Fabrication of buried channel waveguides on silicon substrates using spin-on glass

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A new process for the deposition of thick (=10-μm) films of silica and titania-doped silica on silicon substrates is described. Films are built up by repetitive operation of a simple process cycle in which a layer of sol-gel material is deposited by spin coating, then densified by rapid thermal annealing. Stress-free layers are obtained through careful choice of the anneal temperature. Bilayer structures suitable for waveguide fabrication may also be constructed by performing two successive deposition runs using sol-gel precursors with different titania concentrations. These bilayers may be patterned topographically into ridges by using reactive ion etching, and the ridges may be planarized by applying additional layers of sol-gel material to form buried channel waveguides.

Key words: Spin-on glass, sol-gel, thick films, channel waveguides.

1. Introduction

Optical quality dielectric films of 10–20-μm thickness are a basic requirement for integrated-optic devices that are fabricated on silicon substrates. Because such films are thick by normal coating standards, a number of specialized methods have been developed to form them. These include wet thermal oxidation and thermal nitridation, sputtering, low-pressure and plasma-enhanced chemical vapor deposition, and flame hydrolysis. Each method has its own advantages and disadvantages. In some cases (e.g., wet thermal oxidation), the process is extremely time-consuming and suffers from a limit in ultimate thickness. In others (e.g., plasma-enhanced chemical vapor deposition), the nature of the process makes the deposition apparatus complicated and expensive.

Sol-gel technology offers an alternative method of depositing glassy films based on the hydrolysis and polycondensation of metal alkoxides. As with any sol-gel process, three basic stages are involved: formation of a sol (a stable suspension of particles within a liquid), processing of the sol to form a gel (a continuous solid network permeated by liquid), and drying of the gel to form a porous glass. Typically, the sol is applied to the surface to be coated either by spin coating (in which case the resulting material is referred to as spin-on glass) or by dip coating. Gel formation then follows as a result of solvent evaporation. The drying stage may simply involve heating the gel to evaporate the liquid phase, although higher temperature processing is often employed to remove any residual organic material by combustion and (if the temperature is high enough) to sinter the glass. One commonly used process involves the fabrication of silica (SiO₂) films from a sol based on tetraethylorthosilicate [Si(OC₂H₅)₄] or TEOS. However, a wide range of other metal alkoxides can be used, allowing a corresponding range of dielectric films.

Sol-gel silica films have been used as antireflection coatings and waveguiding layers. Refractive-index variations can be produced either by laser densification or by the introduction of a dopant. For example, titania doping may be achieved by adding to the silica precursor a titania precursor based on tetracyclolortitanate [Ti(OCH₃)₄ or TPOT]. In addition, since sol-gel films can be porous, they can act as host matrices for other materials. Potential guest materials include organic dyes that can be used for solid-state laser or sensor applications. Inorganic microcrystallites are also being considered for nonlinear switching because of the enhanced optical nonlinearity that is available from the quantum size effect when the pores in the host are small.

Unfortunately, the basic sol-gel process suffers from a serious limitation when it comes to depositing thick films, which is that the maximum thickness of a
layer resulting from a single deposition is \( \sim 0.7 \, \mu m \); thicker layers generally crack as a result of shrinkage at the drying stage. Of course, this limitation does not preclude the production of multilayer films in which each layer is spun on and dried before the next layer is deposited. However, it has been found previously that such films also tend to fail by cracking, even when each individual layer is considerably less than 0.7 \( \mu m \) thick.

The aim of this paper is to demonstrate that it is in fact possible to fabricate multilayer films by the method outlined above, but only if the sample is thermally annealed at the correct temperature after the application of each individual layer. This was originally observed in our laboratory by LeMeur and Green. Since then, we have developed a process that allows film thicknesses of greater than 10 \( \mu m \) to be reached with ease. Furthermore, the basic process can be modified to fabricate three-dimensional multilayer structures including buried channel waveguides. Although the process is a serial one, it avoids the use of both vacuum and dangerous process gases and can be implemented with relatively inexpensive equipment.

### Preparation of Sol-Gel Precursors

The sol-gel precursors used in this work are almost identical to those previously described by Martin and Green. We therefore discuss their preparation only briefly, concentrating instead on the new features of thick film deposition and waveguide fabrication.

The preparation of precursors follows the scheme shown in Fig. 1. TEOS and TPOT were both obtained commercially at 99.999% purity. Both were dissolved in an equal volume of ethanol, and an additional hydrochloric acid catalyst was added to the TEOS precursor to take the mixture to a water:alkoxide ratio (denoted \( R \) in Fig. 1) of unity. This mixture was then hydrolyzed by refluxing at 70 °C for 2 h. The TEOS and TPOT precursors were then mixed together to give the required silicon-titania ratio. Further quantities of ethanol and the hydrochloric acid catalyst were then added to take the water:alkoxide ratio to \( R = 2 \), and the mixture was aged, typically for 24 h. A final dilution of ethanol (typically 1.5 parts ethanol:1 part sol-gel by volume) was made to achieve the required viscosity before use.

### Production of Thick Films

Our process for the deposition of thick films on silicon is shown in Fig. 2. Currently we are using 525-\( \mu m \)-thick, 4-in. (10-cm) diameter, (100)-oriented Si wafers. After preparation of the precursors, the wafer to be coated was annealed a number of times to ash any organic surface contaminants and to remove moisture; this promotes adhesion of the sol-gel material to the substrate. A thick film was then built up as a multilayer. At each iteration, the wafer was spin coated with sol-gel material, annealed at a fixed temperature for a fixed time, then cooled. The cycle time is \( \sim 3 \) min at normal work rates, using manual transfer of the wafer between the spinner and the annealer. Important features of the process are described below in some detail.

#### Spin Coating

At the dispensing step, the sol-gel material was filtered to 0.2 \( \mu m \) and applied to the wafer by using a syringe. The wafer was then spun for 30 s at a speed in the broad range of 1000–5000 rpm. The variation of the thickness of single annealed layers with spin speed is as shown in Fig. 3 for silicas doped with 6.25-mol. % titania and diluted with ethanol in the ratios of 1 part ethanol:1 part sol-gel, 2:1, and 3:1. Typically, the layer thickness obtained at a given spin speed decreases with the dilution and increases with the titania concentration. For flat layers, we used a slow spin speed (e.g., 1000 rpm) and a low dilution (e.g., 1.5:1); this yields a relatively fast build-up rate of \( \sim 2000 \, \text{Å}/\text{spin} \) for pure silica and \( \sim 2400 \, \text{Å}/\text{spin} \) for titania-doped silicas.
for silica doped with 6.25-mol. % titania. However, as is explained below, much higher speeds (as high as 5000 rpm) are used for planarizing. Two problems are associated with spin coating: film thickness nonuniformity and contamination by particulate inclusions.

Thickness nonuniformity is manifest in two different guises. The first is a slow radial variation in film thickness \( t(r) \), which may be observed as a concentric interference pattern when the coated wafer is viewed under partially coherent illumination. Figure 4 shows the variation in the normalized thickness \( t(r)/t(0) \) for a typical thick film. Devices are fabricated by using the most uniform central portion of the wafer; in this region (e.g., as high as \( r = 40 \) mm) the thickness variation is \( \pm 0.6\% \), which is relatively unimportant for optical applications. However, outside this region, the thickness falls sharply.

The second nonuniformity is a faster circumferential variation, which may be seen as a pattern of radial striations. Surface profile measurements that were made by using a Sloan Dektak II indicate that the thickness fluctuation in this case is of the order of 100-Å peak-to-peak. Striations were formed on every layer of a multilayer film, leading to cumulative surface roughness. This may cause significant scattering in films that are intended for optical applications. The striations appear to be virtually independent of the spin duration and are smaller at faster spin speeds and for particular sol-gel compositions.

We have no explanation for these observations at present.

Although all our sol-gel processing is performed in a Class 100 clean room, we found that large numbers of particulate inclusions occur in our films unless special precautions are taken. These are primarily silica flakes that arise from the wafer itself and from the spin coater. At spin speeds below 1000 rpm, a significant amount of material builds up at the edge of the wafer, and this tends to crack off during annealing and wafer handling. Also, the excess solution that is deposited on the spin coater in each cycle gets and is then swept up and redeposited on the wafer in later process cycles. These problems have been reduced significantly by frequently cleaning the internal quartzware of the annealer and by continually flushing the bowl of the spinner with ethanol using a recirculating pump.

**Fig. 3.** Variation of single layer thickness with spin speed for silica doped with 6.25-mol. % titania and diluted with different amounts of ethanol.

**Fig. 4.** Variation of normalized layer thickness \( t(r)/t(0) \) over a 4-in. (10-cm) wafer.

**Fig. 5.** Variation of wafer curvature and film stress with annealing temperature.

**Annealing**

Annealing is performed by using an AG Associates Heatpulse 610 rapid thermal annealer. The wafer is heated over a 4-s interval, held at the anneal temperature for 10 s, then cooled to room temperature for 60 s. The substrate temperature is monitored by an optical pyrometer. In initial experiments performed in a nitrogen atmosphere, sooty deposits were observed on the quartz liner of the work chamber after annealing and, more seriously, in the annealed layer itself. All subsequent work has therefore been performed in oxygen, which apparently yields pure silica. Very thick (>10 μm) films of either silica or titania-doped silica can be built up by annealing at \( T_a = 1075^\circ C \). At or near this temperature, wafers emerge from the deposition process virtually flat (a radius of curvature in excess of 3 m at all points is obtained routinely). This indicates that the films are not significantly stressed. Furthermore, the films are dense and homogeneous; individual layers are not discernible in scanning electron microscope examinations, and no delamination has been observed after any further processing. At lower temperatures (\( T < T_a \)), the film surface is generally concave, implying the existence of tensile, balanced principal stresses in the film (\( \sigma_p > 0 \)). Such films typically fail by crazing and peeling after a relatively small number of process cycles (5–10). At higher temperatures (\( T > T_a \)), the film surface is approximately convex, implying the existence of compressive principal stress in the film (\( \sigma_p < 0 \)). Such films do not peel, although they often exhibit the different failure mode that is described below. The overall effects of annealing are summarized in Fig. 5: the transition between the different
regimes of behavior takes place over the narrow temperature range $\Delta T = 100^\circ C$.

We have demonstrated that wafers can survive a considerable number of process cycles (as many as 80). Unfortunately, at high anneal temperatures there can be significant wafer distortion because of the gradual migration of slip lines from damage sites at the periphery of the wafer. In our case, these lines are oriented parallel and orthogonal to the primary flat [i.e., the $x$ and $y$ axes in Fig. 6(a)], and cause saddle-shaped surface distortions. This can induce high local wafer curvature and, if the radii of curvature are different in orthogonal directions, the principal streses become unbalanced ($\tau_{xx} \neq \tau_{yy}$), leading to a nonzero shear stress $\tau_{xy}$ acting at 45° to the $x$ and $y$ axes. Shear cracks are then generated in these directions. Although this failure mode does not cause peeling, the shear cracks render the film useless.

The likelihood of shear cracking can be reduced by using thicker (e.g., 1-mm) Si wafers, since the substrate deformation is reduced. Also, we have noticed that some sol-gel compositions appear less prone to shear cracking than others.

**Fabrication of Buried Channel Waveguides**

The fabrication of buried channel waveguides follows the sequence shown in Fig. 7. First, a bilayer was formed by using two deposition runs [Fig. 7(a)]. The refractive-index difference between the layers needed for waveguiding was obtained by using silica doped with different levels of titania for each layer. By using two different measurement techniques (based on an ellipsometer and an Abbé refractometer, respectively) we found that the refractive index of weakly doped silica–titania films made by our process is $n = 1.43 + (0.008)y$, where $y$ is the titania concentration in mole percent. Note that the index obtained when $y = 0$ (pure silica) is 1.43, which is some way below that found in bulk silica ($n = 1.456$). This suggests that the films may not be completely densified.

Currently, the film compositions are chosen to reduce the effect of surface striations. Typically, for the lower (buffer) layer of a waveguide, we use 7-$\mu$m thickness of silica doped with 0.25 mol. % of titania, giving a refractive index of $n = 1.48$. For the (upper) guide layer, we use 4-$\mu$m thickness of silica doped with 7.5 mol. % of titania, giving $n = 1.49$ (corresponding to an increase of $\approx 0.01$ in refractive index over that of the buffer layer).

A 0.2-μm-thick chromium mask was sputtered onto the guide layer and patterned by using standard photolithography and wet etching techniques. The guide layer was then dry etched to produce 7-μm-/$\lambda$ wide ridge-guide structures [Fig. 7(b)]. We used a Plasma Technology RIE60 reactive ion etcher with a three-gas mixture comprising CHF$_3$, Ar, and O$_2$ at flow rates of 25, 25, and 1 SCCM, respectively. SCCM denotes cubic centimeter per minute at STP. The rf power was 140 W, the dc bias was 460 V, and the pressure was 50 mTorr. Under these conditions, the etch rates were ~670 A/min for SiO$_2$ and ~780 A/min for SiO$_2$ doped with 7.5-mol. % TiO$_2$.

After removal of the chromium mask, the ridges were buried under additional layers of sol-gel material having the same index as the buffer. Planarization of 4-μm-high features appears to pose no intrinsic difficulties, although some care must be taken in choosing the process parameters because the buried layer builds up more rapidly in some regions than in others. For example, for ridges that run orthogonal to the preferred direction of fluid flow during spinning (i.e., the radial direction), coverage is asymmetric, with material accumulating on the upstream side [Fig. 7(c)]. Material is also trapped between closely spaced ridges (e.g., in the center of directional coupler geometries). If the deposition rate is too high in these regions of accumulation, the glass cracks during annealing. We have therefore developed a planarization schedule in which the initial layers are deposited by using dilute solutions spun at high speeds. As burial proceeds, step features become smoother and the viscosity of the solution and the spin speed can gradually be restored to their normal values.

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Fig. 6. (a) Orientation of slip lines and shear cracks in highly distorted (100) wafers; (b) regions of asymmetric ($A, A'$) and symmetric ($B, B'$) coverage during planarization.

Fig. 7. Guide fabrication: (a) initial bilayers, (b) profile after ridge formation by reactive ion etchings, (c) profile at start of burial stage, (d) profile at end of burial stage.
Even with dilute solutions there is some residual variation in the cross-sectional shape of partially buried guides with position on the wafer. In particular, referring to Fig. 6(b), the profiles at points A and A' are generally less symmetric than those at B and B'. However, the profiles of fully buried guides are relatively symmetric [Fig. 7(d)] and smooth by comparison with some other processes (e.g., plasma-enhanced chemical vapor deposition). Figures 8(a), 8(b), and 8(c) are scanning electron microscope photographs of typical ridge-guide structures before, during, and after planarization.

We have measured the propagation losses at 0.633-μm wavelength for a number of buried channel guides by coupling light from a He–Ne laser into each waveguide in turn and by measuring the variation of the scattered light intensity with propagation distance using a traveling microscope. The guides are multimode at this wavelength, and it is not possible to isolate a particular mode. However, the method allows an estimate of the propagation loss, which is \( \sim 2.4 \, \text{dB/cm} \). Sidewall roughness that results from the reactive ion etching process appears to make a significant contribution to this figure, since the initial bilayer exhibits a loss of just 0.6 dB/cm at the same wavelength when it acts as a planar waveguide. We have verified that the guides are single mode at near-infrared wavelengths (1.5 μm). However, because of the relatively small size of the core (and the interfacial scattering mentioned above) they are extremely lossy. We are therefore currently investigating the use of larger cores together with a yellow step to remove sidewall roughness.

Conclusions

We have devised a new process for the fabrication of silica and titania-doped silica films on silicon substrates based on a simple repetitive process that involves spin coating and densification by rapid thermal annealing. This has been demonstrated by using relatively cheap manually operated equipment. However, there is clear potential for an automated industrial process that employs a spinner and an annealer linked by a wafer-track system.

We have identified suitable parameters for the deposition of stress-free films of greater than 10-μm thickness and have shown that bilayers suitable for waveguide fabrication may be constructed by using precursors with different titania concentrations. Similarly, we have demonstrated that these films can survive topographic patterning into ridges by reactive ion etching and that the ridges may be planarized with further spin coating by using dilute solutions to form buried channel waveguides. Using this method, we have fabricated channel waveguides with losses of \( \sim 2.4 \, \text{dB/cm} \) at 0.633-μm wavelength.

The most serious drawbacks of the process appear to be the inclusion of particles in the films and damage to the crystalline lattice of the substrate; these still require investigation. However, the experiments described here should be considered only as a first iteration—there is still considerable scope for optimization of the process parameters to alleviate these difficulties.

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