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Preparation and Characterization of Beryllium Doped Organic Plasma Polymer Coatings

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ABSTRACT

We report the formation of beryllium doped plasma polymerized coatings derived from a helical resonator deposition apparatus, using diethylberyllium as the organometallic source. These coatings had an appearance not unlike plain plasma polymer and were relatively stable to ambient exposure. The coatings were characterized by Inductively Coupled Plasma Mass Spectrometry and X-Ray Photoelectron Spectroscopy. Coating rates approaching 0.7 μm hr^{-1} were obtained with a beryllium-to-carbon ratio of 1:1.3. There is also a significant oxygen presence in the coating as well which is attributed to oxidation upon exposure of the coating to air. The XPS data show only one peak for beryllium with the preponderance of the XPS data suggesting that the beryllium exists as BeO. Diethylberyllium was found to be inadequate as a source for beryllium doped plasma polymer, due to thermal decomposition and low vapor recovery rates.

I. INTRODUCTION

Current Inertial Confinement Fusion (ICF) implosion experiments performed on the NOVA laser at Lawrence Livermore National Laboratory utilize a multilayer, all-organic fuel capsule design. Although this design could be used successfully in experiments being planned for the National Ignition Facility (NIF), implosion performance improvements may be realized if the materials space for capsule fabrication could be expanded. Among the alternatives being considered, wall materials containing beryllium are the leading candidate for ICF applications.

ICF target capsules have stringent requirements on sphericity and surface roughness of both the inner and outer surfaces. In addition, diffusional filling of hydrogenic fuel is a very desirable capability. Without this feature, it becomes necessary to introduce fill tubes or drill-and-plug technologies, with increased chances for leaks and a departure from true spherical capsule symmetry. Characterization of liquid or solid deuterium-tritium fuel layers in the interior capsule wall is necessary and makes some degree of capsule transparency desirable. We have used plasma polymerization to prepare coatings for ICF capsules in current NOVA experiments that meet all of the foregoing criteria.[1] Thus, we are motivated to find out if plasma polymerization can be used to prepare beryllium-containing coatings. In this case, a high degree of beryllium incorporation would satisfy the materials conditions needed for implosion performance while the basic polymer network formed in the deposition process may allow for diffusional fill and optical fuel layer characterization. One key unknown is the ability of the plasma polymerization process to prepare coatings with a high degree of metal content. We recently completed a study of this issue in our systems using germanium as the metal dopant.[2] Germanium-to-carbon ratios as high as 1:1 were achieved, allowing for speculation as to whether a similar result could be obtained using beryllium as the metal dopant. This paper reports the results of the plasma polymerization of an organoberyllium precursor in a hydrogen carrier stream.

II. EXPERIMENTAL

Deposition experiments were performed in a helical resonator plasma polymerization apparatus[3] that had been modified to allow for wide flexibility in handling an organoberyllium precursor. Figure 1 illustrates the coating system.

In order to reduce the occurrence of condensation of the organoberyllium precursor in transit to the plasma applicator, the carrier hydrogen is preheated within the precursor oven by passing it through a short (≈ 1 m long) heated loop before mixing with the organoberyllium vapor. The transfer lines were maintained at approximately 5°C above the temperature of the source oven up to the point of attachment to the helical resonator. When in steady state, the helical resonator plasma applicator itself reaches a temperature of approximately 45°C.

In addition to the 43.56 MHz helical resonator plasma polymerization station, a high power, parallel-plate 13.56 MHz decomposition station and a 450°C thermal decomposition station were added to the coating system for maximum flexibility in handling the organoberyllium precursor. At present, only the coatings made in the helical resonator deposition chamber have been studied.

Diethylberyllium (CAS No. 542-63-2) was purchased from STREM Chemicals and used as received. The vapor pressure of this material can be expressed as $\log 10\, p = 7.59 - (2200/T)$ where p is in units of Torr and T is °K.[4] This corresponds to a room temperature vapor pressure of 1.6 Torr and a vapor pressure of approximately 10 Torr at 62 °C. Since the room temperature vapor pressure is too low for adequate control by our flow equipment, the source bubbler and its associated flow control equipment are maintained in a heated environment. Table I lists the standard deposition parameters used in this study.

The flow rate of the organoberyllium precursor is controlled via an MKS Instruments 148J all-metal control valve and the flow rate is monitored using an MKS 0.5 $\mu \cdot L\ sec^{-1}$ Conductance Flow Element (CFE) and a differential capacitance manometer.[5] An all-metal bellows sealed pneumatic positive shut-off valve (Nupro SS-4BG-TW-3C) completes the organoberyllium handling system within the temperature controlled compartment. The stated flow rate in Table I is based upon an assumption that the organoberyllium vapor is a monomer. This assumption is not strictly correct as the composition of the vapor phase has been shown to be a mixture of monomers and dimers.[6] An additional complication stems from the fact that the method of flow control we typically use can operate as a mass filter in the molecular flow regime. We have not attempted any characterization of the organoberyllium vapor composition in our system at this time. Therefore, the flow rate stated in Table I must be considered only roughly approximate.

Substrates for this study consisted of polished silicon wafers of (100) orientation (1 cm square) placed upon 7.5 cm X 12 cm glass slides. The silicon wafers were cleaned using a CO_2 "snow" cleaning process[7] and the glass substrates were cleaned simply by wiping with ethanol.

Bulk determination of the total beryllium content was obtained by chemical digestion of the plasma polymer followed by characterization in an Inductively Coupled Plasma -

Mass Spectrometer (ICP-MS). Samples of interest were sealed, together with a mixture of 10 ml of 8 M HNO_3 and 0.5 ml of concentrated HCl, into precleaned teflon bombs and heated in a microwave oven. Following dissolution each sample was spiked with 1.25 μg of Li and brought to a total volume of 50.0 ml. The concentration of beryllium in each resultant solution was then determined by an ICP-MS measurement. These measurements were then compared with a series of standard solutions containing between 5 ng/ml Be and 1000 ng/ml Be, each containing 50 ng/ml of Li as an internal standard.

Surface sensitive characterization of beryllium doped plasma polymer films was done via X-Ray Photoelectron Spectroscopy (XPS) analysis using a Perkin-Elmer 5400 ESCA system. A Mg X-ray source operating at 15 KV and 400 watts was used to illuminate a 30 mm^2 area of the sample for analysis. Initially, broad range scans were used to qualitatively identify the surface species present as well as to provide an estimate of the relative abundance of each element. Estimates of surface composition were obtained using a standard set of atomic sensitivity factors.[8] Once the elements present were identified, high resolution scans were accumulated to provide speciation and chemical shift information.

III. RESULTS AND DISCUSSION

Relatively thin films (≈ 1 μm thick) of beryllium doped plasma polymer were deposited on the silicon wafer and glass substrate. The deposition rate for the conditions given in Table I was 0.7 $\mu m\ hr^{-1}$ and was determined by measuring the step height of the coating on the glass slide formed by the masking of the glass by the silicon wafer. The deposition rate is somewhat misleading as it was not possible to maintain a steady flow rate of diethylberyllium precursor. This issue will be discussed in detail below. As a consequence of the plasma polymerization process, coatings are also formed on the inside of the plasma applicator tube within the helical resonator (see figure 1). The appearance of the coatings is very similar to plain plasma polymer, which is a transparent, yellow to yellow brown film. The yellow coloration is typical of the carbon unsaturation in plasma polymer. The coatings on the silicon and glass substrates did not exhibit any obvious instability upon standing in room air and there was no apparent tendency to delaminate. Coatings on the plasma tube did show a slight tendency to delaminate with time. This could be due to compositional changes and/or changes in the residual stress of the coating with exposure to air.

Coatings within the plasma tube are difficult to analyze on a microscopic basis and we have only made bulk beryllium content determinations on these films . The axial distribution of beryllium along the plasma tube is an important indicator in the performance of the coating process. If the beryllium were to be deposited in a narrow zone near the top of the plasma region (away from the substrates), it would necessitate a change in the configuration of the coater to provide for downstream organometallic injection and processing. To characterize the beryllium content axially, the plasma tube was carefully fractured and samples of glass carrying the doped plasma polymer coating were chemically digested and analyzed via ICP-MS. Beryllium was found well above the limit of detection all along the plasma tube where coating was visibly occurring. This trend was similar to was found for germanium content in our previous feasibility study.[2]

XPS analysis of beryllium doped coatings on the silicon wafer substrates has demonstrated both the level and the nature of the beryllium incorporation into plasma polymer. Table II lists the major elements detected, relevant observed XPS peak information and the composition in atom percent. Figure 2a-d contains the XPS spectra for beryllium, carbon, oxygen and silicon.

With regard to ICF applications, the most important result taken from Table II is the nearly one-to-one beryllium concentration relative to carbon. Beryllium incorporation of this magnitude is significant and might be useful as an ICF ablator material, subject to other constraints such as oxygen content, residual stress and surface roughness.[2]

Insulating samples, such as these, typically acquire a steady state charge of several volts owing to the balance that is established between the photoelectrons lost from the sample and those electrons gained by the sample by conduction or from the vacuum space. Such charging causes peaks to shift to apparently higher binding energies by as much as several volts. There are several methods that may be used to correct for charging in insulating samples.[9] The most common method of charge referencing is to use the position of the carbon 1s peak from adventitious hydrocarbon contamination, which has a binding energy of 284.6 eV. In the present case there is considerable uncertainty with respect to which of the two carbon peaks present (figure 2b) represents the adventitious carbon peak inevitably found on samples handled under normal laboratory conditions. If one assumes that the larger of the two carbon peaks is indicative of the adventitious carbon peak this would imply a charge correction of 2.6 eV while an assumption that the smaller of the two carbon peaks represents the adventitious carbon requires a charge correction of 3.9 eV.

There are a number of factors that suggest that 2.6 eV may be a more realistic correction factor. A 2.6 eV binding energy shift on the carbon peaks assigns the larger peak as being or containing the adventitious carbon. The smaller carbon peak then approaches values typically obtained for carbon singly bound to oxygen (such as for alcohols).

Coatings with both high and low beryllium content show the same general behavior in the carbon peaks; a smaller peak at high binding energy and a much larger peak at a lower binding energy. If the 3.9 eV shift correction were used, the smaller peak would be assigned as adventitious carbon and the larger peak would approach binding energy values similar to those obtained for metallic carbides (280.7 to 282.6 eV). However, the relative intensities of the two carbon bands is insensitive to the beryllium content. Thus, it is difficult to assign the large carbon peak to carbide-like carbon in the near absence of beryllium and the 2.6 eV correction is more favorable.

The single beryllium peak is indicative of a uniform chemical environment. A 2.6 eV shift correction would place the beryllium peak just below that generally ascribed to beryllium oxide (113.4 to 114.6 eV). A 3.9 eV correction places the beryllium peak at the edge of values used for beryllium metal (111.2 to 111.8 eV). The amount of oxygen in the coating (Table II) suggests that the beryllium is completely oxidized, with additional oxygen associated with the hydrocarbon polymer network.[10] This hypothesis favors the 2.6 eV shift correction. However, it may well be that the beryllium is not oxidized and is fully incorporated into the polymer network. It is not known to what extent the binding energy of the beryllium peak would be shifted to higher values by the carbon network, but it would not be as great as that for BeO. We tentatively conclude that the formation of BeO in the plasma polymer is reasonable and that the 2.6 eV shift correction is valid.

The most convincing evidence for the 2.6 eV shift correction comes from considering the oxygen XPS peaks. A 2.6 eV shift places the 534 eV oxygen peak very near to that accepted for BeO (531.6 eV). The 535.6 eV oxygen peak then shifts to a region where one typically finds metal hydrates, water and carbon-oxygen linkages such as carbonyls. A 3.9 eV binding energy correction places the smaller 535.6 eV peak at the position of BeO but places the larger 534 eV in a region where one typically finds materials such as chromates. We have found that the oxygen content tracks the beryllium content very closely. This argues that it is more reasonable to assign the 534 eV peak as BeO and further argues for the 2.6 eV shift correction.

The assignment of the silicon peaks is problematic. A 2.6 eV charge correction moves the 104.9 eV peak to a region where one typically finds silicates. In addition, the 107.3 eV peak is moved to a point near the accepted value for silicon in K_2SiF_6. Neither of these peak assignments are very realistic given the nature of the specimen. However, a 3.9 eV shift correction makes the 104.9 eV peak coincident with a line observed for triphenylsilanol and the 107.3 eV peak moves to a binding energy region populated by SiO_2 and silica hydrates. The closer association of these peaks with oxygen species makes more intuitive sense, but the 3.9 eV shift applied to the other, major species in the coating is not as satisfying on chemical grounds as is the 2.6 eV shift. Clearly, more work will be required to make some definitive statements about the chemical binding in this system.

There is no evidence that BeO was simultaneously deposited with plasma polymer during coating formation. Since the gas feed components ($Be(Et)_2$ and H_2) are oxygen free and since there was no evidence of a gross leak in the system during deposition, it is reasonable to expect that the initial coating laid down was also oxygen free. There are two possibilities. First, it is possible that zero-valent metallic Be atoms are incorporated or dispersed into the carbon-based organic coating. The second possibility is that the Be is covalently incorporated into the carbon based plasma polymer network with C-Be bonding of the same general type as found in the $Be(Et)_2$ monomer. In either case one expects that upon exposure to molecular oxygen the Be atoms would oxidize to form the more thermodynamically stable BeO. Though this will be a concern for ICF target applications, it is certainly within our technical capabilities to keep the materials in an oxygen free environment or to apply methods to greatly slow the oxidation step.

As mentioned above, the diethylberyllium source did not perform well during the deposition experiments. Variability in the vapor flow rate during deposition was encountered as well as rapidly decreasing diethylberyllium vapor pressure during processing. There appear to be two main drawbacks to this precursor. The first is an apparent thermal decomposition of the precursor at the highest temperatures used in this study and the second is low vapor recovery times at reduced temperatures. Both of these points are discussed below.

Initial deposition experiments were performed with the source temperature raised to 62°C. This temperature was thought to provide an adequate vapor pressure (10 Torr by calculation) and still be below the temperature cited for the onset of significant decomposition.[4] Figure 3 plots the source vapor pressure as a function of time after evacuating the source well below the calculated vapor pressure of 10 Torr and allowing it to rise.

The bubbler pressure rises above the calculated vapor pressure of 10 Torr and continues to rise such that after 12 hours at 62°C the bubbler pressure is 65 Torr. We interpret this to indicate that the diethylberyllium is subject to thermal decomposition even at this temperature. Therefore, it is quite likely that the diethylberyllium source vapor is diluted with organic decomposition products at the onset of coating formation. This behavior may have important implications regarding the final beryllium content as well as the beryllium content as a function of the depth of the coating.

An attempt was made to arrest the thermal decomposition by lowering the source temperature. During the flow calibration of the system before coating operations, it was determined that a vapor pressure of 3 Torr was the lowest pressure at which our flow system could maintain control. Consequently, we attempted to coat at a source temperature of 42°C. This temperature gives a calculated vapor pressure of approximately 4 Torr, leaving us a comfortable margin of error.

Figure 4 plots the calculated (open squares) and experimental vapor pressure (filled squares) overlaid by the temperature of the source oven (triangles). In the first 100 minutes, we see the vapor pressure over the diethylberyllium rise to a steady pressure of 6 Torr. Although the oven temperature is somewhat unstable as one crudely approaches the desired 42°C operating point, the source vapor smoothly rises and reaches saturation. The liquid and vapor are well shielded from rapid thermal transients by the significant thermal mass of the stainless steel container; this explains the smooth pressure rise to steady state. Additional data were collected after 200 minutes and are included in figure 4. The increase from 6 to 7 Torr between 100 and 200 minutes is ascribed to continued equilibration with the source oven. Note that the calculated vapor pressure also rises about one Torr between the 100 and 200 minute mark due to the increase in oven temperature from 40 to 46°C. These data demonstrate that the thermal decomposition of diethylberyllium is negligible at approximately 42°C.

Although it is possible to operate the coating system at a vapor pressure as low as 4 Torr, it is not possible to carry on a practical coating operation because the source container is depleted of vapor species faster than can be liberated from the liquid phase. Using our chosen initial flow settings, the diethylberyllium vapor pressure drops by 0.5 Torr min^{-1}, corresponding to a consumption rate of 5 μmole min^{-1}. Thus, even with a vapor pressure of 6 Torr one quickly drops below the critical vapor pressure of 3 Torr that maintains a controlled flow rate. The vapor recovery time was measured by stopping the flow and plotting the vapor pressure as a function of time; the results are presented in figure 5.

The data from figure 5 coupled with some simple calculations shows that the vapor recovery rate is only 0.07 μmole min^{-1}. It is unclear why the vapor pressure is so slow to equilibrate. It may be that there is a slow equilibrium in the liquid phase to form monomers and dimers which then would be liberated into the gas phase. It is not likely that heat transport is the limiting factor due to the large thermal mass of the steel cylinder and the small amount of liquid present. A detailed study of this phenomenon has not been carried out.

IV. CONCLUSIONS AND PLANS FOR FUTURE WORK

A plasma polymer material with a significant beryllium content has been demonstrated. The coatings have an appearance very near to that of undoped plasma polymer; they are transparent and yellow to yellow-brown in color. These coatings do not show any tendency to react violently with ambient air. The beryllium-to-carbon ratio in coatings produced in the afterglow region is approximately 1:1.3 and might be useful in ICF applications. The beryllium is bound within a uniform chemical environment. The chemical shift data in the XPS results are not completely consistent but the preponderance of the data suggests that the beryllium exists as an oxide, which was likely formed after deposition due to exposure of the coating to air. Diethylberyllium is not a preferred source for vapor phase processing of organoberyllium coatings, due to apparent thermal decomposition of the source and very slow vapor recovery times.

A continued investigation into the formation of these coatings is planned. The emphasis will be on using alternate organoberyllium precursors with a goal of producing a thick film of material. Another important goal is producing a definitive picture of the chemical state of the beryllium as deposited as well as to find methods to reduce the level of oxidation. Finally, it will be necessary to determine the hydrogen permeability to discover whether this material truly could be a candidate as an ICF ablator.

V. ACKNOWLEDGMENTS

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Table I

Operational Parameters for Organoberyllium Coatings

H_2 flow rate	12 sccm
Et_2Be flow rate	0.3 sccm[§]
Et_2Be source temperature	42 - 62°C
Chamber Pressure	70 mTorr
RF Frequency	43.56 MHz
RF Power	12 W
Deposition time	60 - 90 min

[§] - Assumed flow rate; see text for discussion

Table II

XPS results on beryllium doped plasma polymer coatings

Element	No. peaks	Observed Energy (eV)	Composition (at %)§
Be	1	115.7	27
C	2	287.2 ; 288.5	36
O	2	534.0 ; 535.6	35
Si	2	104.9 ; 107.3	1

§Trace background impurities make up the last 1% of the observed species.

FIGURE CAPTIONS

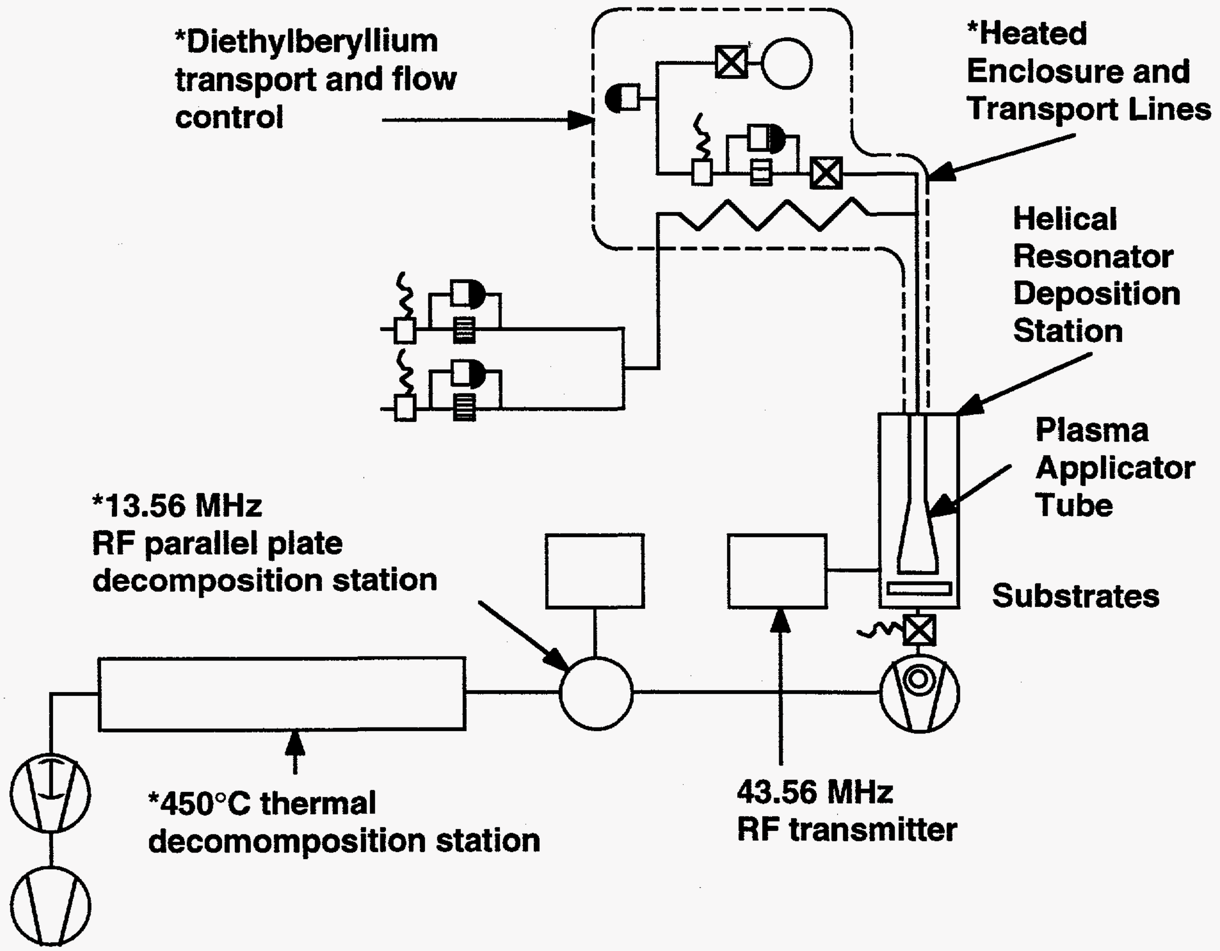
Figure 1. Schematic component diagram of the organoberyllium plasma polymerization system. Sections labeled with a "*" are new or modified from the standard plasma polymerization configuration.

Figure 2. XPS spectra for (a) beryllium, (b) carbon, (c) oxygen and (d) silicon in beryllium doped plasma polymer.

Figure 3. Plot of the diethylberyllium bubbler pressure as a function of time after reaching a steady state oven temperature of 62°C and freshly evacuating the head space.

Figure 4. Plot of the diethylberyllium vapor pressure (experimental and calculated) and source oven temperature as a function of time.

Figure 5. Plot of the diethylberyllium vapor pressure versus time at 42°C. The container was evacuated and the pressure allowed to come to equilibrium again.



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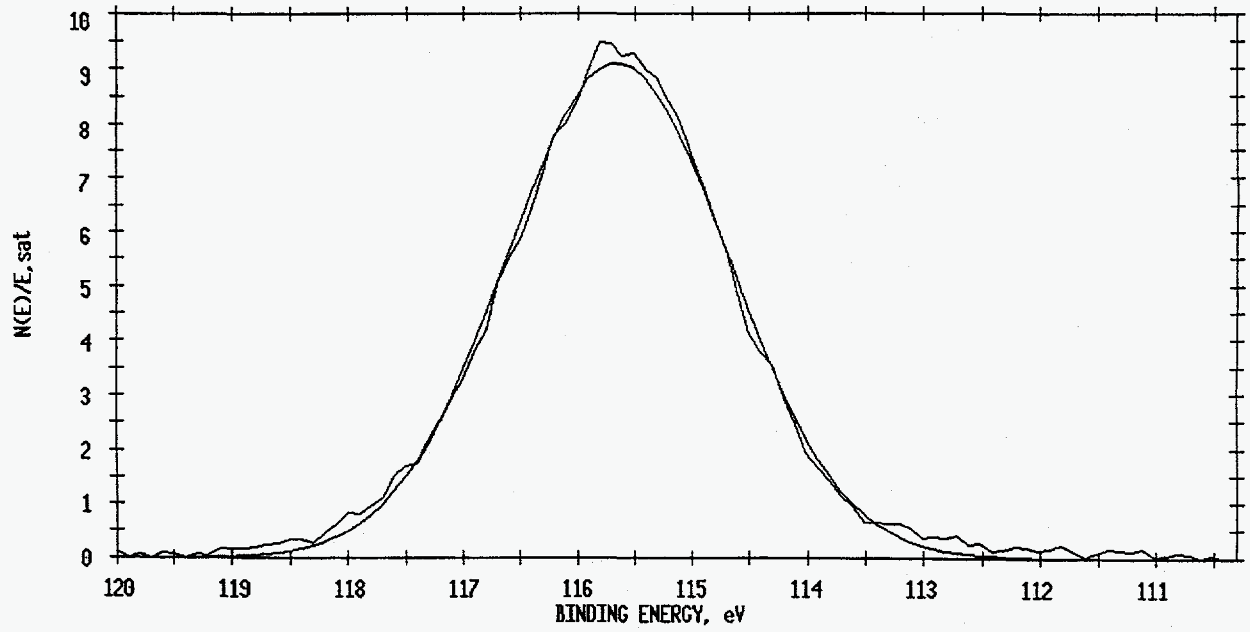
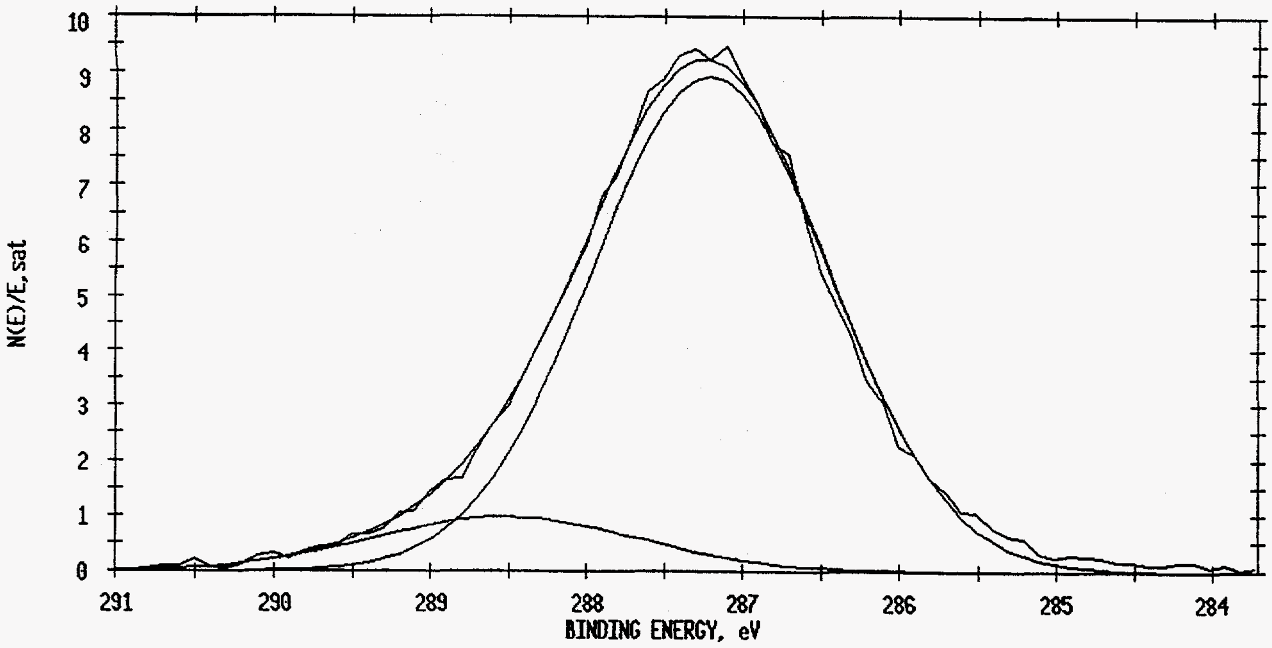


2a

Figure 2. XPS spectra for (a) beryllium, (b) carbon, (c) oxygen and (d) silicon in beryllium doped plasma polymer.


N(E)/E,sat
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9
8
7
6
5
4
3
2
1
0
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290
289
288
287
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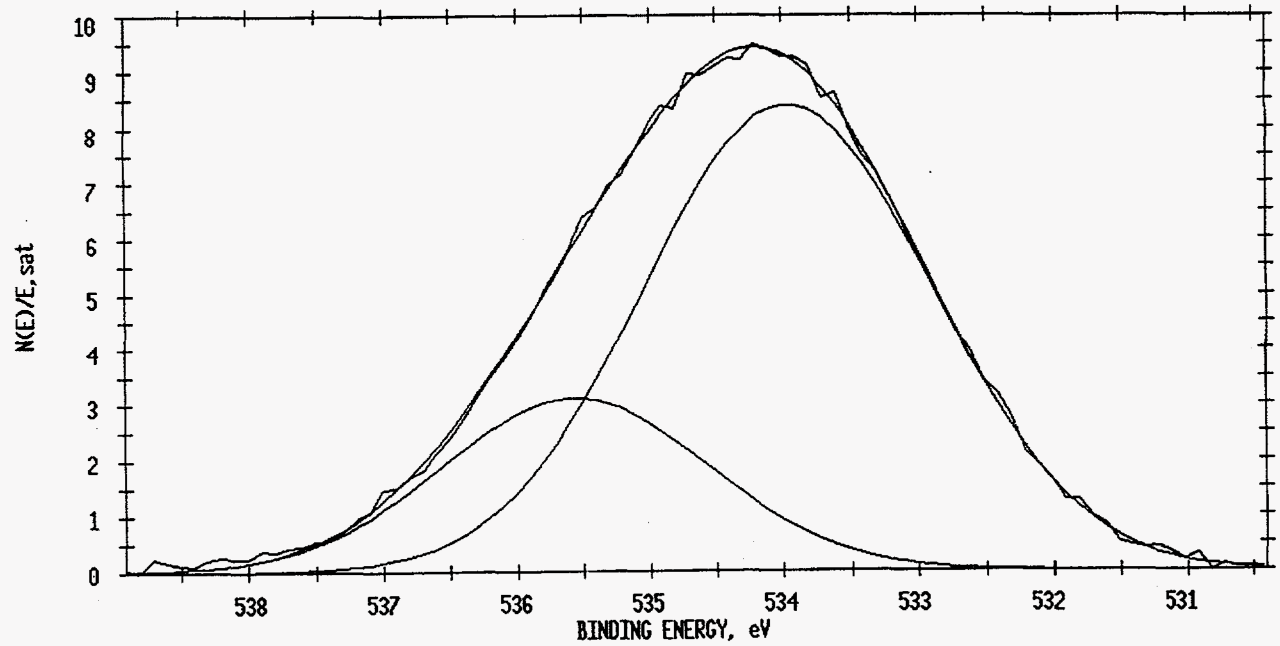
285
284
BINDING ENERGY, eV

2b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5
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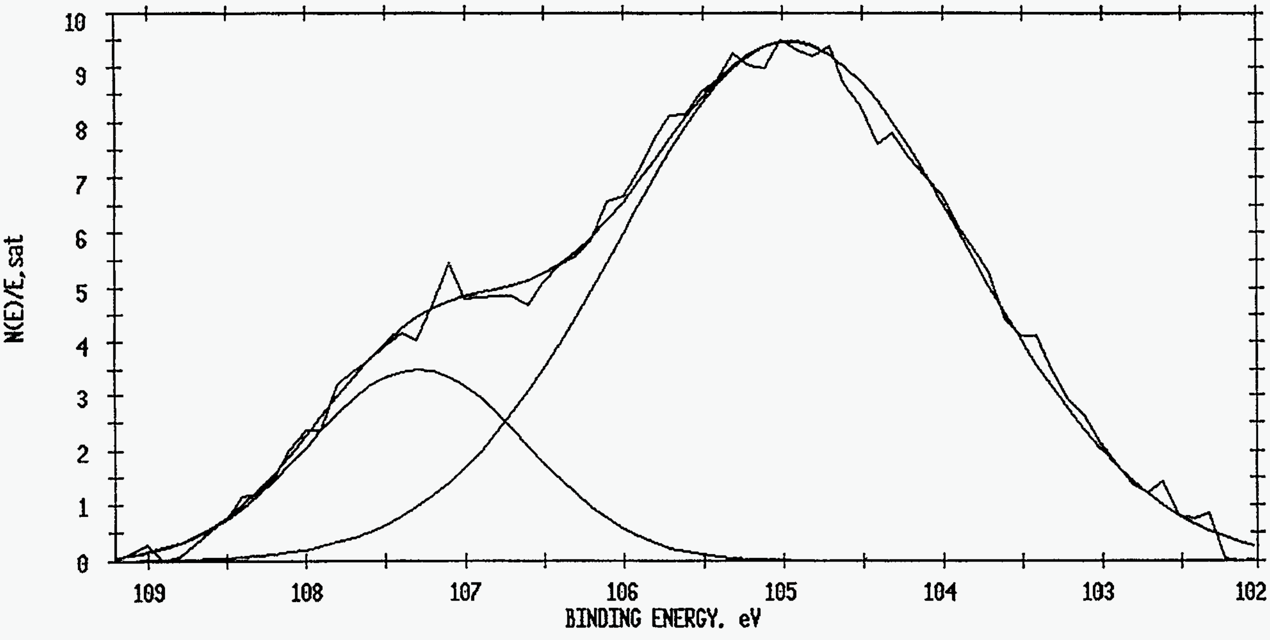
2c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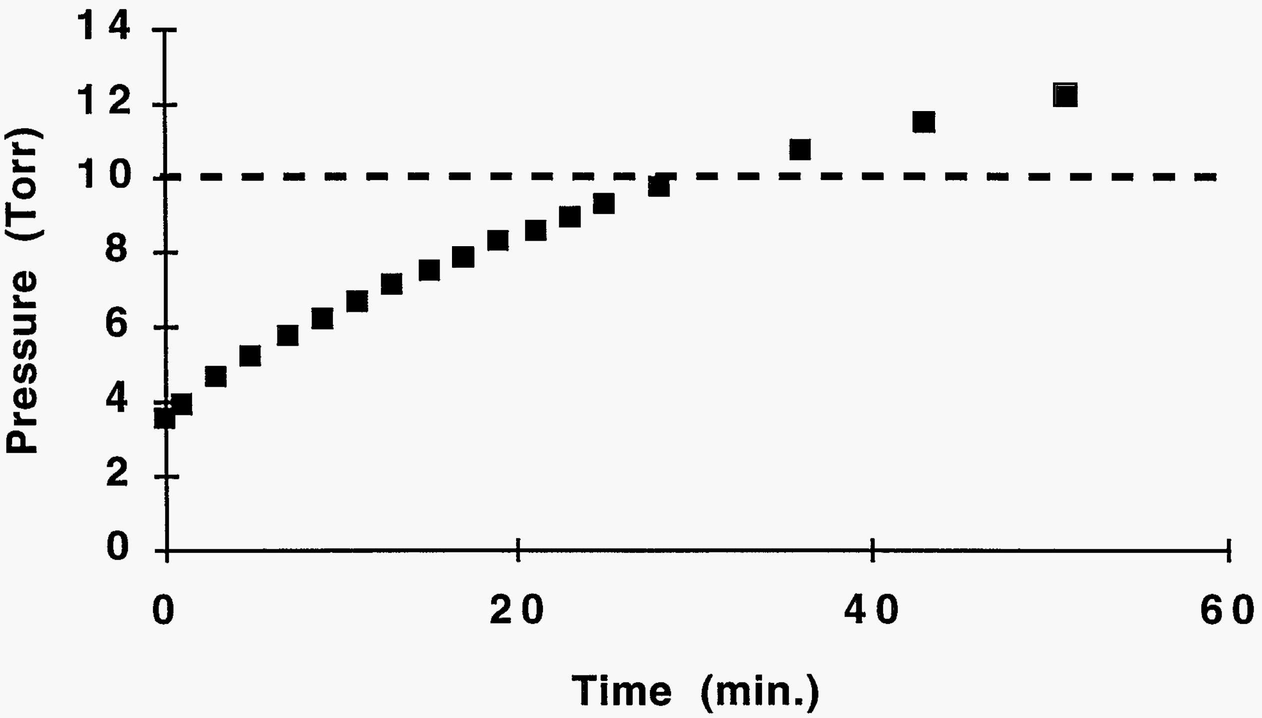
102
BINDING ENERGY, eV

2d



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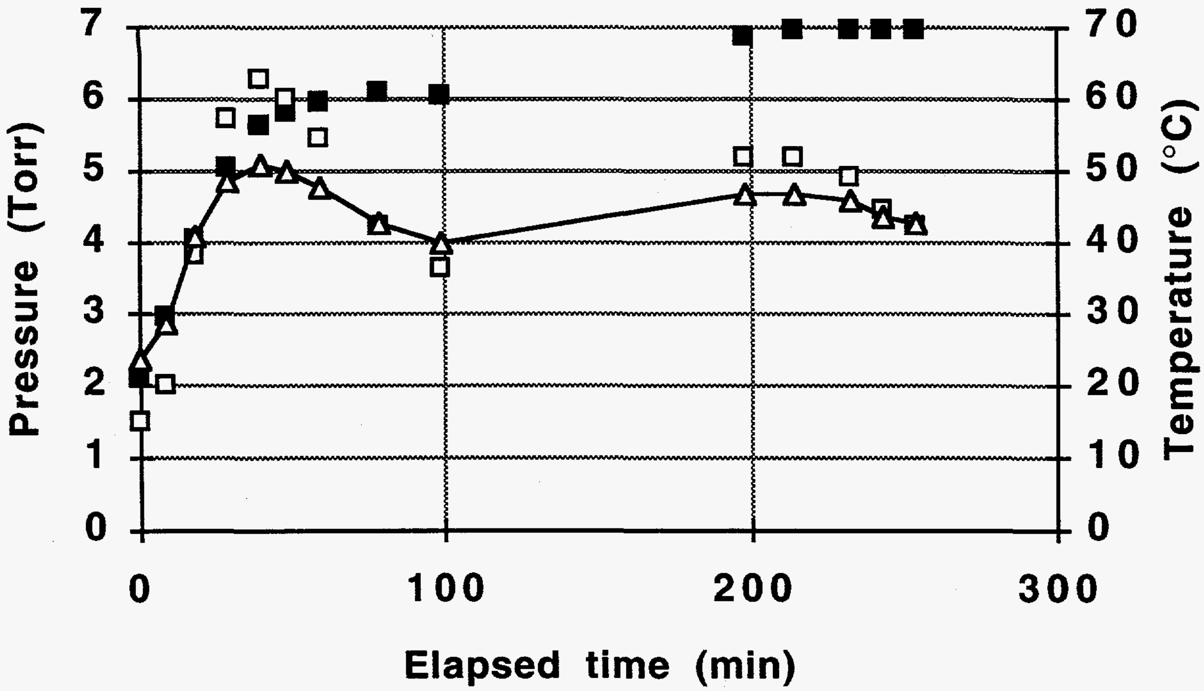

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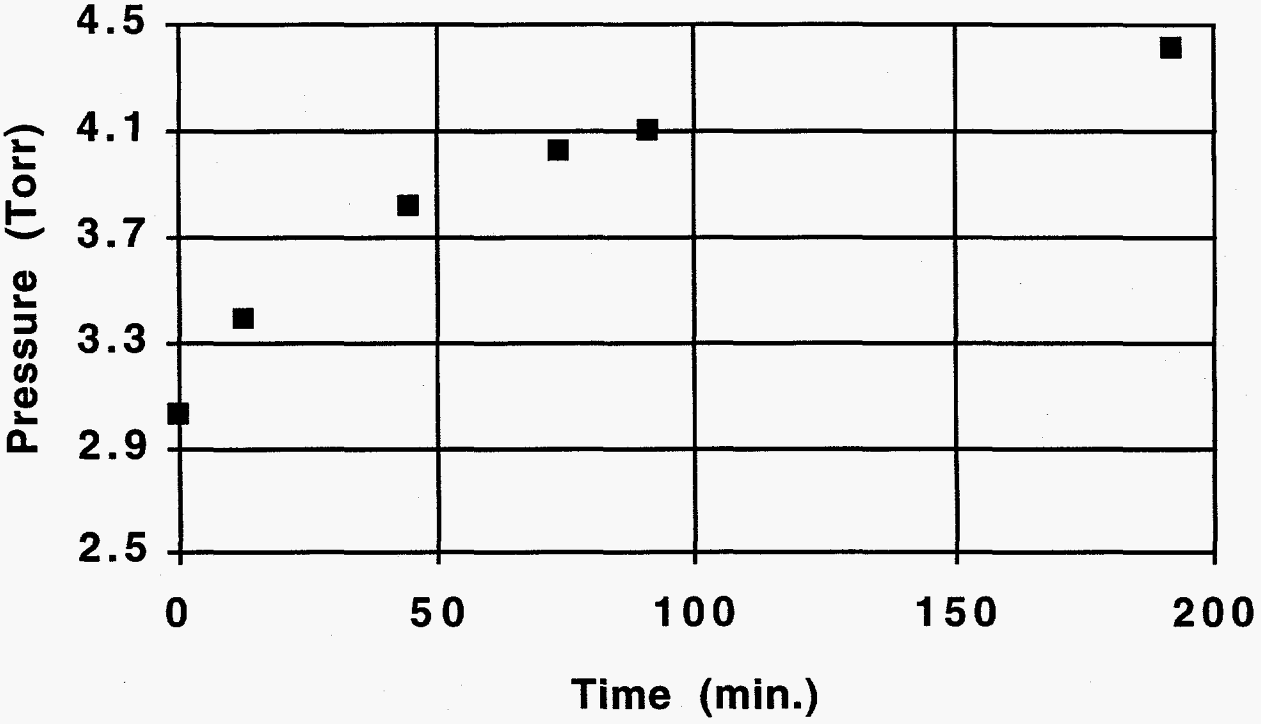

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