and positive. We have found that very thick films can only be formed when $T_a$ increases above a further critical value, $T_{AC} \approx 1075°C$, at which $\sigma_i$ falls to zero. Under these conditions, the stress in the film is compressive at all temperatures. Behaviour of this type was observed in sol--gel phosphosilicate glass (PSG) multilayers; however, the annealing temperature required for thick-film deposition of PSG was less (950°C) [15].

3.4. Cumulative densification

If consolidation is omitted, we have found that measurements of multilayer films yield inconsistent results due to variations in the degree of densification with depth. For example, Fig. 10

![Graph showing the variation of film thickness and curvature difference with annealing cycles at 1075°C.](image-url)

Fig. 11. Variation of film thickness, $t_f$, and curvature difference, $1/r_f - 1/r_s$, with number of additional annealing cycles at 1075°C for an unconsolidated single-layer film of 6.25 mol% TiO$_2$-SiO$_2$. Points are experimental data; lines are exponential fits to the data as described in the text.
shows the results of timed etching in buffered HF of films annealed at 1075 and 1175°C. For $T_a = 1175°C$, the etch depth varies linearly with time, indicating that the film is almost completely and uniformly densified. However, for $T_a = 1075°C$, the etch rate is not only much higher but also variable: for short etch times (i.e., near the surface) the rate is higher than for longer times (close to the substrate).

These variations arise because the annealing of each additional layer of material increases the densification of the layers beneath it. Cumulative densification was investigated by annealing films several times after spin-coating. For example, Fig. 11 shows the variation in thickness of one film with the number, $n$, of extra anneal cycles at $T_a = 1075°C$. To reduce the effect of surface striations (which cause random variations in thickness), a two-layer film was used here, and the thickness data obtained were scaled by a factor of two to simulate the behaviour of a single-layer structure.

To a good approximation, the layer thickness decreases exponentially with $n$, following

$$t_n = t_{0n} + (t_0 - t_{0n}) \exp\{-\beta n\}. \tag{4}$$

Here $t_{0n}$ is the thickness obtained without additional annealing, $t_0$ is the value obtained as $n \to \infty$ and $\beta$ is a constant. The data have been compared with Eq. (4), using the following best-fit values: $t_0 = 0.23 \mu m$ and $t_{0n} = 0.195 \mu m$ (corresponding to a final shrinkage of 15%) and $\beta = 0.108$. As can be seen, the thickness tends to a constant value after 25–30 cycles. Although this behaviour shows that full densification of each layer can be performed immediately after coating, we have found that the increase in cycle time required is not justifiable for thick films. Further, we noticed some variation in the value of the parameter $\beta$, depending on the age of the sol and the spin-coating conditions.

3.5. Cumulative variation in film stress

Cumulative densification also affects the stress of deposited films. Fig. 11 also shows the variation in curvature difference $1/r_1 - 1/r_2$ with the number of additional anneal cycles for a single-layer film. The effect of additional annealing is to increase the film curvature considerably, indicating that the film stress becomes more compressive as annealing proceeds.

The curvature data in Fig. 11 may be modelled with a similar exponential variation to that used for the thickness data. In this case, the best-fit value for the parameter $\beta$ was 0.064. Although this value is not identical to that previously found for the thickness variation, it is similar enough to indicate a common mechanism for densification and stress changes.

![Fig. 12. Refractive index versus composition for TiO$_2$:SiO$_2$ films after different thermal treatments.](image-url)
3.6. Variations in refractive index with composition

For waveguides, refractive indices must be controlled to 0.1% (by contrast with thicknesses, for which variations of 1.0% are acceptable). However, we found that the indices of multilayer films varied considerably. We have previously shown that residual porosity depends on the annealing schedule. Since porosity in turn affects the refractive index, the indices measured for single-layer, multilayer and consolidated multilayer films differ. In all cases, the index varies with composition as \( n(y) \approx n(0) + \frac{\partial n}{\partial y} \times y \), where \( y \) is the titania concentration in mol\%.

The following variations were observed:
- (a) single-layer films \( n(y) \approx 1.430 + 0.008y \);
- (b) multilayer films \( n(y) \approx 1.440 + 0.006y \);
- (c) consolidated multilayer films \( n(y) \approx 1.445 + 0.005y \).

These variations are shown in Fig. 12. Single-layer films are porous, with a relatively low value of \( n(0) \). Multilayer films have undergone additional annealing cycles, which densify the lower layers, so that \( n(0) \) increases. Finally, consolidated films have \( n(0) \) close to the refractive index of pure silica. An additional effect of densification is to decrease the sensitivity of refractive index to TiO\(_2\) concentration. We assume that this independence is caused by a reduction of composition-dependent porosity.

4. Discussion

The evidence presented in Section 3 – namely, discrepancies between the thickness values measured for single-layer and multilayer films, the variation of wet etch rate with etch depth and unexpected variations of film curvature with film thickness – indicates that the failure of the rapid thermal annealing process to densify each layer immediately after it is deposited has a significant effect on the consistency of film properties. In an attempt to explain some of these observations, we have therefore constructed a simple model of the deposition process.

In an \( N \)-layer multilayer film, the lowest layer has undergone \( N-1 \) additional anneals, and so on, until the uppermost layer has undergone no extra anneals. From the results of Section 3.4., we would expect the thickness of each layer to decrease exponentially with annealing time, so that the thickness of the \( i \)th layer would be

\[
t_i = t_{in} + (t_{in} - t_{in-1}) \exp\left\{ -\beta(N-i) \right\}.
\]

The total layer thickness is then

\[
t = \sum_{i=1}^{N} t_i = Nt_{in} + (t_{in} - t_{in-1}) \times \exp\left\{ -\beta(N-1)/2 \right\} \sinh(\beta N/2) / \sinh(\beta/2).
\]

The predictions of this model based on the data of Fig. 11 are shown in Fig. 13. The main feature is that the thickness does not vary linearly with the number of layers, thus explaining the observed thickness variability. For large \( N \), \( t_f \) is less than the value of \( Nt_{in} \) expected from simple multiplication of the single-layer thickness, and slightly more than the value of \( Nt_{in} \) obtained after consolidation. For thick (e.g., 10 \( \mu \)m) films, the error in the single-layer estimate may be large (\( \approx 1 \mu \)m), so if accurate knowledge of the final thickness is required, consolidation is essential.

Although we have not investigated this in detail yet, we feel that further extensions to the model (that link layer thickness to residual porosity, and porosity to etch rate) will account for the
observed variation in etch rate with etch depth shown in Fig. 10. However, using the exponential stress variation, we have constructed a model for the cumulative curvature of multilayer films, following an approach similar to that of Eqs. (4)–(6). This model shows that variations of curvature with film thickness or number of layers are not linear functions passing through the origin, providing an explanation for the behaviour previously shown in Fig. 6.

5. Conclusions

We have demonstrated that a sol–gel process based on the iterative use of spin-coating and rapid thermal annealing can be used to fabricate crack-free thick films of titania-doped silica on silicon substrates, provided the annealing temperature is above a critical value (1075°C). The use of rapid thermal processing reduces the cycle time to a few minutes, making the method viable as a production technique. However, a short (10 s) anneal time does not yield completely densified films, and causes variability in important film properties. While complete densification can be achieved by increasing the anneal time or temperature, the former results in a large increase in the cycle time, and the latter can cause substrate damage. However, a simple consolidation step can be used to produce consistent behaviour from material previously annealed for shorter times at lower temperatures.

The financial support of the Furukawa Electric Co. Ltd. for this work is gratefully acknowledged.

References