DEPOSITION AND CHARACTERISTICS OF CHLORINE-DOPED GLOW DISCHARGE POLYMER FILMS

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Abbas Nikroo
Inertial Fusion Division
General Atomics
P.O. Box 85608, San Diego, Ca 92186-9784
(619) 455-2931

ABSTRACT

Shells coated with chlorine-doped polymers deposited in a plasma are needed for diagnostic purposes for the OMEGA experiment. We have deposited chlorine-doped plasma polymer films by using a number of different chlorinated hydrocarbons. Chlorine concentrations between ≤ 1 to ≈ 35 at.% were obtained. Several characteristics of Cl-GDP films such as color, stress, chlorine concentration homogeneity and thermal stability are discussed.

I. INTRODUCTION

Polymers deposited by the polymerization of a hydrocarbon in a glow discharge (GDP) are used as the ablation layer for the inertial confinement fusion (ICF) micro-shell targets. These coatings are normally made using a pure hydrocarbon with no impurities. However, sometimes elements with higher atomic numbers at concentrations of a few atomic percent (at. %) are desired in these coatings. For example, germanium-doped GDP coatings are extensively used on Nova targets.[1] Bromine-doped[2] and silicon-doped[3] GDP target overcoatings have also been developed. Recently, there has been a need for chlorine-doped GDP (Cl-GDP) coatings on OMEGA targets. These coatings are used as the ablation layer with the chlorine acting as a diagnostic tool for studying shot characteristics. Targets containing both undoped and chlorine-doped GDP layers are also needed. Chlorine concentrations of approximately 6 at.% chlorine are desired in the doped layer. The chlorine concentration should be homogeneous throughout the coating. In addition, for multiple layer films there should be no diffusion of the dopant from the doped layer to the undoped layer. With the depolymerizable mandrel

(PAMS) technique[4] having reached production phase, the Cl-GDP films must also be thermally stable against dopant loss during heat treatment to depolymerize and extract the mandrel. Finally, the doped coatings must meet the usual surface finish criteria used for undoped GDP shells.[5]

II. EXPERIMENTAL

Cl-GDP coatings were deposited on flat silicon substrates as well as polystyrene shells using the standard coating apparatus normally used in depositing undoped coatings.[6] However, the manner in which the radio frequency (rf) power is input to the helical resonator coil was modified for some of the experiments. Normally, rf power is tapped into the resonator coil at the seventh turn from the bottom and the top and the bottom of the coil are grounded. In some of our experiments, rf power was tapped in at the third turn and the bottom and all of the turns above the seventh were grounded. This was done to confine the plasma in the lower part of the coating plasma tube. RF powers used in the experiments ranged between 2 to 4 W. Trans-2-butene (T2B) and hydrogen were used as feed gases along with a chlorinated hydrocarbon serving as the dopant precursor. The chlorinated hydrocarbons used were all volatile enough (boiling point of about 100°C at 760 Torr) to be used without heating gas lines in the coating system. The chlorinated hydrocarbons used included methyl chloride, dichloromethane, dichloroethylene (DCE), chloro-butene, chloro-benzene and chlorostyrene. However, chloro-butene and DCE were used in most of the experiments for reasons discussed below. Flow rates were between 0 and 0.2 sccm for T2B, and the chlorinated hydrocarbons and between 0 and 10 sccm for hydrogen. The chlorine concentration in the films was measured by X–ray microfluorescence (XRF) calibrated by combustion analysis.[7] Energy-dispersive

X–ray analysis (EDAX) in a scanning electron microscope was used to determine the sample homogeneity with a spatial resolution of ≈3 µm. High resolution (10 nm) homogeneity measurements near the surface as well as interlayer diffusion measurements were performed by Rutherford Backscattering (RBS). The amount of stress in the coatings was determined qualitatively by noting how long it took for films deposited on glass slides to wrinkle after deposition.

III. RESULTS AND DISCUSSION

We obtained a range of doping levels in our coatings depending on the combination and relative flow rates of the precursor gases. The maximum doping for each chlorinated feedstock was obtained when the chlorinated feedstock was the only feed gas in the process (Table I). Introduction of hydrogen into the coating system severely reduced the chlorine content of the films (Fig. 1). The introduction of T2B had a similar effect but to a much smaller extent. Hydrogen is normally used in excess in undoped coatings to reduce stress in the films and improve surface finish.[8] The introduction of argon, however, did not affect the chlorine concentration. This seemed to indicate that chlorine was being removed from the deposition process by hydrogen through the formation of HCl. Coatings made using a combination of a chlorinated hydrocarbon and hydrogen and/or T2B, in general, were very dark in color, sometimes black, and highly stressed (Fig. 2). When only the chlorinated hydrocarbon was used as the feed gas, the films were stress free and amber colored as with undoped GDP. Therefore, only a chlorinated hydrocarbon precursor was used when coating targets, and the dopant level was controlled by the choice of the precursor. Chloro-butene was used to make coatings with 6 at.% chlorine. RF input power was limited to 2– 4 W because of excessive gas phase polymerization at higher powers that produced falling flakes of polymer covering the coated substrates.

Table I
List of some of the chlorinated hydrocarbons (C1–HC) used in the experiments and the maximum chlorine concentration obtained with each dopant

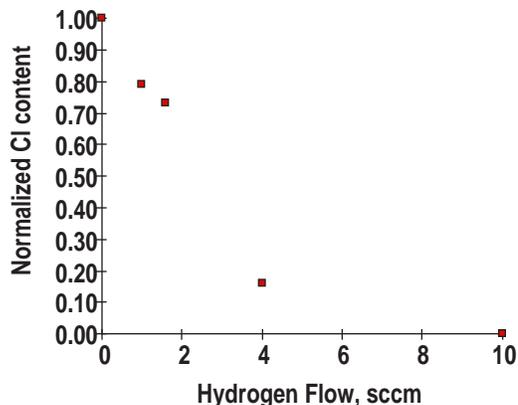| Cl-HC	Max Cl Atom %
Chlorobutene	6
Chloromethane	17
Dichloromethane	22
Dichloroethene	35
Chlorobenzene	6

Fig. 1. Plot of the chlorine concentration of Cl-GDP films normalized to unity as a function of hydrogen flow in the coating process for a fixed chloro-butene flow (0.2 sccm). Presence of hydrogen sharply reduces the chlorine content of the Cl-GDP films.
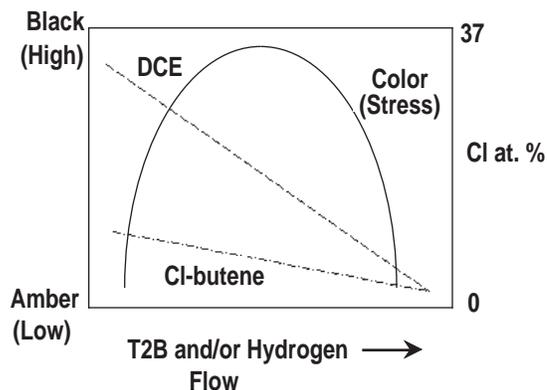

Fig. 2. Qualitative plot of the effect of mixing of chlorinated hydrocarbons with T2B and hydrogen. The dashed lines represent the chlorine content for two different dopants. Coatings made with the chlorinated hydrocarbon alone have the highest Cl content and are at the same time light colored and stress free. As more and more T2B and/or hydrogen are added to the coating process films become darker and more stressed and contain less Cl. Films made with little relative chlorinated hydrocarbon flow are also stress free and light colored but contain little chlorine (undoped GDP).

The surface finish of the Cl-GDP was poorer than that which is produced with undoped GDP under similar conditions. The RMS background surface finish was about 20 nm (0.3 µm/h coating rate, 20 µm thick film). By comparison, the RMS background surface finish of 50 µm thick undoped GDP films is usually 1 nm at the same coating rate. More importantly, the surface of the coatings was covered with numerous domes even on very smooth starting mandrels [Fig. 3(a)]. Occasionally, large (10 µm)
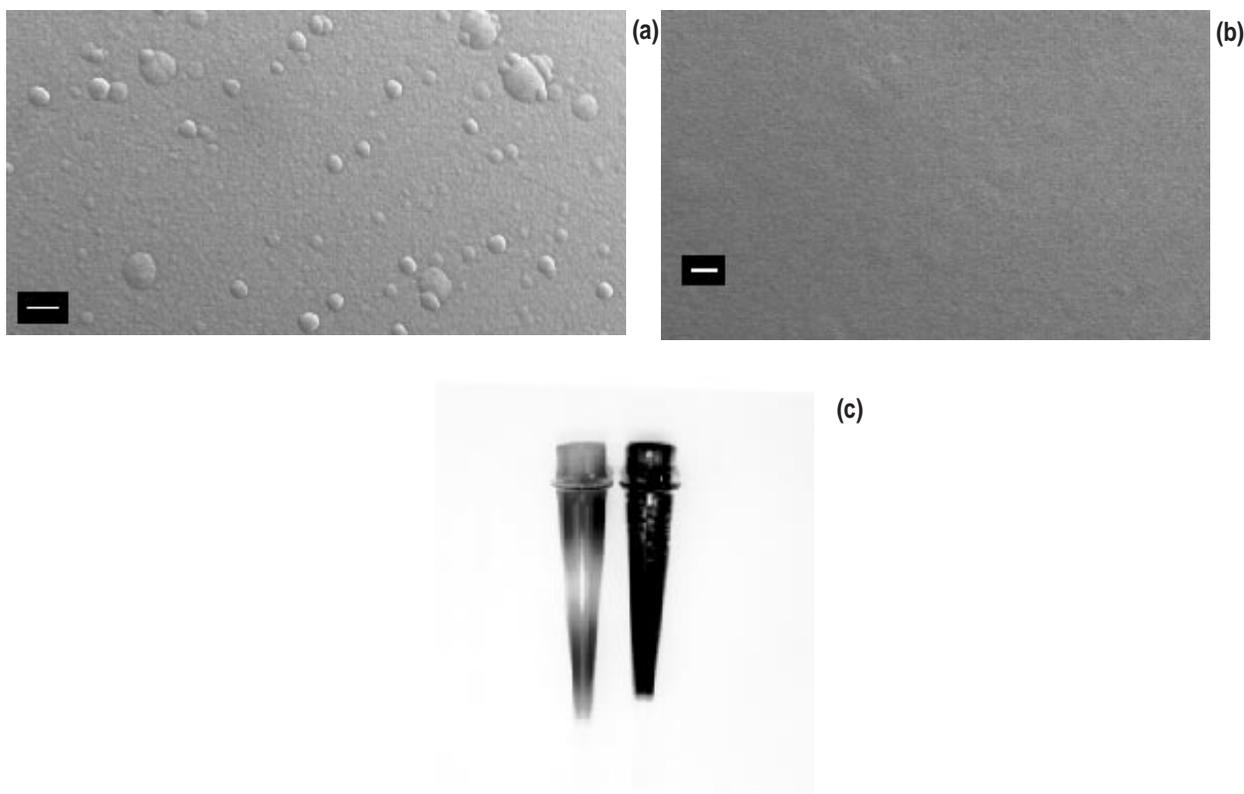
Fig. 3. Scanning electron microscope (SEM) image shows that the surface of Cl-GDP coatings using the standard resonator rf power input configuration had many domes (a). The coating tube in this configuration was completely black after deposition (c-right side). The new resonator setup lowered the plasma in the coating tube and avoided excessive coating and gas phase polymerization within the tube (c-left side). The surface of the resulting coatings are mostly free of domes (b). Scale bars are 3 and 1 μm in (a) and (b), respectively.

spherical polymer beads were found attached to the shells after deposition indicating gas phase polymerization. The plasma tubes were covered with a black coating even after short (24 h) runs. There appeared to be an excessive amount of coating taking place in the tube compared to the substrates. This indicated that the plasma needed to be lower in the tube in order to distribute the coating more evenly between the plasma tube and the substrates. Lowering of the plasma had proven beneficial in previous studies as well.[6] Modification of the resonator as described above resulted in coatings that had fewer domes and no beads [Fig. 3(b)]. The coating tube was not black in this resonator configuration even after runs as long as 90 h [Fig. 3(c)].

Coatings 60 μm thick were deposited for cross-sectional examination by EDAX to determine the bulk homogeneity of the films. No major *bulk* inhomogeneity was observed. However, high resolution RBS measurements revealed chlorine depletion near the surface in the top 2 μm of the films. This was consistent with the lower Cl content seen in thin ($\approx \leq 2$ μm) films by

XRF (Fig. 4). Undoped GDP films are known to oxidize[9] rapidly because of trapped free radicals embedded in the coatings.[10] In particular, the top 2 μm are especially susceptible to oxidation.[11] Therefore, it is plausible that the chlorine was depleted quickly near the surface by oxidation after exposure to air. RBS measurements also revealed that chlorine diffused about 10 μm into an undoped GDP overcoating of a Cl-GDP layer during deposition indicating that the chlorine in Cl-GDP is highly mobile.[7]

Many chlorine containing polymers are thermally unstable at temperatures of about 300°C, which is the temperature used in the PAMS-GDP mandrel production process. Cl-GDP films pyrolyzed for this process were no exception. They lost about 80% of their chlorine content, probably through liberation of HCl. Loss of hydrogen in this manner would lead to conjugation of carbon bonds and the heated Cl-GDP films were indeed black. However, thermogravimetric analysis[12] of these films indicated that the remaining 20% of chlorine atoms are bound very stably. Therefore, there may be two types of chlorine
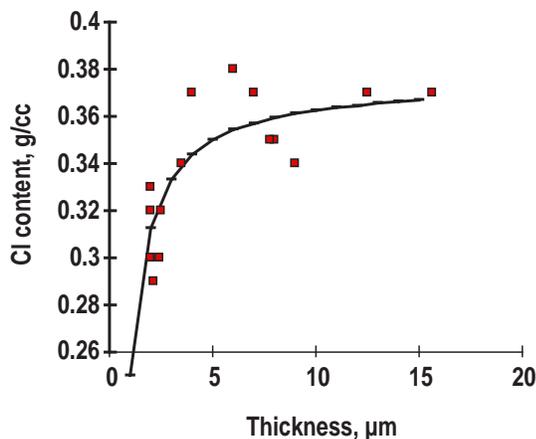
Fig. 4. Chlorine concentration as a function of coating thickness for chlorobutene films. Coatings thinner than ≈ 2 μm have lower chlorine content possibly because of liberation of HCl as the film oxidizes.

binding sites in Cl-GDP, one thermally stable and the other unstable.[13] This requires further investigation. Thermal instability of chlorine in Cl-GDP may explain the observed mobility of chlorine from a Cl-GDP layer into an adjacent undoped layer during plasma deposition where temperatures of about 100°C are encountered.

IV. CONCLUSION

Chlorine-doped GDP films containing a wide range of chlorine concentrations have been deposited. The best quality films are obtained when a chlorinated hydrocarbon is the only feed gas into the plasma created with a modified resonator configuration. Films have good bulk homogeneity, but chlorine is depleted near the surface. Most chlorine in Cl-GDP is poorly bonded, but a second more stable binding site for chlorine may exist within the coating, leading to some chlorine that is thermally stable. Thermal instability of chlorine apparently leads to diffusion of chlorine into adjacent undoped layers.

ACKNOWLEGEMENTS

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