Stress in thick sol–gel phosphosilicate glass films formed on Si substrates

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(Received 1 March 1993; revised manuscript received 24 June 1993)

Abstract

It is shown that thick (> 10 μm) films of phosphosilicate glass may be formed on silicon substrates by repetitive spin-coating and rapid thermal annealing of commercial sol–gel material. The viability of the process is explained in terms of film stresses, and it is demonstrated that annealing above a critical temperature is necessary to prevent stress failure.

1. Introduction

Thick (> 10 μm) films of silica and doped silica on Si substrates are essential in two technological fields: silica-on-silicon integrated optics, and micromechanics. In the former, they are required for their optical properties, and in the latter they are used as sacrificial materials. Thermal oxidation, sputtering, chemical vapour deposition (CVD), plasma-enhanced chemical vapour deposition (PECVD), sputtering and flame hydrolysis have all been used for integrated optics [1–3]; however, in micromechanics, CVD and PECVD have been almost universally popular [4].

Optical waveguides have also been produced by laser densification of sol–gel glass [5]. A key problem with sol–gel materials has been the difficulty of producing thick films: generally, films fail by cracking at thicknesses well below 10 μm, especially on Si substrates (although cracking was not observed in a 2 μm-thick multilayer dielectric filter formed on Si [6]). Recently, however, a complete process for the fabrication of SiO₂/Si integrated optic devices has been described, using titania-doped silica sol–gel glass [7]. This involved the deposition of thick films as multilayers, by repetitive spin-coating and rapid thermal annealing at a high temperature (1075°C). In this paper, we describe the extension of the method to a different sol–gel material, phosphosilicate glass (PSG), and provide an explanation for the viability of the process in terms of film stress.

2. Experimental procedure

The aim of the experiments described here was to investigate the use of commercial PSG
sol–gel for thick film deposition. Two compositions from the Allied Signal Accuglass® P-XXY series [8,9] were investigated: P-112A (containing 2 mol% P₂O₅) and P-114A (4 mol% P₂O₅). All films were deposited on 4" diameter (100) p-type Si wafers, with a nominal thickness of 525 µm.

Initial layers were deposited on native oxide. Thick films were then built up by iterative deposition of thin layers. Each layer was spin-coated at 2000 rpm for 30 s, and then annealed for 10 s in O₂ using a rapid thermal annealer (AG Associates Heatpulse). The use of a rapid thermal annealing (as opposed to furnace heating) allows thick films to be built up in a reasonable time; with manual wafer handling, the cycle time is 3–4 min per layer [7]. Individual layer thicknesses were 125–135 nm for P-112A and 130–145 nm for P-114A. These values are higher than the manufacturer’s data for material cured at 425°C (123 nm for P-112A and 131 nm for P-114A) [8].

In previous experiments [7], the annealing temperature, Tₐ, was found to be critical for the avoidance of cracking, so Tₐ was considered a variable. In particular, the aim was to determine the effect of Tₐ on the film stress, σ. Film stress was determined from film curvature, by using Stoney’s formula [10–13]:

\[
\sigma = \frac{E_s t_s^2}{6(1 - \nu_s)} \left[ \frac{1}{r_f} - \frac{1}{r_i} \right],
\]

where \( 1/r_i \) is the curvature of the substrate without film, \( 1/r_f \) is the curvature with film, \( E_s \) and \( \nu_s \) are the thickness, Young’s modulus and Poisson’s ratio of the substrate, and \( r_f \) is the thickness of the film. Following the standard convention [10–13], tensile stresses are taken to be positive, and compressive stresses negative. In the latter case, the film surface is typically convex and \( r_f \) is positive.

Curvatures were deduced from the parabolic shapes of films, which were measured by an auto-leveling Dektak IIA surface profiler. The data presented are averages of two measurements per wafer, taken from surface profiles made in orthogonal directions. The initial wafer curvature, \( 1/r_i \), was normally small (of order \( 5 \times 10^{-3} \) m⁻¹) compared with the curvature measured after deposition of the film (which reached \( 2.5 \times 10^{-1} \) m⁻¹ for thick films). However, lack of symmetry in the initial shape of the wafer placed a limit on measurement accuracy of \( \pm 1.25 \times 10^{-3} \) m⁻¹. Measurements were made 2 min after annealing. However, no variations in curvature were observed over a period of several months. In addition, no systematic changes in film thickness or curvature were observed when films were sintered at 950°C in air for 30 min after deposition.

Film thicknesses were established by measurement of step features formed by photolithography and wet chemical etching. The data given are each average of eight measurements. In this case, a limit of \( \pm 2.5 \) nm is placed on accuracy by the presence of surface striations formed during spin coating [9].

3. Results

Some variations in thickness with radial position, \( R \), were observed. Generally, the film thickness was highest at the centre of the wafer, and approximately constant for \( 0 \) mm < \( R \) < 40 mm. However, it decreased sharply for \( 40 \) mm < \( R \) < 50 mm. Fig. 1 shows the radial thickness variation for single-layer films of the two materials when annealed at \( T_a = 950°C \). This variation (\( \approx 2.5\% \)) is also rather higher than the manufacturer’s data (2% total variation) [8]. Measurements were therefore taken from the most uni-

![Fig. 1. Radial variation, \( R \), of layer thickness, \( t \), for P-112A and P-114A phosphosilicate glass deposited at 2000 rpm and annealed for 10 s in O₂ at 950°C.](image)
form central portion of the wafer. Further slight variations in thickness with annealing temperature were also observed; however, these were not significant over the range of $T_A$ considered.

Fig. 2 shows the variation of curvature difference $1/r_{12} - 1/r_{23}$ with annealing temperature for the two materials, for five-layer films (thinner films gave different and variable results, as described below). The curvature difference is positive over the entire range considered, implying a compressive film stress. For both materials, the curvature difference increases approximately linearly with $T_A$.

There is some variation in published data [3, 10, 11] for $E_s/(1 - v_s)$; here we have assumed the value $1.8 \times 10^{11}$ N/m$^2$. Using this value and other known geometric parameters, the variation of $\sigma_r$ with $T_A$ may be deduced. This variation is shown in Fig. 3 for P-112A material, together with a best-fit linear function. The film stress becomes increasingly compressive as the annealing temperature is increased; this trend is consistent with the behaviour of oxide films formed by other methods. For example, the stresses in silica and PSG films deposited on Si substrates by PECVD increase when annealed below a temperature of ~800°C, but decrease when annealed above it [11, 12, 14].

Assuming that tensile film stresses are the primary cause of cracking, this suggests that it should be possible to deposit thick films with annealing temperatures higher than a critical value $T_{AC}$ at which $\sigma_r = 0$. From Fig. 3, $T_{AC} \approx 850°C$. However, films of P-112A deposited at 850°C failed at 20 layers ($t_f = 2.6 \mu$m), while films deposited at 900°C failed at 48 layers (6.24 µm). Typically, failure involved the appearance of cracks mainly oriented at 45° to the intersection of the (111) planes with the wafer surface (although other orientations were observed near inclusions).

From the crack orientations, it was deduced that the predominant failure mode was shear failure; however, the exact failure mechanism is currently unclear. One possibility is that dislocation migration from the wafer edges, a significant problem in our earlier process [7], causes wafer distortion, which could in turn result in unbalanced principal stresses in the film, and hence give rise to shear stress.

It was necessary to increase $T_A$ to 950°C for the deposition of films as thick as 10 µm. For example, Fig. 4 shows typical variations in curvature difference $1/r_{12} - 1/r_{23}$ with $T_A$, measured for the two different materials as the number of layers increased during deposition of thick films. Best fit linear functions for the two sets of data are also shown. In each case, agreement with the
data is good, suggesting that a linear variation of stress with thickness is a good approximation, and hence that the film stresses must be almost constant throughout the process. Further, since the slopes of the functions are similar, the film stresses must be comparable for the two materials.

The thickness of the P-114A layer reached 10 \( \mu \text{m} \) after 75 process cycles. At this number of cycles, the radius of curvature of the film is approximately 4 m. The distortion to the Si substrate caused by dislocation migration was reduced compared with wafers processed in a similar way at \( T_A = 1075^\circ \text{C} \) [7].

4. Discussion

The film stress, \( \sigma_f \), generally has two components. The first is caused by the mismatch between the thermal expansion coefficients of the film and the substrate, and appears as the wafer is cooled from \( T_A \) to a final temperature, \( T \). Assuming approximately constant thermal expansion coefficients (true to reasonable accuracy [10–13]), this is given by

\[
\sigma_{th} = E_t (\alpha_f - \alpha_s) (T - T_A)/(1 - \nu_t),
\]

where \( E_t, \nu_t \), and \( \alpha_t \) are the Young’s modulus, Poisson’s ratio, and thermal expansion coefficient of the film, and \( \alpha_s \) is the expansion coefficient of the substrate. Knowing these parameters, the value of \( \sigma_{th} \) at room temperature may be calculated. For simplicity, we have taken the values for pure silica for the PSG films considered here. Again, there is some variation in available data, and we have assumed \( E_t(1 - \nu_t) = 8.5 \times 10^{10} \) N/m\(^2\), \( \alpha_f = 0.55 \times 10^{-6}/^\circ \text{C} \) and \( \alpha_s = 2.6 \times 10^{-6}/^\circ \text{C} \). Figure 3 shows the resulting variation in \( \sigma_f \) with \( T_A \) for P-112A. It is almost constant over the range of \( T_A \).

The second contribution is an intrinsic stress, \( \sigma_i \), which is the stress at the deposition temperature. This can be estimated as \( \sigma_t = \sigma_f - \sigma_{th} \) [10–13]. The variation of \( \sigma_i \) with \( T_A \) is also shown in Fig. 3, together with a best-fit linear function. Note that \( \sigma_i \) changes sign at a critical temperature \( T_{AC} \) (\( = 950^\circ \text{C} \)), being tensile below this value and compressive above it. This is the explanation for the failure of some films. Annealing at temperatures above \( T_{AC} \) is insufficient to prevent tensile stresses, since these may arise as the material is actually being annealed for all values of \( T_A \) between \( T_{AC} \) and \( T_{AC'} \). Only when \( T_A \) is increased above \( T_{AC'} \) is the film stress compressive throughout the process. Thus, for this material, 950°C is the minimum annealing temperature for thick film deposition.

The description above explains most of the observed behaviour of thick sol–gel films. However, there is evidence that different effects occur in films containing only a small number of layers. For example, the variations of \( 1/r_t - 1/r_s \) with \( t_t \) shown in Fig. 4 do not pass through the origin, which suggests that the stress in films containing few layers is less compressive than that in films containing many. For PSG, we find that the film stress reaches its final value, to good approximation, after deposition of five layers. However, the stress in the first layer can be significantly different.

5. Conclusion

We have demonstrated that the spin-coating and rapid thermal annealing process previously demonstrated [7] for deposition of titania-doped
silica sol–gel glass on silicon is applicable to other similar materials. From measurements of curvatures as the deposition proceeds, the film stresses can be established, and hence process parameters can be chosen for crack-free deposition.

The financial support of the Science and Engineering Research Council and of the DTI under the LINK project ‘POINTS – Passive Optical Interconnects on Silicon’ is gratefully acknowledged.

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