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VACUUM DEPOSITED POLYMER/SILVER REFLECTOR
MATERIAL

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Vacuum deposited polymer/silver reflector material

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ABSTRACT

Weatherable, low cost, front surface, solar reflectors on flexible substrates would be highly desirable for lamination to solar concentrator panels¹. The method to be described in this paper may permit such reflector material to be fabricated for less than 50¢ per square foot. Vacuum deposited Polymer/Silver/Polymer reflectors and Fabry-Perot interference filters were fabricated in a vacuum web coating operation on polyester substrates. Reflectivities were measured in the wavelength range from .4 μm to .8 μm . It is hoped that a low cost substrate can be used with the substrate laminated to the concentrator and the weatherable acrylic polymer coating facing the sun. This technique should be capable of deposition line speeds approaching 1500 linear feet/minute². Central to this technique is a new vacuum deposition process for the high rate deposition of polymer films. This polymer process involves the flash evaporation of an acrylic monomer onto a moving substrate. The monomer is subsequently cured by an electron beam or ultraviolet light. This high speed polymer film deposition process has been named the PML process - for Polymer Multi-Layer.

1. The Monomer Evaporation Process

The technique used to evaporate the monomer is really quite simple. Monomer fluid is 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 an ultrasonic atomizer, fuel injector, or by dripping onto a high speed rotating disc. Dispersion with an ultrasonic atomizer yields 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 photographs³ 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.

2. BACKGROUND ON THE POLYMER MULTILAYER (PML) FILM DEPOSITION PROCESS

As the PML process is likely to be new to most readers at this time, some background material seems in order. The basic process, and relevant comparisons to conventional vacuum web coating, will now be discussed.

The types of acrylic polymers that have been deposited to date are very clear for wavelengths between about 0.35 μm and 2.5 μm . In this wavelength range, the polymers have extinction coefficients of $k \approx 10^{-7}$, while conventional, vacuum deposited, optical materials only have $k \approx 10^{-4}$ at best. Commercially available monomers produce polymers with refractive indices

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Top View of Sputter Terminated Strip

Side View of Sputter Terminated Strip

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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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 chamber³. 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 photographs³ (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).

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 known⁴, 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.

2.1 PML Deposition Systems

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 used⁵. Figure 3 is a schematic of the vacuum web coater at the Pacific Northwest Laboratory. 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 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; rod fed e-beam evaporation - reactive or non-reactive; plasma enhanced chemical vapor deposition; and monomer extrusion - 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, and any combination of deposition zones can be biased with fixed or rotating magnetic fields.

2.2 Important Process, Hardware, And Economic Differences Between PML And Conventional Vacuum Web Coating

The main difference between a conventional web coater and a Polymer Multilayer web coater is the replacement, or supplementation, of the sputtering or evaporation sources with monomer evaporators and cure systems. In terms of initial hardware investment there is not much cost difference.

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.

The operational costs could be much lower for the polymer system than for conventional 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 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, $n \approx 1.5$ 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 METHOD

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/sputtered metal were continuously deposited in much the same fashion as the earlier capacitor work³. 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 5×10^{-6} Torr. During the depositions the main chamber pressure would rise to the mid 10^{-5} Torr range while the sputter enclosures were maintained between 0.05 millitorr and 2.5 millitorr depending upon the process. There have been reports⁶ of crossed field magnetrons 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.

Reflectance measurements were made with a Beckman model UV 5270 dual beam spectrophotometer calibrated against an aluminum standard mirror.

4. 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 $0.12\text{ }\mu\text{m}$ thick and the polymer layers are $1.5\text{ }\mu\text{m}$ thick. As discussed by Shaw² 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 film².

Figure 4. Ag sputtered directly onto polyester (dashed line) and PML/Ag repeated multilayer deposited on polyester. The Ag layer is $0.12\text{ }\mu\text{m}$ thick in each case.

When the silver layer is made thinner ($0.03\text{ }\mu\text{m}$ 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.

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.

While monomer additives have worked well to promote adhesion of the PML layer to aluminum layers, as of this writing, adhesion to silver layers is marginal. A standard tape test will pull pieces of the plastic away from the silver. Work is still proceeding on this front.

5. 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.

6. ACKNOWLEDGEMENTS

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