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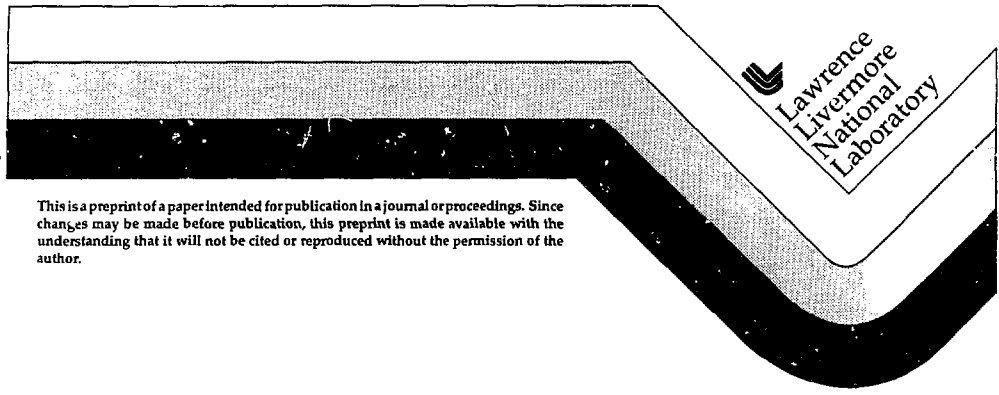
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PREPRINT

Preparation of Germanium Doped Plasma Polymerized Coatings as ICF Target Ablators

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Preparation of Germanium Doped Plasma Polymerized
Coatings as ICF Target Ablators

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ABSTRACT

Targets for Inertial Confinement Fusion (ICF) experiments at the Lawrence Livermore National Laboratory (LLNL) utilize an organic (CH) ablator coating prepared by plasma polymerization. Some of these experiments require a mid-Z dopant in the ablator coating to modify the opacity of the shell. Bromine had been used in the past, but the surface finish of brominated CH degrades rapidly with time upon exposure to air. This paper describes the preparation and characterization of plasma polymer layers containing germanium as a dopant at concentrations of between 1.25 and 2.25 atom percent. The coatings are stable in air and have an rms surface roughness of 7-9 nm (modes 10-1000) which is similar to that obtained with undoped coatings. High levels of dopant result in cracking of the inner mandrel during target assembly. Possible explanations for the observed cracking behavior will be discussed.

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INTRODUCTION

Targets for use in Inertial Confinement Fusion (ICF) experiments at the Lawrence Livermore National Laboratory (LLNL) have multilayer configurations. The outermost layer, whose role is as an ablator to initiate compression of the target, is fabricated exclusively by plasma polymerization of organic precursors. In some implosion experiments it is necessary to control preheat in ignition capsules and the ablation front instability by doping the ablator layer with a small quantity of high Z material.¹ Calculations have shown that germanium would make a good dopant in this regard. In addition to altering the composition of the ablator coating, careful attention must be paid to the surface roughness of the coating, as perturbations of the right size and shape can lead to Rayleigh-Taylor instabilities which subsequently degrade capsule performance.² This paper will discuss the successful incorporation of germanium as a dopant in ablators prepared by plasma polymerization.

The recent literature contains several examples of the preparation of organogermanium films.^{3,4,5} Since our requirements are for very low doping concentrations (of the order of a few atom percent) our strategy is to co-react a germanium-bearing precursor with our standard polymerization starting material, *trans*-2-butene (T2B) during ablator deposition.

EXPERIMENTAL

Coatings of germanium doped plasma polymer (CHGe) were prepared in a helical resonator plasma polymerization coater which has been in use at LLNL for many years.⁶ In our implementation of a helical resonator, a coil of wire surrounds a tapered silica reaction tube. RF energy is fed into a fixed tap on the coil and is impedance matched to the load via a π -type impedance matching network. The operating frequency is 43.5 MHz. Precursor gases of hydrogen and T2B flow down the tube and encounter a plasma in the tapered region. Figures 1 and 2 illustrate the design of the helical resonator coater.

¹C.J. Keane, R.C. Cook, T.R. Dittrich, B.A. Hammel, W.K. Levedahl, O.L. Landen, S.H. Langer, D.H. Munro, and H.A. Scott, "Diagnosis of pusher-fuel mix in spherical implosions using x-ray spectroscopy", to be published in *Review of Scientific Instruments*.

²M.J. Dunning and S.W. Haan, "Analysis of Weakly Nonlinear Three-Dimensional Rayleigh-Taylor Instability Growth," in *ICF Annual Report 1993*, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-LR-105820-93 (1993), pp. 179-187.

³Gazicki, M., J. Schalko, F. Olcaytug, M. Ebel, H. Ebel, J. Wernisch and H. Yasuda, *J. Vac. Sci. Tech. A*, **12**(2), 345, 1994.

⁴Tyczkowski, J., P. Kazimierski and H. Szymanowski, *Thin Solid Films*, **241**, 291, 1993.

⁵Sadhur, R.K., H.E. Saunders and W.A. Byers, *Polym. Eng. Sci.*, **33**(10), 645, 1993.

⁶Johnson, W.L., S.A. Letts, C.W. Hatcher, L.E. Lorensen and C.D. Hendricks, *ACS Symp. Ser. No. 108*, Plasma Polymerization, 315, 1979.

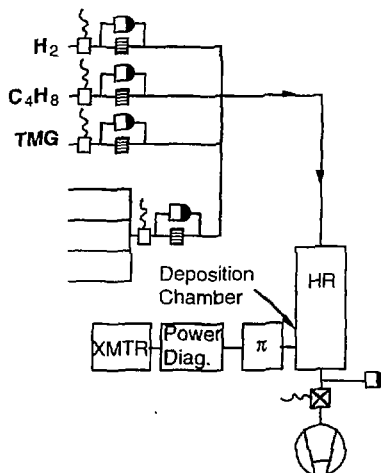


Figure 1.

Schematic diagram of the helical resonator plasma polymerization device (overall construction and flow system).

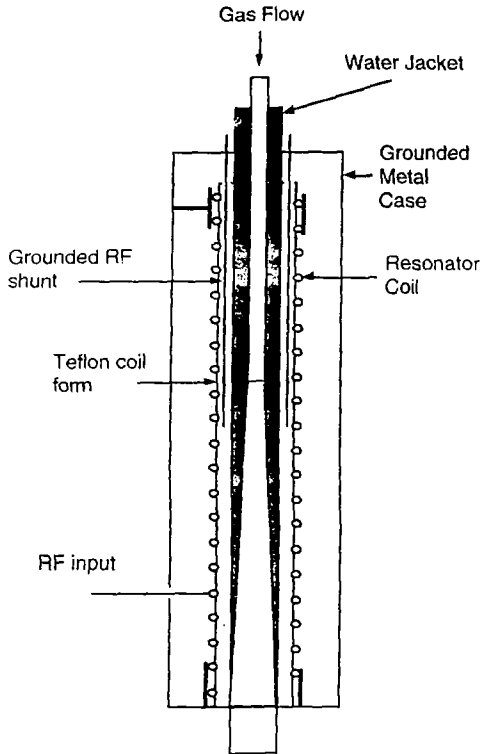


Figure 2. Schematic diagram of the helical resonator plasma applicator.

Doping of the plasma polymer with germanium is achieved by adding a small amount of tetramethylgermane (TMG) vapor to the gas flow. Depending upon the germanium level desired, the flow rate of TMG varies between 0.074 and 0.144 sccm. Table I lists the constant operating parameters of the coater.

Substrates used in this work consisted of spherical target mandrels, silicon wafer substrates and thin fused silica disks. Target mandrels are formed from spherical shells of polystyrene approximately 410 μm in diameter and 2-3 μm in thickness. These shells are overcoated with 2-3 μm of polyvinyl alcohol, then placed in the plasma polymerization coater. Silicon wafers are 1 cm^2 square and are precleaned

before deposition using CO₂ "snow" as a cleaning agent.⁷ A wafer is placed on a 5 cm X 8 cm glass microscope slide when loaded into the deposition chamber. Fused silica disks, 25.4 mm in diameter and 400 μm thick, are used as substrates in the qualitative determination of residual coating stress. They are first coated on one side with approximately 2000 Å of aluminum as a reflector; the other side is then coated with plasma polymer to a thickness of 1.7 μm.

Coating thickness on spheres is measured using interferometry. Thickness determinations on flat substrates are performed using a Tencor stylus profilometer. Roughness measurements on spheres are made using a circumferentially scanning atomic force microscope (AFM) technique.⁸ The roughness power spectrum is computed using the height versus azimuthal angle data for each trace in the AFM scan and then averaging the spectra.

The determination of germanium content is accomplished using an X-ray microfluorescence method.⁹ A brief description of the technique is given here. Glass slides coated with CHGe are analyzed for X-ray emission from germanium in the polymer and trace amounts of calcium in the glass using a Kevex Omicron X-ray microfluorescence analyzer. The calcium emission is attenuated by the hydrocarbon matrix and germanium atoms. The thickness at the point of analysis is measured. The degree of Ca absorption from the hydrocarbon matrix is calculated from the thickness of the coating and the known density of plain plasma polymer. Additional Ca X-ray attenuation is ascribed completely to germanium. The concentration of germanium is determined utilizing the mass absorption coefficient and assuming a uniform distribution of Ge which is assumed to simply replace C in the polymer matrix. When several different samples are analyzed, a calibration curve of germanium X-ray counts versus germanium concentration (via Ca X-ray attenuation) is generated which is then applied in the determination of germanium in target mandrels. An estimate of the error in germanium concentration by this method is ≈ 5% of the concentration value obtained.

The density of one sample of CHGe was determined by forming a shape controlled deposit on a pre-weighed silicon wafer. The wafer was weighed again just after the deposition using a Cahn microbalance with 1 μg precision. The shape of the deposit was then analyzed to obtain the volume.

⁷R. R. Zito, "Cleaning large optics with CO₂ snow," in *Advanced technology optical telescopes* (SPIE-The International Society of Photo-Optical Instrumentation Engineers, Bellingham, WA, 1990; *Proc. SPIE* 1236) pp. 452.

⁸R.L. McEachern, C.E. Moore and R.J. Wallace, "The Design, Performance and Application of an Atomic Force Microscope-Based Profilometer," this proceeding.

⁹R.C. Cook, T.P. Bernat, G. Collins, S.A. Letts, R. MacEachern, G.E. Overturf and R.E. Turner, "Production and characterization of ICF capsules," in *Plasma physics and controlled nuclear fusion research* 1992 Vol 3, p 449-454 (1993).

Qualitative measurements of residual stress in coatings were made by measuring the deformation of a fused silica stress disk coated with plasma polymer using a Zygo interferometer. A greater deformation at constant coating thickness is a qualitative indicator of greater residual coating stress after deposition.

The deformation of the stress disk results in the formation of a concave, rather than planar, substrate. Assuming the substrate is bent into a segment of a sphere, the distortion can be quantified by calculating the radius of curvature via equation 1,

$$R = \frac{S}{2\pi h} \quad [1]$$

where S is the surface area of the disk (a constant) and h is the height of the segment found by interferometry.

RESULTS AND DISCUSSION

Deposition rate and surface roughness

Germanium doping levels of approximately 1.25 and 2.25 atom percent have been utilized in the Hydrodynamically Equivalent Physics (HEP) experimental program at LLNL. Figure 3 plots the repeatability, in both deposition rate and germanium content, for identical runs in the two germanium concentration regimes. The reproducibility is very good.

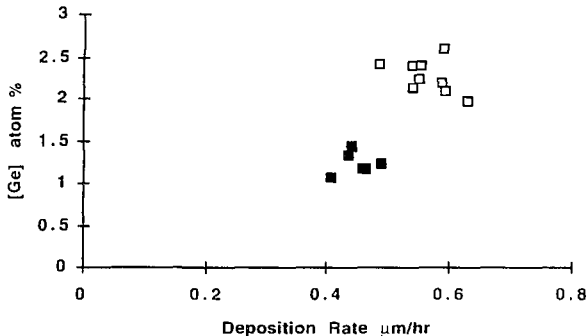


Figure 3. Plot of the germanium content and deposition rate for several identical experiments preparing 1.25

atom percent (filled symbols) and 2.5 atom percent (open symbols) doped plasma polymer on target mandrels. The reproducibility on shells is very good.

The deposition rate varies between $0.45 \mu\text{m hr}^{-1}$ at 1.25 atom percent germanium and up to $0.56 \mu\text{m hr}^{-1}$ when the TMG flow rate is increased to provide 2.25 atom percent doping. Presumably at least part of the increased deposition rate is due to the additional carbon introduced into the system by virtue of the organic ligands on the germanium precursor, however a detailed deposition mechanism is as yet unknown.

Figure 4 plots the roughness power in nm^2 versus mode frequency obtained for typical plasma polymer coatings on target spheres. The gray line shows the result for plain, undoped plasma polymer and the black line represents plasma polymer doped with germanium. It can be seen that the surface roughness of the two are very similar, with rms roughness values typically in the range of 7 to 9 nm when computed from mode 10 to mode 1000.

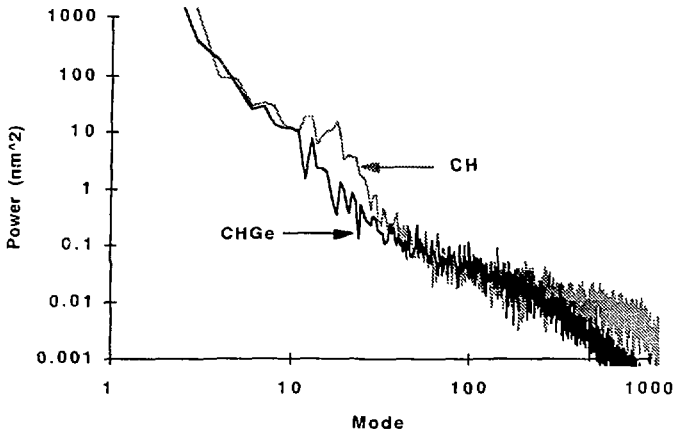


Figure 4. Plot of the power spectra for plain, undoped plasma polymer (gray line) and germanium doped plasma polymer (black line) on spherical mandrels.

Previous to this time, bromine had been used as an ablator dopant.⁹ This material suffered from an aging mechanism which caused the surface to roughen over time. An investigation into the nature of this phenomenon revealed that the cause was due to the crystallization of NH_4Br from the polymer matrix.¹⁰ Figure 5 plots the rms roughness of bromine and germanium doped plasma polymer versus time after completion of the coating in days. In comparison to the bromine seeded material, germanium doped plasma polymer shows no significant tendency to roughen over long periods of time.

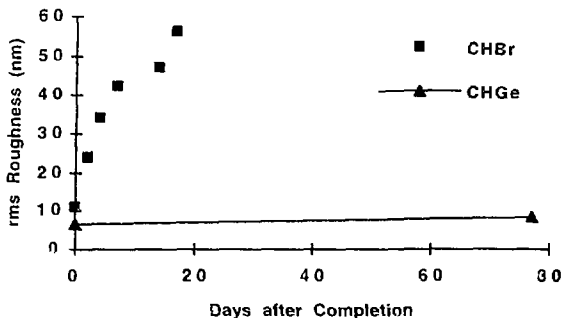


Figure 5. Plot of the rms roughness versus time after completion for bromine seeded (squares) and germanium seeded (triangles) plasma polymer coatings.

Density determination

The determination of density proceeded from a straightforward analysis of the weight and shape of a small amount of germanium doped plasma polymer. The weight of a microdot of CHGe (doped to 2.8 atom percent) deposited on a pre-weighed silicon wafer was determined by difference. The shape of the deposit was determined by taking four thickness scans across the dot diameter separated by 45° using the Tencor stylus profilometer. Figure 6 plots the results of the four thickness traces. The thin lines are the individual traces and the thick line represents the average of the eight radial traces. The height data was taken at $5 \mu\text{m}$ intervals, thus the slightly greater than 5000 micron width represents 1015 measurements.

¹⁰S.A. Letts, R.C. Cook, P. Welch, R. McEachern and E. Fearon, 205th American Chemical Society National Meeting, Denver, CO, Report CONF-930304, p 323, 1993.

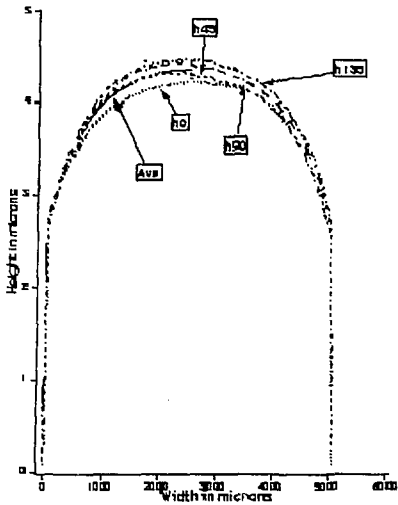


Figure 6. Plot of the height versus width of a specimen of CHGe used in determination of the density.

With 1015 data points, the center of the dot is at data point 508. The average height as a function of distance from the center is calculated by,

$$h_{ave}(r_i) = \frac{1}{4} \sum_{\text{trace } i} (h_i(r_i) + h_i(r_{1016-i})) / 2 \quad [2]$$

The volume of the specimen is then calculated as,

$$V = \sum_{i=1}^{507} (\pi r_{i+1}^2 - \pi r_i^2) (h_{ave}(r_{i+1}) + h_{ave}(r_i)) / 2 \quad [3]$$

where the index i now counts out from the center of the dot. From this we determined the volume to be $7.30 \times 10^{-5} \text{ cm}^3$. The weight of the specimen was determined to be $93.2 \text{ } \mu\text{gram}$ (1% error). Thus, the density of the specimen becomes 1.227 g cm^{-3} . This value compares favorably with the plot of density versus germanium content in the paper by Gazicki, et al.³

Cracking and stress

One troubling feature of preparing ablaters with germanium doping lies in an increased propensity for finished target mandrels to crack during processing that takes place after ablator fabrication. It has been observed generally that cracks occur only in the inner polystyrene layer of the mandrel, that the cracks never propagate through the polyvinyl alcohol diffusion barrier layer¹¹ and that cracking is most likely to occur in a post-deposition step that exposes the shell to an asymmetric thermal gradient. We have found that the seriousness of the cracking problem is a function of the germanium concentration in the plasma polymer; more germanium incorporation results in more cracking. The composition of the polystyrene inner mandrel magnifies the tendency to crack, i.e. when the polystyrene is doped with titanium for spectroscopic measurements during a target implosion, the cracking problem becomes more severe than that for a plain polystyrene mandrel.

There are many possible explanations for such behavior, ranging from undesirable thermomechanical properties of the ablator to residual stress after coating. To begin addressing this issue, qualitative measurements of residual coating stress were made. We find that the radius of curvature for stress disks varies from 500 m for plain plasma polymer down to a value of 100 m at the highest incorporation levels. The absolute values of the stress have not been determined and the precise relationship between residual stress and cracking behavior has not been investigated. Some techniques described in the literature^{12,13,14} may be useful for quantitation, but the applicability of these techniques to our system has not been done. More work in this area is called for. Current efforts are focussed on preparing ablator coatings with the minimum amount of germanium needed and increasing the robustness of the inner polystyrene mandrel when doped for spectroscopic purposes.

CONCLUSIONS

It has been established that small amounts of germanium can be reproducibly incorporated into plasma polymer coatings. The coatings have been deposited to thicknesses of 45 μm with surface roughness of 7 to 9 nm rms on spherical substrates. The coating rates generally are 0.45 to 0.56 $\mu\text{m hr}^{-1}$. The density of the coating doped to a level of 2 atom percent is 1.23 g cm^{-3} and is in agreement with density values for similar coatings reported in the literature. There have been problems with shell cracking with increasing amounts of germanium and pusher dopants exacerbate the problem.

ACKNOWLEDGMENTS

¹¹This means that, although the shell is cracked on the inside, hydrogenic fuel does not leak out after fill.

¹²R.W. Hoffman, *Physics of Thin Films Volume 3*, Academic Press, NY, 1966, pg. 211.

¹³Blech, I.A. and P. Wood, *J. Vac. Sci. Technol. A*, **11**(3), 728, 1993.

¹⁴Lahav, A., K.A. Grim and I.A. Blech, *J. Appl. Phys.*, **67**(2), 734, 1990.

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TABLE I

Operating parameters for the helical resonator coater

I ₂ flow rate	13 sccm
T2B flow rate	0.3 sccm
Total pressure	70 mTorr
RF power	12 W