VACUUM DEPOSITED POLYMER FILMS - PAST, PRESENT, AND FUTURE APPLICATIONS

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Two extremely high rate processes have been developed for the vacuum deposition of polymer thin films. Dubbed the PML (for Polymer Multi-Layer) and LML (for Liquid Multi-Layer) processes, the PML technique was originally developed for the manufacture of polymer/aluminum surface mount capacitors while the LML method arose from a need to fabricate lithium polymer batteries. These processes have since been found to be compatible with most other vacuum deposition techniques in, integrated, in-line coating processes. Battelle has developed an extensive program, and a great deal of hardware, to pursue a wide variety of PML and LML applications which integrate these two process technologies with other, conventional, vacuum deposition methods. The historical development of the technologies will be reviewed and the Battelle PML/LML facilities will be described. Current Battelle work involving solar thermal control films, PML QWOTs, and polymer/metal high reflectors will also be discussed. Battelle PML work that is just starting, involving non-linear optical materials/devices, lithium polymer battery fabrication, electrochromic devices, and polymer/oxide multilayers, will be discussed as well.

1. INTRODUCTION

This paper will discuss work under way at the Pacific Northwest Laboratory (PNL) to develop applications of two new vacuum processes for the deposition of polymer films. The first technique involves the vacuum flash evaporation of monomer fluids which are subsequently condensed as a liquid film then radiation cross linked to form a solid film - this method has been named the Polymer Multi-Layer (or PML) process. The second process involves the vacuum “coating” of reactive liquids, mixtures, or slurries directly onto the substrate which are subsequently radiation cross linked to form the solid film. The “coating” can be accomplished by a variety of means such as extrusion, gravure rollers, spraying, or any of the standard - atmospheric - roll coating processes regularly employed in the converting, or printing, industry today. We have chosen to call this second technique the Liquid Multi-Layer (or LML) process in order to distinguish it from the flash evaporation process. Each of these processes is compatible with the simultaneous, high rate, in-line deposition of other layers by conventional vacuum coating processes like sputtering, evaporation, or Plasma Enhanced Chemical Vapor Deposition (PECVD). The rate actually exceeds that of all of the conventional techniques for the deposition of dielectric films. In fact, for most product applications involving polymer/metal layers, the polymer rates even exceed metal deposition rates. In these cases the throughput is limited by the metal film deposition rate and not, as is traditionally the case, the dielectric film deposition rate. As these processes are likely to be new to most readers at this time, some background material seems in order. The basic processes, and relevant comparisons to conventional vacuum web coating, will now be discussed.

The PML Process: The technique used to evaporate the monomer is really quite simple. Monomer fluid is first degassed - stirred while the vapor is pumped away - to a suitable base pressure. The degassed monomer is then sprayed into a very hot tube that has a very hot, pressure baffling, expansion nozzle on one end. By very hot, it is meant that the tube is hot enough to instantly vaporize the monomer spray, yet not hot enough to crack and/or polymerize the monomer on contact. Under these conditions the monomer evaporates as quickly as it is introduced into the tube - there is no pool of liquid in the tube. The baffles in the tube/nozzle system serve to build the pressure (of the molecular gas of monomer molecules) in the nozzle expansion chamber. Building the pressure serves to make the molecular gas stream, exiting the slit in the nozzle, more uniform across the length of the nozzle slit.
The flow of monomer, into the hot tube, is controlled with a precision metering pump. The monomer spray can be created with a variety of techniques, including an ultrasonic atomizer, fuel injector, or by dripping onto a high speed rotating disc. To date, dispersion with an ultrasonic atomizer has yielded the best layer thickness uniformity. However, 2% uniformity has been attained on capacitor runs of several thousand layers, by just allowing the precision metered monomer flow to drip into the hot tube. The SEM photographs of figure 1 demonstrate the layer uniformity of this "drip" process for PML capacitor material deposited on a substrate moving at 500 feet per minute. Film thicknesses obtainable with the PML process range from a few tens of angstroms up to mils, with the limit largely imposed by the penetration depth of the cross-linking radiation employed.

Degassing of the monomer is not carried out in order to maintain the vacuum condition of the chamber, although it is always good practice to minimize the amount of these vapors in order to minimize contamination of concurrent processes. Rather, the degassing step is necessary in order to properly introduce the liquid to the vacuum environment. If the liquid is not degassed prior to injection into the vacuum, violent expansion occurs as the gassy liquid enters the vacuum. This causes pulsing and spitting at the injection port, which leads to large pulses in the flow of liquid into the evaporator, which subsequently leads to time variations of the film thickness.

The LML Process: This process also begins by degassing the reactive liquid in order to prevent violent expansion when the liquid enters the vacuum chamber. However, the liquid is directly applied to the substrate without evaporation. The choice of reactive liquids that can be used in the LML process is much wider than that which can be employed in the PML process. Since the liquid does not need to be evaporated without degradation, higher molecular weight materials can be employed. As well, solutions (like monomers with dissolved salts) or slurries (like monomer/oxide, monomer/graphite, or monomer/high molecular weight, solid, polymer powders) in which the additional components will not evaporate in the range of temperatures compatible with the monomer liquid can deposited. However, the lower thickness limit, and thickness uniformity, obtainable with the LML process is not expected to be much different than the atmospheric deposition processes that it derives from. Therefore, the lower thickness limit of LML layers shouldn't be much less than about a half mil, with uniformity of a few percent.

2. PRODUCT APPLICATION AREAS FOR PML AND LML FILM DEPOSITION PROCESSES

PML Applications: The types of acrylic polymers that have been deposited to date are very clear for wavelengths between about 0.35 μm and 1-2.5 μm, making them attractive for optical thin film applications. In this wavelength range, the polymers have extinction coefficients of \( \kappa = 10^7 \), while conventional, vacuum deposited, optical materials only have \( \kappa = 10^4 \) at best. Commercially available monomers produce polymers with refractive indices between 1.31 and 1.71. PML technology has already been reduced to practice in a manufacturing process to produce multilayer polymer/aluminum capacitors in a single vacuum chamber. Due to the rather broad acceptable limits on layer thickness with the capacitor product, layer to layer thickness uniformity is not as critical as for optical interference coatings. Nonetheless, in typical capacitor runs, of 5000 layers deposited at 500 feet per minute, published SEM photographs of figure 1 show layer to layer thickness uniformity is roughly 2%. Capacitor films have been deposited in multilayer configurations from a few to more than 24,000 layer pairs, with total stack thicknesses greater than 2 millimeters. (NOTE that this 24,000 layer pair film was greater than 10 square feet in area, and took less than 4 hours to deposit - including pump down, venting, and removal of the film from the chamber). These, demonstrated, thickness uniformities are already adequate for some interference coating applications while the rates exceed conventional processes by more than two orders of magnitude.
Figure 1. **In the side view:** the tear drop shapes are sputter coated Al leaves exposed by plasma ashing then sputter coated with copper for wave solder electrical termination of the device. The white lines are Al layers and the black are polymer layers. **In the top view:** you are looking down on the sputter coated Al Leaves. These capacitors were routinely deposited at line speeds of 500 linear feet per minute.
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The PML technique can be applied to batch coating operations for rigid substrates as well as to web coating. In a batch mode operation the rates, while still much higher than for conventional processes, must be reduced relative to the web mode due to mechanical fixturing restrictions.

The PML process can be used to deposit any radiation cross-linkable polymer, or mixtures of various radiation cross-linkable polymers. Poly-functional acrylates and methacrylates have been the focus to date since they just happen to have the highest cross-linking rates. However, the weatherability and environmental stability of the acrylates and methacrylates is very well known, making them perfect choices for the outdoor service conditions that a solar reflector will experience. Furthermore, the PML process utilizes pure monomers. This means that corrosive chemicals, such as those required to extrude or cast a polymer web substrate, are not present to attack the silver film.

For the reasons cited above, PNL is actively developing PML processes for solar thermal control films, solar reflectors, multilayer interference optics, and PML/sputtered optical multilayers. As well, PML and hybrid PML/metal, PML/oxide or PML/metal/oxide multilayer materials are under development for EMF mitigation, radar absorption, packaging barrier layers, paper coating, and release layers.

**LML Applications:** The LML process does not lend itself to optical interference coatings, or most of the PML applications listed above, due to the lower limit on thickness being relatively large, over 10 \( \mu \text{m} \). However, the areas where it is being developed may have even larger economic impact. Monomer/salt solutions allow the deposition of polymer electrolytes. Further addition of an electron conductor (like graphite) with an intercalation compound (like cobalt oxide) permits deposition of polymer cathode materials. Some polymers will store lithium directly and require only the electron conducting additive to form polymer cathode materials. Polymer/graphite layers can form intercalation anodes as well.

In the area of electrochemical applications described above, PNL is actively developing LML process technology for complete vacuum fabrication of lithium polymer batteries as well as switchable electrochromic windows and mirrors. The technology has already been licensed for the battery application and production facilities are being prepared. The production process will employ proprietary polymer electrolyte, lithium salt, and polymer cathode materials. In production, the battery application will use LML, PML, and electron beam evaporation technology. The LML process will be used to deposit the polymer cathode and electrolyte layers while the lithium metal anode, and current collecting metal layers, will be electron beam evaporated. A final hermetic sealing layer will be applied by the PML process.

Index matched polymer crystal composites are being developed for detector and heads up display technology as well, and data from this process will be discussed below.

### 3. PML AND LML HARDWARE REQUIREMENTS

Figure 2 shows the geometry of the manufacturing system used to deposit alternating layers of polymer and aluminum for the capacitor application discussed above. In the capacitor application the substrate is simply a rotating drum. However, other substrates, such as flexible polyester, polyethylene, metal foils, and various types of paper, can be used. Figure 3 is a schematic of the vacuum web coater at PNL. The chamber is shown configured as it would be for depositing Polymer/Silver/Polymer on polyester with the PML process used in concert with sputtered silver.

Some system specifications for the chamber in figure 3 are: 0-500 feet/min web speed; bi-directional operation; deposition source enclosures isolate process atmospheres; roll-to-roll, closed loop, and drum only operation; and system is fully automated. The chamber in figure 3 is set up in a modular fashion that permits multiple process enclosures to be mounted in any order for fabrication of multilayer structures. One of the closed-loop web paths has nothing in contact with the front
Figure 2. Schematic of deposition system used to deposit polymer/aluminum capacitor material.

Figure 3. Schematic of new Battelle deposition system shown in a configuration to make polymer/metal/polymer multilayers such as solar reflector or window film coatings.
surface. This last feature will permit fabrication of large area, high performance, dielectric only laser filters and broadband
dielectric only reflectors without the danger of scratching due to multiple passes over idlers. The current process capability
includes: PML flash evaporation - with e-beam or UV cure; sputtering - reactive or non-reactive; e-beam evaporation -
reactive or non-reactive/rod fed or crucible; PECVD; and LML (extrusion type) - with e-beam or UV cure. Further, the entire
drum can be biased with rf or dc electric fields, any deposition source enclosure may contain rf or dc bias electrodes, rf glow
discharge cleaning modules can be placed before and after any deposition source, and any combination of deposition zones
can be biased with fixed or rotating magnetic fields.

3.1 Hardware, And Economic, Differences Between PML/LML And Conventional Vacuum Coating Processes:
The main difference between a conventional vacuum web coater and PML/LML vacuum web coater is the replacement, or
supplementation, of the conventional deposition sources with monomer evaporators (or LML sources) and cure systems. In
terms of initial hardware investment there is not much cost difference.

The operational costs could be much lower for the PML/LML system than for conventional vacuum roll coaters when one
is directly substituting a polymer layer for a sputtered or evaporated dielectric layer. Compare several hundred to as great
as 1500 feet per minute for polymer coatings to 1 to 20 feet per minute for conventional dielectric coatings. It is true that
some of the newer metallizers can flash evaporate aluminum at 2000–3000 feet per minute, depending on thickness. However,
they can not deposit optical grade dielectric materials, of useable thicknesses, at even 50 feet per minute - usually much less
than 25 feet per minute. What value can be placed on being able to increase the rate of a manufacturing process more than
100 fold? Particularly a process where there are such large initial capital and ongoing maintenance costs as with vacuum roll
coating.

The material costs are the same, or much lower, for polymer films than for conventional dielectric films as well. For instance,
the per pound costs for optical grades of indium oxide, magnesium fluoride, or silicon dioxide are roughly $500, $700, and
$500, respectively. Many acrylic monomers, unlike standard optical grade materials, are commodities. With, in some cases
very few, additives, acrylic monomers are polymerized into such things as floor wax, disposable diapers, or the smooth
coating on many types of paper. HDODA (Hexane Diol DiAcrylate, n=1.5 for the cross linked polymer) costs about $3 per
pound. For monomers containing only carbon, hydrogen, and oxygen, prices are in the $3-$10 per pound range. Most of the
polymers, created from these monomers, have 1.45<n<1.55. Adding fluorine atoms to the monomer molecules can lower the
refractive index to the 1.31 range, while adding bromine atoms can raise n to the 1.7 range. The fluorinated, and brominated,
monomers are not in mass production at the present time. The fully fluorinated monomers are commercially available though.
These fluorinated monomers, which are not mass produced, are comparable in price to conventional optical grade starting
materials.

3. Experimental Methods and Results

PML Reflector Materials Experimental Method: PML/Silver reflectors and Fabry-Perot etalons have been fabricated and
tested. For this work, a length of 18 cm wide polyester substrate was simply attached to the rotating drum. The drum
temperature was maintained at 4 °C. Multiple layers of polymer/spattered metal were continuously deposited in much the
same fashion as the earlier capacitor work. The top and bottom layers were always polymer. Hexane Diol DiAcrylate
(HDODA) was used as the monomer in this experiment. The HDODA was stirred and degassed in a cylindrical reservoir
that formed the cylinder of a syringe pump. When the monomer was degassed to a base pressure of 50 millitorr the piston
was lowered to the level of the liquid. At this point the monomer was metered, through an ultrasonic atomizer, into the
evaporator. The evaporator was held at 205°C. The ultrasonic atomizer was a Sono-Tek model 8700-120ms operated at
120 kHz. The evaporator aperture was 12.7 cm long and .2 cm wide. Substrate speed was maintained at 35 meters per
minute.
Monomer curing was accomplished via an electron beam from an, in-house built, hollow anode plasma gun. This device is essentially a diode sputtering cathode contained in a metal box. The working gas, Ar, enters through a pipe fitting and electrons exit through a narrow slit. The cathode is operated between 10 kv and 15 kv, and currents from 10 mA to 250 mA. Secondary electrons from the plasma escape from the box through a 12.5 cm long slit that is .2 cm wide and impinge upon the substrate.

The sputtering targets (round, 20 cm OD/12.5 cm ID, crossed field magnetrons) were contained in enclosures with 15 cm wide by 20 cm long. The apertures above the targets were held within .1 cm of the substrate surface. Thus, the aperture formed a differential pumping seal to the sputter enclosure and allowed the metal layers to extend about 1 cm further than the polymer layers on each side. The target surface-to-substrate distance was 25 cm. Chamber base pressures were about 5x10⁻⁵ Torr. During the depositions the main chamber pressure would rise to the mid 10⁻⁴ Torr range while the sputter enclosures were maintained between 0.05 millitorr and 2.5 millitorr depending upon the process. There have been reports of crossed field magnetrons that are capable of self-sputtering with Ag targets above about 45 watts/cm². In this work the Ag target power density was held between 50 and 55 watts/cm² and we were able to sputter with the Ar flow turned completely off. This self-sputtering mode promises to provide films with exceptional reflectivity due to the reduction of trapped Ar gas in the film.

![Figure 4. Ag sputtered directly onto polyester (dashed line) and PML/Ag repeated multilayer deposited on polyester. The Ag layer is 0.12 μm thick in each case.](image)

*Figure 4. Ag sputtered directly onto polyester (dashed line) and PML/Ag repeated multilayer deposited on polyester. The Ag layer is 0.12 μm thick in each case.*
Reflectance measurements were made with a Beckman model UV 5270 dual beam spectrophotometer calibrated against an aluminum standard mirror.

**PML Reflector Materials Experimental Results:** Figure 4 shows the reflectivity curves for a Polymer/Silver repeated multilayer deposited on a polyester substrate and the reflectivity of Silver sputtered directly onto a polyester substrate. The silver layers are 0.12 μm thick and the polymer layers are 1.5 μm thick. As discussed by Shaw et al., and evidenced in figure 4, the leveling effect of the monomer/polymer layers can increase reflectivity by providing a much smoother surface. As well, the polymer layers serve to reduce pin holes in the metal film.

When the silver layer is made thinner (0.03 μm as in figure 5), multiple reflections are seen between successive polymer/silver cavities below the first surface of the multilayer stack. This permits the structure to act as a multiple cavity Fabry-Perot interference filter. Comparison of figure 5 with an optical model indicates that significant reflections are being returned from as deep as the 4th silver layer below the surface. This means that the three repeated peaks in figure 5 are higher order, resonant, transmission lines from a three cavity Fabry-Perot interference filter.

![Reflectivity Curve](image)

**Figure 5.** A polymer/Ag (1.5 μm/0.03 μm) repeated multilayer. The reflectance spectra matches a model for a 3 cavity Fabry-Perot interference filter.

**LML Polymer Composites and Index Matched Materials Experimental Method:** Polymer/CaF$_2$ composites, index matched and non-index matched, were vacuum deposited to thicknesses in excess of 0.5 cm. For this work, monomer/CaF$_2$/photoinitiator mixtures were stirred and degassed then the resulting slurry was metered through an ultrasonic atomizer onto the substrate. The substrate was continuously, and sequentially, rotated by the atomizer and a UV light source which cross-linked the slurry to form a solid polymer/crystal composite. The individual layer thicknesses were adjusted to approximate the average crystal size (about 25 μm) and thicker composites were built up from multiple layers. The substrate temperature was ambient. The ultrasonic atomizer was a Sono-Tek model operated at 25 kHz. The light source was a Fusion UV (300) system with a D type bulb. The air cooled UV source was outside the chamber and exposed the sample
Figure 7. A very low index polymer film material used at PNL. Much of the UV absorption may be due to the photoinitiator used to polymerize the monomer. The monomer molecule is inset in the $n$ vs. $\lambda$ plot.
through a fused quartz window. The monomers used were Polyethylene Glycol Dimethacrylate and a perfluoro polyether diacylate from 3M (see figure 7). The photoinitiator was a trimethylbenzophenone blend.

Monomer/photoinitiator mixtures were also vacuum extruded, through a slotted die head, onto a web substrate and UV cured. For this work, a roll-to-roll configuration was used in which an 18 cm wide polyester web was used. The drum temperature was maintained at ambient temperature. The extrusion die was built at PNL. The die assembly consisted of the die head and a special idler rigidly attached to the die mounting bracket. The web was lifted from the chill drum and passed over the idler for extrusion then returned to the chill drum for UV cure. The rigid die/idler combination is required to maintain the die/substrate distance to the necessary accuracy for the extrusion process. A single pass was made in which material was vacuum extruded and UV cured. Diethylene Glycol Diacrylate was used as the monomer and a trimethylbenzophenone blend was used as a photoinitiator. Substrate speed was maintained between 1 and 10 meters per minute.

**LML Polymer Composites and Index Matched Materials Experimental Results:** Vacuum atomized, UV cured, monomer/CaF₂ slurries were successfully deposited in multilayer stacks of more than 100 layers in excess of 0.5 cm total thickness. Using a single monomer (no index match attempted) it was found that slurry flow, dispense, and cure conditions could be obtained in which, for 0.5 cm thick multilayers, one could not detect crystal dispersion inhomogeneity in the composite with the naked eye. Due to vapor pressure differences between the fluorinated and non-fluorinated monomers, it was extremely difficult to degas the index matched slurry and obtain consistent results in the index of the final material.

Figure 7 shows two samples of polymer/CaF₂ composites. One sample has a very good index match while the other is made from a single, non-fluorinated, monomer. The indexed matched sample has a refractive index of approximately 1.43. Thus it has low front surface reflection. Similar composites, with fluorescing crystals may make very good material for a heads up display. Since they are very clear, and reflect little, one could see through them without a lot of reflective interference. However, if they were written on with a diode laser they could be made to emit light to display information.

The vacuum extrusion form of the LML process was carried out in a roll-to-roll configuration. While thickness uniformity was very poor (due to poor die head/substrate alignment and the home made nature of the die head) this first attempt did show that the process can be carried out in vacuum under conditions compatible with simultaneous, in-line, deposition by conventional deposition techniques.

### 4. CONCLUSIONS

Excellent reflectivity can be obtained from polymer/silver/polymer coatings vacuum deposited on polyester web. The reflectivity is significantly better than that obtained by direct deposit of Ag onto the polyester substrate. The high rate and low absorption of PML deposited polymer layers should permit a wide variety of optical interference type coatings to be deposited, in a cost effective manner, on wide area flexible substrate. PNL is presently working on PML processes to fabricate solar thermal control film, solar reflector material, quarter wave stack reflectors, PML/sputtered optical multilayers, and hybrid PML/metal, PML/oxide or PML/metal/oxide multilayer materials are under development for EMF mitigation, radar absorption, packaging barrier layers, paper coating, and release layers. LML process technology has been demonstrated and will shortly be implemented in commercial production of lithium polymer batteries and R&D fabrication of electrochromic devices. Figure 8 shows a photograph of PNL's vacuum web coater with two sputter cathodes, one PML evaporator, one e-beam cure gun, and one extrusion die head installed. One sputter cathode is mounted without enclosure while one has the front door removed from the enclosure to show the cathode within. This modular machine design, where all sources are contained in enclosures, in which individual process atmospheres can be isolated from each other, will permit the process development for a wide variety of elaborate hybrid multilayer films involving a multitude of deposition processes.
while the one on the bottom employs only non-fluorinated monomer.
The top is made by blending fluorinated and non-fluorinated monomers.

Figure 7. Comparison of two samples, each 10 weight % CAF, where the one on
Figure 7. Comparison of two samples, each 10 weight % CaF₂, where the one on the top is index matched by blending fluorinated and non-fluorinated monomers while the one on the bottom employs only non-fluorinated monomer.
Figure 8. PNL's vacuum web coater with two sputter cathodes (bottom), one e-beam cure gun (left side), one PML evaporator (above e-gun on left), and one extrusion die head (upper left) installed. One sputter cathode is mounted without enclosure while one has the front door removed from the enclosure to show the cathode within.
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6. REFERENCES


