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ABSTRACT

Plasma deposition techniques have been examined for production of air-stable films consisting principally of beryllium and carbon. By plasma polymerization of diethylberyllium, films have been made with Be content above 50%, O content near 1%, excellent composition uniformity and reasonable surface smoothness. It appears necessary, for oxygen stability, to deposit these films at T>250°C; at that temperature, the Be is incorporated, at least in part, as a carbide; the measured film densities— 2.1–2.5 g/cm^3, are near that of Be$_2$C. Permeability to H$_2$ is suffcient to allow microballon filling at 105°C without subsequent loss of H$_2$ at room temperature.

Combined sputtering of Be and deposition of a methane plasma polymer has been found similarly effective in forming beryllium/carbon films with Be content above 50 at. % and O content near 1%. These films have not been as extensively studied.

I. INTRODUCTION

The goal of the proposed National Ignition Facility (NIF) is to ignite a target containing DT fuel using inertial confinement, and to study the behavior of material in the high energy regime that ignition produces. The DT fuel is contained in and compressed by a capsule whose walls are driven inwards by up to 2 MJ of laser energy. This compression is not easily accomplished because Rayleigh-Taylor instabilities, among others, cause mixing of the dense wall with the less dense fuel, and limit the achievable compression. Currently, such capsules are composed primarily of carbon and hydrogen, with dopants to control x–ray opacity and for generating diagnostic signals. There are ongoing studies of the utility of other low-Z materials in mitigating instability problems and in allowing access to a wider range of implosion parameters; beryllium has been identified as one of the possibilities.

We have been studying the feasibility of producing targets of a beryllium-loaded CH material made by a plasma polymerization process analogous to the current techniques.[1] The goal of this work was to deposit a film containing Be, C and H, with Be present in high proportion (Be/C atomic ratio > 0.4) which did not contain significant amounts of oxygen. The thermodynamic constants for Be, BeO and Be$_2$C indicated that Be$_2$C was more stable, in the presence of oxygen, than Be and would be formed preferentially at elevated temperatures. Preliminary scoping experiments, carried out in the fall, winter and early spring of 1995–1996 demonstrated that Be containing films that met and exceeded the Be/C requirement could be deposited from a diethylberyllium (DEB) plasma. We also found that a film deposited at a substrate temperature of about 250°C, in many cases, contained very little oxygen, while this was never true for films deposited at room temperature. The work, described below, was intended to provide a basis for a better understanding of the effect of the many experimental variables at our disposal. This work discusses the

feasibility of producing such films based on an exploratory investigation by three separate processes:

- Plasma Polymerization of Diethylberyllium (DEB)
- Be vapor deposition through a Trans-2-Butene Plasma (Be vapor/T2B)
- Be sputtering into an Ar/Methane Plasma (Be sputter/Me)

These deposition systems will be discussed in Section II, and the films they produce in Section III. In the final section we compare these properties with those required for successful target production.

II. EXPERIMENTAL

A. Deposition Systems

The diethylberyllium (DEB) plasma polymerization reactor is shown in Fig. 1. The Be–containing plasma polymer films were prepared by introducing degassed diethylberyllium {$Be(C_2H_5)_2$, from Strem Chemicals, Inc} and H_2 (research purity, from Matheson Gas Products) at various flow rate ratios into an inductively coupled glow discharge. The DEB flow rate was controlled at about 1.0×10^{-3} cm^3/s (STP). Al foils, KBr pellets and Kapton® 30H (DuPont) films were used as substrates. The substrates were etched by Ar plasma for 1 hour before the deposition process. After that process, at room temperature, the background pressure is stable and < 10 mTorr in a sealed system, implying leaks, virtual or otherwise, are less than < 10^{-6} sccs. Films were typically
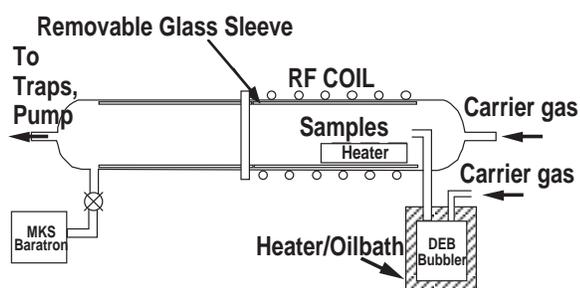
Fig. 1. Schematic diagram of reactor used for DEB plasma polymerization. The reactor cell is a 7 cm i.d. glass cylinder wound with a coil which creates the plasma. Substrates are on a heater plate, and 2 to 8 cm downstream of the DEB entry nozzle. The DEB bubbler is maintained at 50–55°C with an oil bath; the DEB delivery line is heated with tape to 2–3°C hotter than that of the thermal oil bath. After cleaning with an Ar plasma, the background pressure with the reactor sealed is stable and < 10 mTorr.

deposited at a substrate temperature of 250°C. At that temperature the deposition rate at 4 cm from the monomer inlet is about 0.10 μm/h. In some cases a small flow of H_2 gas (DEB/H_2 ~ 1/1) is added to help relieve strain in the coating. Operating parameters of the deposition process are summarized in Table I.

The reactor for Be vapor/T2B is shown in Fig. 2. In early work, T2B plasma polymer and Be were co-deposited, producing Be incorporated in a plasma polymer matrix. In our latest work, Be and T2B plasma polymer have been deposited sequentially, producing a multi–layer structure. Films deposited on Al foil were used for Auger electron spectroscopy. Films deposited on glass were for gravimetric determination of deposition rate. Films deposited on Kapton® were used in the permeation experiments.

The magnetron reactive sputtering system is shown in Fig. 3. The substrate was not heated except by the plasma.

B. Analyses

The films produced in this study were analyzed for characteristics important for their use as fuel holders: elemental composition, molecular structure, morphology, and hydrogen permeability.

Table I
Experimental parameters for depositing diethylberyllium (DEB) plasma polymer films

Base pressure	7–8 mTorr
Ar flow rate (etching)	$1.0–1.2 \times 10^{-3}$ cm^3/s (STP)
Ar etching duration	60 min.
Ar etching pressure	25–30 mTorr
DEB flow rate	$0.8–1.2 \times 10^{-3}$ cm^3/s (STP)
H_2/DEB flow rate ratio	0/1.0–2.5/1.0
R.F. power input	35 W, 3.9 MHz
Substrate temperature	250°C
Plasma Pressure	70–75 mTorr
Deposition duration	8 h for 1 μm films
	120 h for 10 μm films

Elemental composition of the film (on Al substrate) was determined with Auger spectroscopy using a PHI 545,

manufactured by Physical Electronics Industries, Inc. Typical sputter rates were approximately 3 to 4 nm/min. The sputter area was approximately a 4 × 4 mm square, with a detection diameter of 50–100 μm.
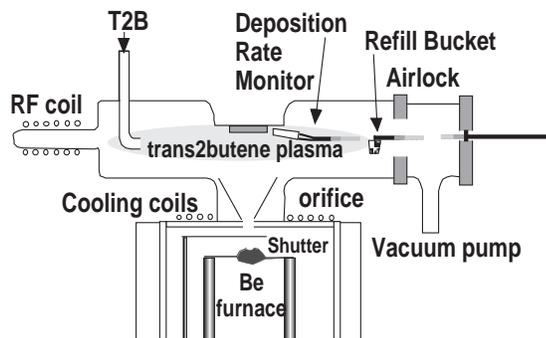
Fig. 2. Schematic diagram of the two chamber reactor used for deposition of evaporated Be/T2B plasma polymer films. The lower chamber (6" i.d. glass cross) contains a W oven heated BeO crucible operating at 1278–2000°C. The pressure is < 1 mTorr. Adjacent components are protected by heat shields, water cooled current conductors, and a cooling coil on the Al top of the reactor. Be diffuses through an 8 mm orifice into the upper chamber (a custom glass Tee) which contains the T2B plasma. The substrates are mounted on the ceiling of the Tee and can be heated by a radiant heater external to the Tee. An rf coil on the narrow end of the Tee maintains the plasma. An airlock on the opposite end allows introduction of a mass deposition monitor or a loading bucket, for reloading the Be furnace without air exposure. The T2B flow rate is ~10^{-2} sccs and the pressure ~2 mTorr.
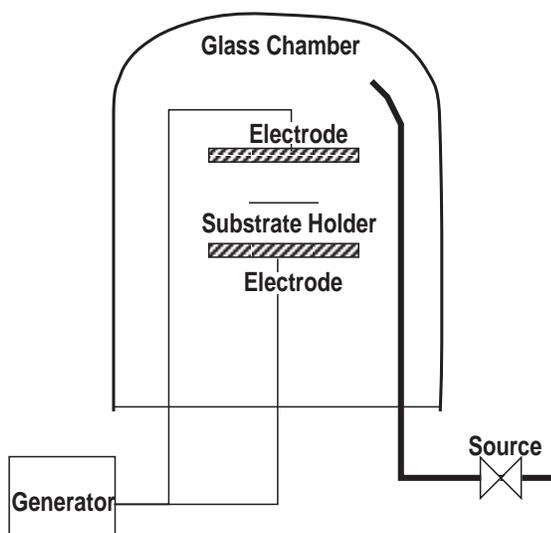
Fig. 3. Schematic diagram of reactor used for deposition of films by Be sputtering into an Ar/Methane plasma.

The x–ray diffraction spectra were obtained on a Scintag XRD 2000.

Molecular structure was determined by FTIR spectroscopy of films (on KBr substrates) was measured by transmission using a Perkin–Elmer model 1760X spectrometer.

The surface morphologies of 10 μm thick films were observed by scanning electron microscopy with a Leica Stereoscan 440. By measuring the thickness of a broken edge, we could deduce the density of the films.

Permeability measurements were made on a custom built device at UMR. It measures the flux of gas from one sealed volume to another through the membrane to be tested (plasma deposit on Kapton®, i.e., a composite film). The permeability coefficient of the composite film is given by

$$P_c = \frac{dp}{dt} \times \frac{Vol}{760 \text{ Torr}} \times \frac{l_c}{A \times \Delta p_c} \qquad (1)$$

here dp/dt is the rate of pressure increase, Vol is the volume of the low pressure side, l_c is the composite film thickness, A the membrane area, and Δp_c the pressure difference across the composite film. The permeability of a bare Kapton® film is also measured (the bare film having been underneath the coated film during deposition, so having had the same thermal history), and used to extract the permeability of the plasma polymer film from that of the composite. The permeability of the Kapton® film is ~10× that of the plasma polymer film, but the Kapton® was also ~10× thicker than the DEB plasma polymer, so the impedance they present to the gas flow is similar.

III. RESULTS AND DISCUSSION

A. DEB Plasma Polymer

Several trends had been observed in early trials and were clarified in this work. It was found that the maximum Be/C ratio was found at deposition sites 4–6 cm from the monomer inlet (Fig. 4). We systematically varied the deposition temperature and H_2 flow rate to optimize film composition at this location; we found deposition temperature 250°C and no added H_2 flow gave the highest Be/C and lowest O/Be ratios (Figs. 5–7). The Be/C ratio also appeared to be function of the nature of the substrate on which deposition occurred (Fig. 4). The addition of H_2 to a monomer mixture is known to decrease internal stress in hydrocarbon plasma polymerization;[2] unfortunately it was also found to decrease Be/C ratios (Fig. 5), precluding the use of large H_2/DEB feed ratios.
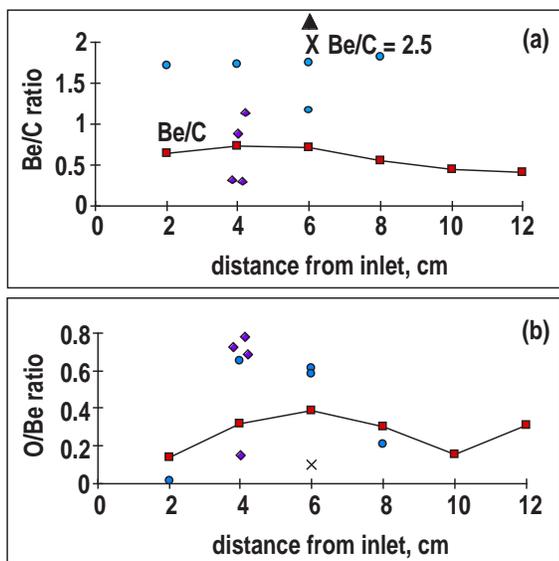
Fig. 4. (a) Be/C and (b) O/Be ratio for films deposited in the DEB reactor as a function of distance from the DEB inlet. The lines connect data on <1 µm thick films deposited in one deposition run. One substrate in that run (X) had 10 µm of plasma polymer predeposited on the Al substrate. The composition of films deposited in other runs—10 µm thick films and of films deposited on Kapton, are marked with O, and ◊, respectively. Note the substantial, systematic composition difference between those latter films and the 1 µm thick films on A1.
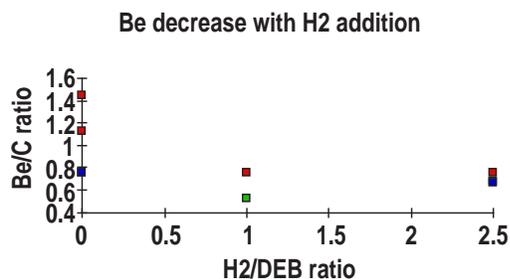
Fig. 5. Be/C ratio for films deposited in the DEB reactor 4 cm from the DEB inlet onto aluminum substrates at 250°C for various flow rates of H_2.

We discovered, however, that the film composition was not so simply determined. Films deposited on Kapton[®] are anomalously high in both Be and O in three out of four cases (◊ in Fig. 4), and the ~10 µm thick films have high Be and O contents (avg. Be/C ~1.7, O/Be = 0.2–0.6) in five out of six cases (o in Fig. 4). That this is not just random variability in run conditions is shown Fig. 4 where the composition of film deposited on a 10 µm plasma polymer coated Al substrate (X), as opposed to bare Al (the connected points) deposited in the same run, is unmistakable.
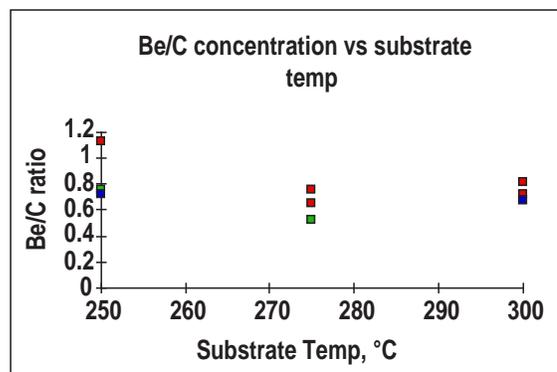
Fig. 6. Be/C ratio for films deposited in the DEB reactor 4 cm from the DEB inlet onto aluminum substrates for various substrate temperatures.
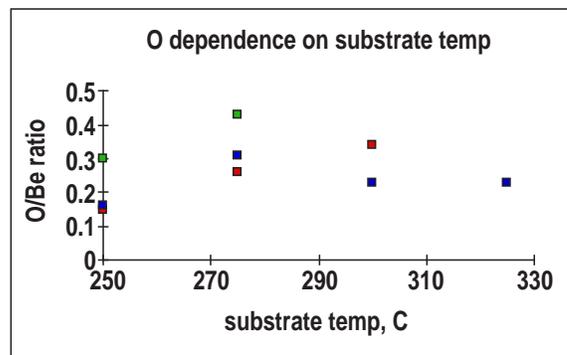
Fig. 7. O/Be ratio for films deposited in the DEB reactor 4 cm from the DEB inlet onto aluminum substrates for various substrate temperatures.

On the basis of our survey, 10 µm thick films were deposited using a substrate temperature of 250°C and no hydrogen. Their compositions are shown as O in Fig. 4. All of them have a much higher Be/C ratio (~1.7) than the 1 µm thick films (~0.7). The oxygen concentration in these thick films follows much the same pattern as for the thin films, but is much more exaggerated. In particular, the sample deposited 2 cm from the inlet seems unusually stable against degradation by exposure to oxygen and atmospheric humidity. We obtained an x–ray diffraction (XRD) pattern for it which showed the presence of crystalline Be_2C (size = 6 nm); much more than seen in other films (Fig. 8). The beryllium-carbide bond should be stable against oxidation in dry air on the basis of the Gibbs free energies of formation of beryllium -oxide and -carbide, respectively. It appears that beryllium-carbide is the preferred form of deposition from molecules immediately after they enter the plasma.

FTIR gave further information about the way that the molecular structure in these films vary with location in the
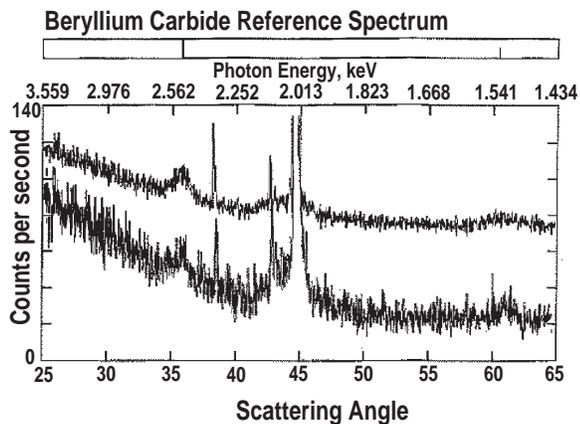
Fig. 8. X–ray diffraction spectra for DEB plasma polymer films deposited at 250°C and 0/1 H$_2$/DEB flow rate ratio. The top spectrum is of the film deposited at 2 cm from the monomer inlet. The bottom spectrum is at 6 cm. In addition to the sharp diffraction peaks from the aluminum substrate, the only other features are one obvious broad peak which can be identified as the (111) reflection of Be$_2$C and another barely visible peak at the location where the (220) reflection of Be$_2$C should be.

reactor. Figure 9 shows spectra for films deposited at 4 and 8 cm. (T$_{dep}$ = 250°C, H$_2$/DEB = 0/1). There are two trends to observe: A broad band caused by carbonyl groups (resulting from reaction of free radicals with oxygen) is present at about 1800 cm^{-1} for the 2, 4 and 6 cm sample but is absent for the 8 cm. sample. On the other hand, a shoulder at about 1066 cm^{-1} (caused by an organic C-Be[3] or C-C or C-O, all organic) gains strength as one goes from 2 to 8 cm. This suggests the film is changing from an inorganic structure containing many trapped free radicals to a less highly cross-linked organic
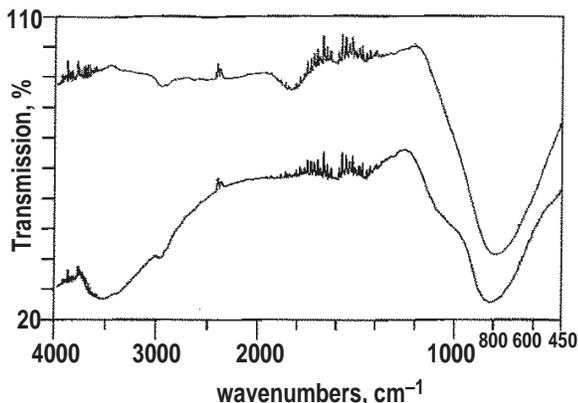
Fig. 9. FTIR spectra for DEB plasma polymer films deposited at 250°C and 0/1 H$_2$/DEB flow rate ratio. The top spectrum is of the film deposited at 4 cm from the monomer inlet. The bottom is at 8 cm.

structure (or at least more mobile structure) with fewer trapped free radicals along the length of the reactor.

These thick films were not intact; they had severe stress problems (Fig. 10). We had not had that problem with previous runs using H$_2$ (Fig. 11). The cracking caused by this stress prevented us from measuring densities (we had calculated film densities 2.1–2.5 g/cm^3 for the cleanly broken edges of films made with H$_2$ added), and we were not able to measure permeability of these films.
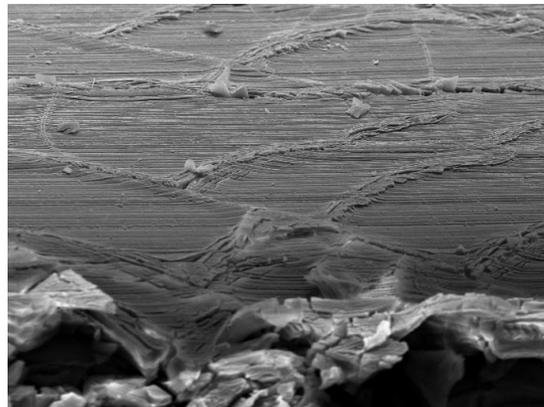
Fig. 10. SEM photograph of DEB plasma polymer sample which was deposited at 250°C and 0/1 H$_2$/DEB flow rate ratio at 4 cm from the monomer inlet.

We did determine the permeability of thinner films for samples deposited at 6 cm from the monomer inlet. The data are remarkably consistent; all plasma deposit permeabilities are in the range 0.11–0.13 barrers (A barrer is the gas flow rate across a membrane for a given pressure difference. 1 barrer = 10^{-10} (cm^3 (STP) cm)/(cm^2 s (cm Hg)). This equates with filling a microballoon, having a 200 μm thick plasma polymer shell, with enough hydrogen to grow a 200 μm thick ice layer (500 atm., STP) in 550 days using a 10 atm driving pressure. Assuming the usual doubling of rate with every 10°C increase in temperature, the fill could be completed in 24 days at 105°C. However the permeability is low enough that the microballoon would retain its charge well at room temperature.

B. Be vapor/T2B Plasma Polymer

The Be vapor reactor was used to make a microlayered film containing pure Be layers thick enough to avoid oxidation, but spaced irregularly enough by T2B plasma polymer that permeation was feasible. Preliminary studies in which pure Be was evaporated on Kapton$^{®}$
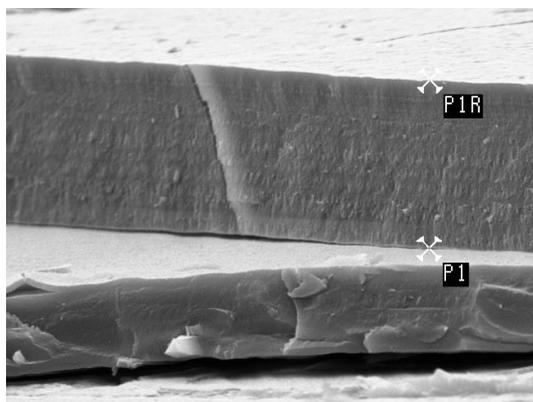
Fig. 11. SEM photograph of DEB plasma polymer sample which was deposited at 250°C and 1/1 H_2/DEB flow rate ratio at 8 cm from the monomer inlet. A film of thickness 11 μm was initially deposited, and the reactor was opened, exposing the sample to the laboratory atmosphere in order to remove other samples for analysis. The sample was then placed under vacuum again, the Ar plasma cleaning process was repeated, and an additional 21 μm of DEB plasma polymer was deposited on top of the original 12 μm thick film.

showed that a 0.1 μm thick coating was not a barrier to H_2 permeation but a 0.2 μm layer was.

The layered structure was formed by alternately shuttering the Be furnace while depositing plasma polymer, and then turning off the plasma while evaporating Be. The cycle was calculated to form 0.1 μm layers alternating between Be and T2B plasma polymer (assuming a density of 1.85 and 1.3 g/cm^3, respectively). Auger depth profiling shows we achieved this structure, though the Be layer contained substantial C (max Be/C ~2.5), and the entire film contained a high level of O (O/Be ~1). This multi–layer structure was found to have a H_2 permeability of 1.36 barrers at 55 C–10× that of the homogenous films deposited from a DEB plasma.

C. Be sputter/Me Plasma Polymer

Films containing high Be/C ratios and low O/Be ratios were obtained at deposition rates of approximately 1 μm/day by the Be sputter/Me method (Fig. 12). Particularly noteworthy is the fact that low O/Be atomic ratios are obtained in films that contain Be/C ratios that exceed 2. The O/Be ratio is apparently stable for at least a week (the time taken for measurements), but not a month; Additional samples measured after 22 and 30 days, had O/Be ratios ~0.8. These samples were not placed on a heated substrate, but the high plasma power (200 W) heated the substrates to 110–150°C after an exposure of
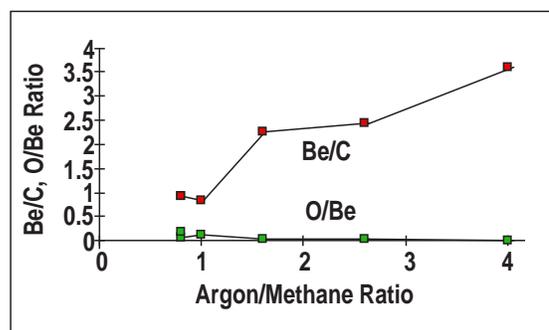
Fig. 12. Be/C and O/Be ratios for films produced by reactive sputtering of Be in an argon/methane plasma. The Be/C ratio is nearly proportional to the Ar/Me ratio, and the O/Be ratio is very low for all conditions. The films were produced at ~1 μm/day, with a 200 W plasma in a pressure of ~200 mTorr.

4 h. Use of a deliberately heated substrate (300°C) led to high oxygen content.

Under the certain conditions, it has been shown that a water vapor barrier can be deposited from a methane plasma.[4] If the carbon part of the deposited film acts as a water vapor and oxygen barrier, we should obtain the observed resistance to oxidation. We are in the process of obtaining hydrogen and nitrogen permeability data for such films.

IV. CONCLUSIONS

DEB-produced plasma polymer films have been stable against oxidation if the Be is deposited in the form of Be_2C. This has proved feasible for <1 μm thick films deposited near the DEB inlet onto substrates at 250°C. Thicker films (10 μm) deposited on Al manifest higher Be/C and O/Be ratios than the thinner films. This is caused by a substrate effect of unknown origin. Films deposited from pure DEB showed excessive stress build-up. Adding H_2 (DEB/H_2 = 1/1) reduces stress in these films without an excessive decrease in Be/C ratio.

Permeability of H_2 through 1 μm thick films was measured and found to be consistent with charging of microballons in 24 days at 105°C. Their low permeability to H_2 at room temperature indicates that hydrogen could be stored in the microballoons for an extended period of time.

Multilayer Be vapor/T2B films showed good H_2 permeability, and no signs of internal stress, but also showed exhibited no resistance to oxidation.

Reactive Be sputtering in methane has produced a wide range of Be/C ratios (up to Be/C = 3.8) with low oxygen content. There is no information on stress or permeation.

Further research into these films will require modification of the DEB plasma reactor[5,6] to enhance the deposition of the oxygen-free Be films. It may be desirable in the future to switch to the reactive sputtering system, for its combination of simple operation and cheap components, if we can show it produces permeable, low-stress films.

ACKNOWLEDGMENTS

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