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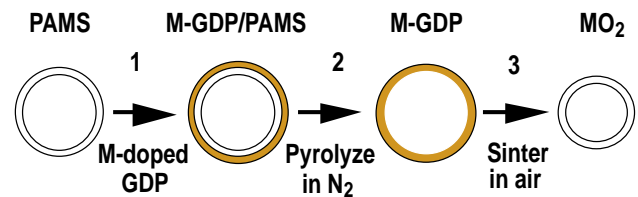
ABSTRACT

An entirely new process was discovered starting from M-doped glow discharge polymer (GDP) deposited by plasma polymerization¹ (where M = Si or Ti) to make M-oxide shells. This process utilizing Si-GDP was developed to make large, uniform, thick-walled glass shells which are suitable for use in cryogenic layering experiments at LLNL and are unobtainable by the routinely utilized drop-tower method. We have found that in addition to controlling the geometry, the permeability and opacity may be controllable over very wide ranges by varying the processing conditions. Preliminary tests to determine the strength of SiO₂ glass shells made by this process are consistent with that expected of pure silica glass.

I. INTRODUCTION

We discovered last year that it was possible to make high quality glass shells by adding another step to the GDP/PAMS technique developed by Letts.² In step one, doped GDP is deposited on Poly(α -methylstyrene) PAMS shells. The dopant needs to be one that forms a suitable oxide, such as silicon or titanium. In step two the shell is pyrolyzed at about 300°C in an inert gas, such as nitrogen, to remove the PAMS. In the final step, the doped GDP shell is pyrolyzed in air atmosphere to convert it into a glass shell (Fig. 1).

Following the discovery that we could convert silicon doped GDP into high quality glass shells (Fig. 2) less than 1 mm in final diameter we began attempts to make even larger glass shells. Large, strong glass shells with excellent concentricity and surface finish would be of great advantage for DT layering experiments since they could be handled at room temperature and would not



Where Metal (M) = Si or Ti

Fig. 1. Doped GDP shells are converted to glass shells.

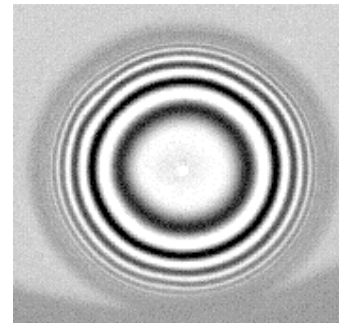


Fig. 2. An interferometric image of an SiO₂ shell resulting from the pyrolysis of Si-GDP confirms this process is capable of producing highly uniform shells.

require a fill tube. The wall thickness and diameter requirements (i.d. \geq 1400 μm ; wall \geq 12 μm) for the desired shells were outside of the range which could be made using the drop-tower method.

The largest high quality PAMS mandrels we had available for this project were near 2100 μm in outer diameter with \sim 12 μm walls. However, substantial shrinkage (\sim 30% in o.d. and wall) that occurs in the sintering step of the process, meant that even if we were successful in optimizing the process we would only be

able to make glass shells near the low end of the desired specification (1400 μm o.d.).

Three substantial difficulties had to be overcome in order obtain glass shells starting from the ~ 2100 μm PAMS mandrels we had available: preventing the Si-GDP mandrel from collapsing or shattering during the PAMS removal step; preventing the Si-GDP mandrel from turning black and becoming opaque during the air pyrolysis step; and preventing the mandrel from fracturing during the conversion of Si-GDP to glass.

II. EXPERIMENTAL

All beginning PAMS mandrels were made by the droplet generator technique.³ The PAMS mandrels were coated with Si-doped GDP in a number of different coatings runs to determine the optimal silicon concentration for this process. All shells were bounce coated in a plasma polymerization system based on a helical resonator and piezo bouncer described by previous authors.^{1,4} Tetramethyl silane (TMS), trans-2-butene (T2B) and hydrogen were used as feed-stock gases for the plasma coater. After the GDP coating step was completed the PAMS mandrel was removed by a controlled heating process in which the temperature was slowly ramped to 290°C under nitrogen to decompose and volatilize the PAMS polymer.

The resulting Si-GDP mandrel was then converted into a glass shell by slow pyrolysis and sintering in air up to 1000°C in a conventional box oven. Permeation and strength tests were conducted using helium and hydrogen on shells sintered to either 700 or 1000°C. Interferometric measurements of the shells were made to ascertain the wall thickness, index of refraction, and wall uniformity. A spheremapper (a specially developed atomic force microscope⁵ (AFM)) and scanning electron microscope (SEM) were utilized to ascertain sphericity and outer surface finish information on shells at various stages in their manufacture.

III. RESULTS AND DISCUSSION

Resolution of the problems encountered during PAMS removal were accomplished by adjusting the silicon concentration in the silicon-doped GDP and optimizing pyrolysis conditions. Control of silicon concentration proved to be crucial. Utilizing TMS as the dopant gas we were able to obtain Si-GDP coatings with up to ~ 13 at.% silicon. High silicon concentration minimizes shrinkage and adds rigidity to the mandrel helping to eliminate deformation or collapse of the shell during PAMS removal. However, too high a concentration

of silicon leads to a brittle shell which shatters during the PAMS removal step. A compromise concentration was found to be about 8 at.% silicon in Si-GDP. In addition to controlling the Si concentration, utilizing PAMS mandrels with as thin a wall as possible and slowing the PAMS removal process to a two day procedure also proved beneficial. Figure 3 illustrates the quality of the Si-GDP mandrels which can be made by this process. The AFM spectra of the free-standing Si doped GDP mandrel is essentially identical to that of the PAMS mandrel.

Once PAMS-free Si-GDP mandrels of suitable size and wall thickness were made, the key to making clear and colorless glass shells was optimizing the pyrolysis conditions (Fig. 4). If the temperature in the oven is raised to 600°C before all of the hydrocarbon has burned away formation of carbides and/or graphite results and the resulting shell is black Fig. 4(a). If instead the temperature is maintained at 550°C in air for a sufficient length of time the resulting glass shell is clear and colorless Fig. 4(b). Since C-H bonds generally are not stable in excess of 600°C this result is not entirely surprising.

The final problem, that of shell fracturing during air pyrolysis, has not been fully resolved. This failure mode frequently results in the formation of hemishells (Fig. 5).

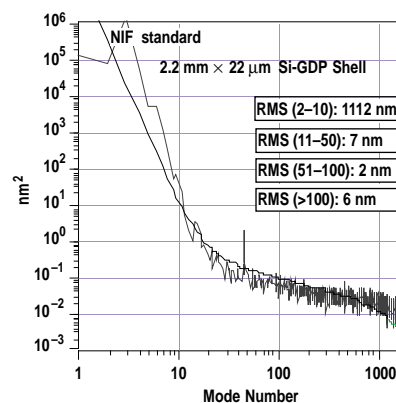


Fig. 3. AFM power spectrum of Si-GDP.

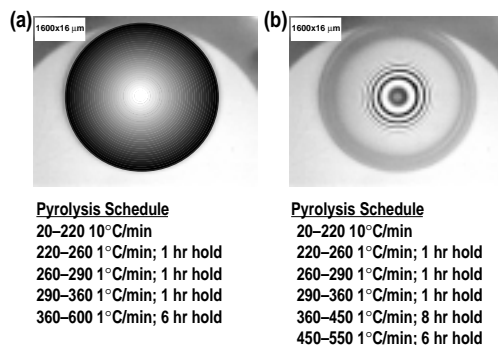


Fig. 4. Pyrolysis conditions can determine whether the resulting shell is opaque or transparent.

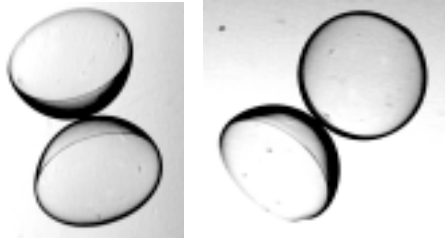


Fig. 5. Hemishell formation is a common failure mode during conversion of thick walled Si-GDP shells into glass shells.

The yield of this air pyrolysis step currently is around 30% for glass shells ~1400 μm o.d. with walls ~13 μm thick.

The Si-GDP shells that survive the conversion to fully dense SiO₂ shells at 1000°C can be made with very low geometrical deformation as illustrated in this AFM of a 1350 μm o.d. × 13 μm wall glass shell (Fig. 6).

Utilizing an SEM allows us to obtain a detailed picture of what the surface structure of the glass shells look like. It is not surprising to find that the surface structure of the glass looks essentially identical to that of the GDP from which it came. Figure 7 illustrates the surface finish of a fully pyrolyzed (1000°C) glass shell and that of a typical GDP type surface.

Glass shells resulting from Si-GDP pyrolyzed to 600°C in air are not yet fully dense. He permeation through these glass shells at room temperature has a half-life of seconds, and deuterium only minutes (Fig. 8).

However, after sintering to 700°C these shells are essentially impermeable to oxygen and water as is confirmed by the formation of water droplets inside a shell during an attempt to fill one such shell with deuterium at 360°C. After sintering at 1000°C for an extended period of time the resulting fully dense shells exhibited permeation properties expected of pure silica glass⁶ shells (Fig 9).

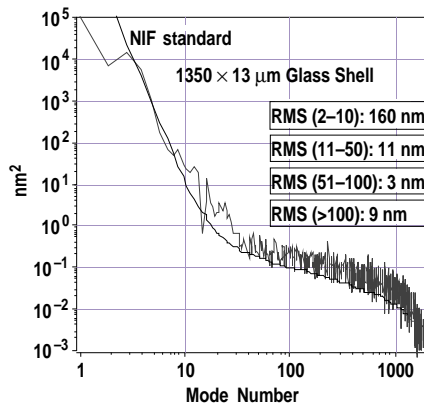


Fig. 6. AFM demonstrates the high quality of SiO₂ shells which can be made from Si-GDP.

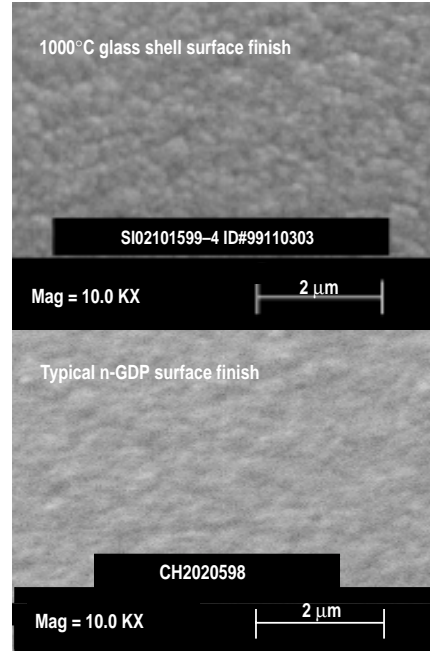
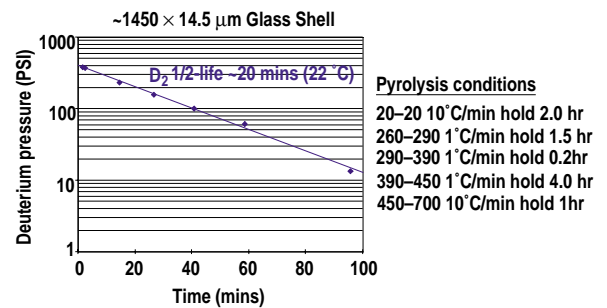


Fig. 7. SEM surface structure of n-GDP and glass are similar.

Strength tests (compression and burst) utilizing helium gas on a few fully densified shells made by this process, although not yet tested to full strength, are consistent with that expected of fully dense glass. Glass shells of two different diameters and wall thickness, were pressure tested by filling with He gas at room temperature in a single pressurization step. The larger o.d. shell (~1400 μm o.d.) also had an overcoat of ~100 μm of GDP which enhances the wall strength.⁷ The results were plotted as Fill Pressure versus Aspect Ratio (A.R. = o.d./w) with the expected 50% survival pressure expected for full strength glass as a reference (Fig. 10).

IV. CONCLUSIONS

We have demonstrated that it is possible to manufacture high quality, transparent glass shells starting from the PAMS/GDP process. The shell size and



* Note: He 1/2-life was only seconds for the same shell while water is essentially impermeable.

Fig. 8. Deuterium permeation thru glass shell sintered at 700°C.

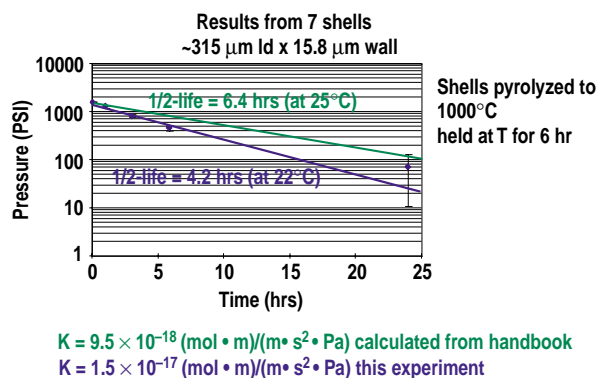
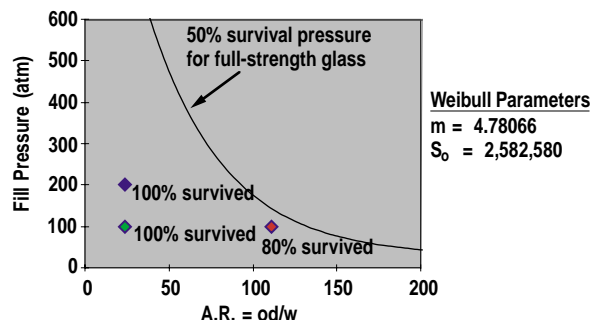


Fig. 9. Helium permeation properties after sintering to 1000°C are consistent with fully dense silica.

uniformity produced by this technique are superior to other previous methods used to manufacture glass shell for the national ICF program. The sphericity of the glass shells can be very good, especially in the lower modes, as shown by spheremapper AFM measurements. The high order modal structure appears to be very similar to that of the GDP from which it came as shown by SEM, with perhaps a slight increase in the amplitude of the features as shown in the spheremapper measurements. The permeability of the glass produced by this method varies widely depending on the sintering conditions – from extremely permeable to hydrogen to the low permeability expected of fully dense silica. The strength of the glass shells produced has not been fully tested but results so far are consistent with that of fully dense silica.

ACKNOWLEDGMENTS

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- ◆ 7 of 9 shells ~1450 μm od x 13 μm glass wall with 100 μm D-GDP
- ◆ 7 of 7 shells ~350 μm od x 15 μm glass wall survived
- ◆ 12 of 12 shells ~380 μm od x 16 μm glass wall survived

Fig. 10. The results of the He pressure test illustrate that the shells made by this process have good wall strength.

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