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Optical Multilayers with an Amorphous Fluoropolymer

R. Chow, G. E. Loomis, and E. F. Lindsey

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R. Chow, G. E. Loomis, and E. F. Lindsey
Lawrence Livermore National Laboratory, P. O. Box 808, Livermore, CA, 94551

ABSTRACT

Multilayered coatings were made by physical vapor deposition (PVD) of a perfluorinated amorphous polymer, Teflon AF2400, together with other optical materials. A high reflector at 1064 nm was made with ZnS and AF2400. An all-organic 1064-nm reflector was made from AF2400 and polyethylene. Oxide (HfO_2, SiO_2) compatibility was also tested. Each multilayer system adhered to itself. The multilayers were influenced by coating stress and unintentional temperature rises during PVD deposition.

Key words: optical multilayers, fluoropolymer, physical vapor deposition, coatings, laser damage threshold, AF2400

1. INTRODUCTION

Amorphous fluoropolymers, like Teflon AF2400, are attractive candidates for optical multilayer coatings. This particular material shows a high transmittance range from 200 nm to 2000 nm, and a low refractive index, n. In fact, the bulk n of 1.29 for AF2400 is lower than any dielectric compound currently used for optical coatings.[1] A low refractive index facilitates the fabrication of optical multilayers because, for a given optical performance, fewer layers are required and the optical bandwidth is wider. Using a high reflector as an example, a wide reflectance window which meets the reflectance specification minimizes the effects of process variations.

Single layer coatings of AF2400 are typically deposited using either a spin or dip solution technique. In these cases, a solution of AF2400 dissolved in an expensive (hundreds of U.S. $ per gallon) fluorinated solvent are required.[2,3,4] Also, multilayering AF2400 in a liquid deposition technique has not been done. Recent work demonstrated that this material can be physically-vapor-deposited (PVD) [5,6] as a corrosion barrier for extra-terrestrial equipment,[7] a possible insulator for submicron electronic devices,[8] and laser-resistant anti-reflective coatings.[9] If the compatibility of PVD AF2400 can be demonstrated in optical multilayered coatings, the material should have increased applications in the optical coatings community. In this paper, the compatibility of PVD AF2400 with other dielectric optical materials is described. The optical and morphological properties of PVD AF2400 are discussed.

2. EXPERIMENTAL

The chemical composition, mechanical, and optical properties of PVD AF2400 single layers were described in detail previously. In brief summary, the first major point was that the refractive index obtained could be intentionally made as low as 1.13. The second major point was that an anti-reflector made of this material had a high laser-resistance at 1064 and 355 nm test wavelengths with 3 ns-pulse widths.[9]

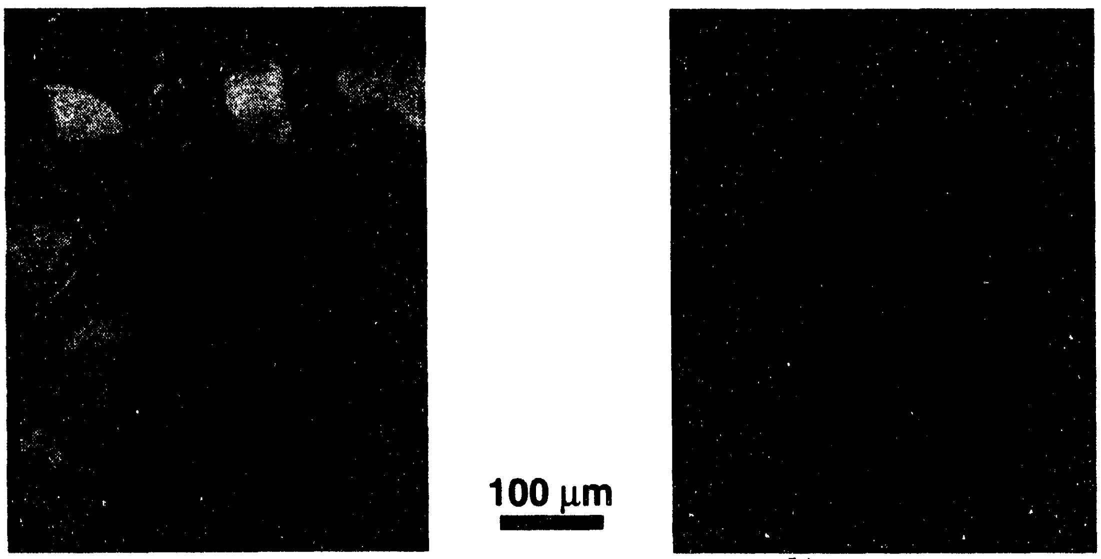
The material compatibility of PVD AF2400 with other optical materials was tested. All the materials were evaporated in a vacuum chamber with dimensions of 2 ft diameter by 2 ft height. The chamber was diffusion pumped with a liquid nitrogen trap. The polymer was place in a Ta boat and resistance heated. An electron beam gun or another resistance heater was used for evaporating the higher refractive index materials. The higher refractive index materials were HfO_2, SiO_2, ZnS and polyethylene. The HfO_2 source were 5 mm diameter pellets and evaporated with an electron beam gun. The SiO_2 source was a boule of Dynasil machined to fit the crucible of the electron beam gun. The ZnS was in the form of chips. The polyethylene source material was a powder and had a density of 0.94 gr/cc. Other polymers [poly(2-vinyl naphthalene), poly(n-vinyl carbazole), parylene, poly(phenyl methacrylate), and poly(methyl methacrylate)] were investigated but polyethylene coatings deposited by a resistance heater had the most transparency in the visible range. The evaporation rates of the oxides were 3 Å/s, of ZnS was 10Å/s, and the polymers were 20-30 Å/s.

The multilayers were examined using optical and electron microscopes, and an optical spectrophotometer (Varian Cary 2390).

3. RESULTS

3.1. Oxides

Initial attempts at multilayering thin films of AF2400 with oxides showed crazing. Based on the observation that many of the craze lines intersected at 90° angles to each other, both of the multilayers were stressed in tension.[10] The HfO_2/AF2400 material combination failed soon after the second HfO_2 layer was deposited (Figure 1a). Up to 21 layers were deposited in the AF2400/SiO_2 system. Crazing was not observed in the AF2400/SiO_2 system (Figure 1b) until after these multilayers were exposed to atmosphere for a couple of days. From then on, the crazing worsened with time.



(a) (b)

Figure 1. Crazing in two AF2400/oxide material systems. Theses pictures were taken with a Normarski microscope. In (a), the layer sequence was HfO_2/AF2400/HfO_2. In (b), the layer sequence was (AF2400 • SiO_2)^{10} SiO_2.

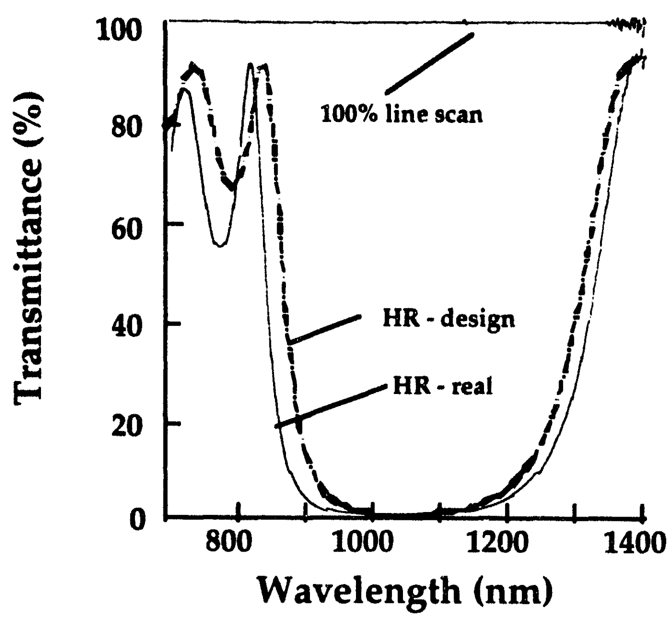
3.2. ZnS

Multilayers with ZnS were more successful. A high reflector (reflectance > 99%) was made with nine layers of quarter wave optically thick ZnS and AF2400: (AF2400 • ZnS)^4 AF2400. The design wavelength was 1064 nm and the full-width at half-maximum bandwidth was over 470 nm. The ZnS layers were evaporated from an electron beam gun. These high reflectors showed no signs of crazing after several months. The damage thresholds from this HR was less than 2.8 J/cm^2 at a test wavelength of 1064-nm wavelength with 3-ns pulse widths.

3.3. Polyethylene

The next material system tried was an all-organic reflector made of AF2400 and polyethylene. A 1064 nm reflector was made from 10 quarter wave optically thick layer pairs: (AF2400 • polyethylene)^{10} (AF2400)^2. The performance of the actual reflector falls below that of the design because the design program did not take into account dispersion and absorption bands of the polymers. The AF2400 stops transmitting at wavelengths greater than 4000 nm.

Figure 2. Transmittance scan of a ZnS/AF2400 high reflector. The design consisted of quarter wave optically thick layers of ZnS and AF2400. The top scan is the spectrophotometer 100% line, taken with an empty sample compartment. The thin line scan is that of the actual high reflector. The dark line scan is an overlay from a design program where the refractive indices of ZnS and AF2400 were 2.17 and 1.3, respectively.



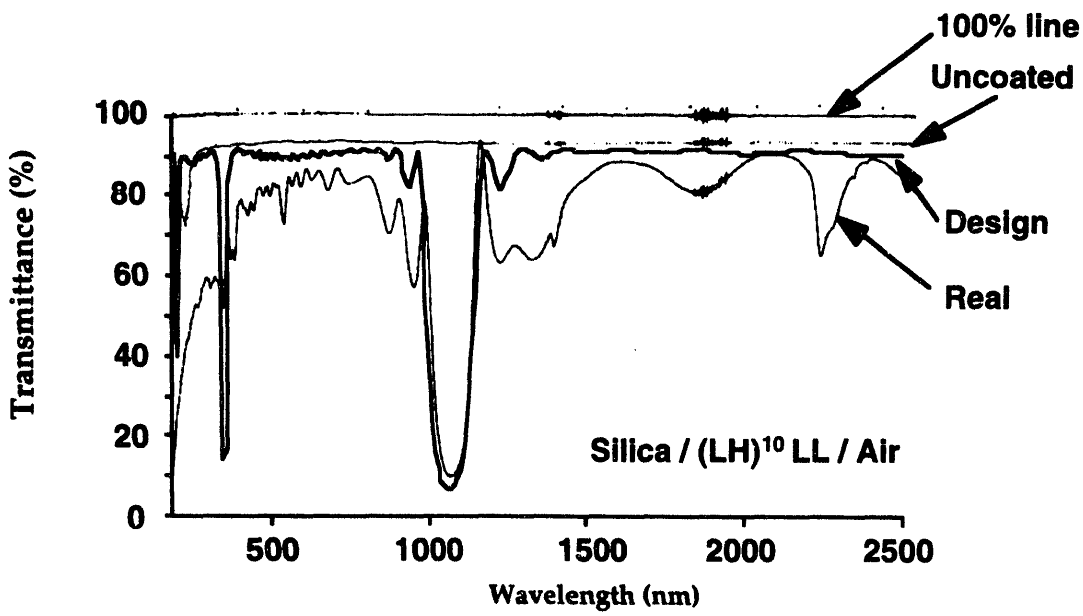


Figure 3. Transmittance scan of an all-organic reflector. The multilayer consisted of AF2400 (L) and polyethylene (H). The 100% line is the spectrophotometer performance with an empty sampling compartment. The scan of the uncoated fused silica substrate is gray. The dark scan is that from a design program where the refractive indices of the polyethylene and AF2400 were 1.52 and 1.3, respectively. The thin line scan is that of the real part.

4. DISCUSSION

4.1. Oxide crazing

The stress cracks in the oxide/AF2400 systems indicate that these multilayer systems are in tension. This was expected for coatings with HfO_2 but not with SiO_2. Normally, SiO_2 layers with optimal optical properties require deposition onto a hot substrate and the resultant stress is compressive. In this case, the substrates were not heated intentionally in order to minimize the re-evaporation of the AF2400 layers. Depositing SiO_2 onto a cold substrate may have resulted in tensile stresses.

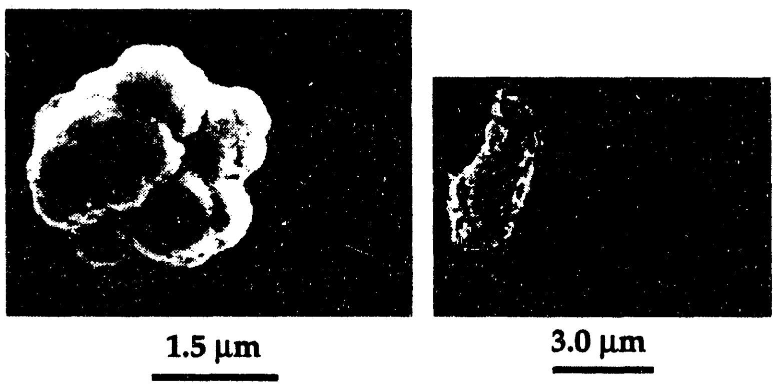
4.2. Defects

The defect density in the ZnS/AF2400 multilayered coatings were rather high, (> 1300 defects/mm^2) where the smallest defect counted was 1 μm in length. The defects were assumed to have come from the ZnS evaporation process since defects were not observed on the single layer work with AF2400 coatings. Reference 11 reported that defects are detrimental to the resistance of coatings to high power laser fluences. It is also known that ZnS dissociate during physical vapor deposition and thereby the ZnS coating becomes highly adsorbing. The low damage threshold of the mirror was probably due either to the ZnS coating material or the defects generated during the ZnS evaporation. A Ta boat was used to evaporate ZnS in an attempt to eliminate the ZnS defects. However, another problem arose and is described below.

4.4. All organic reflector morphology

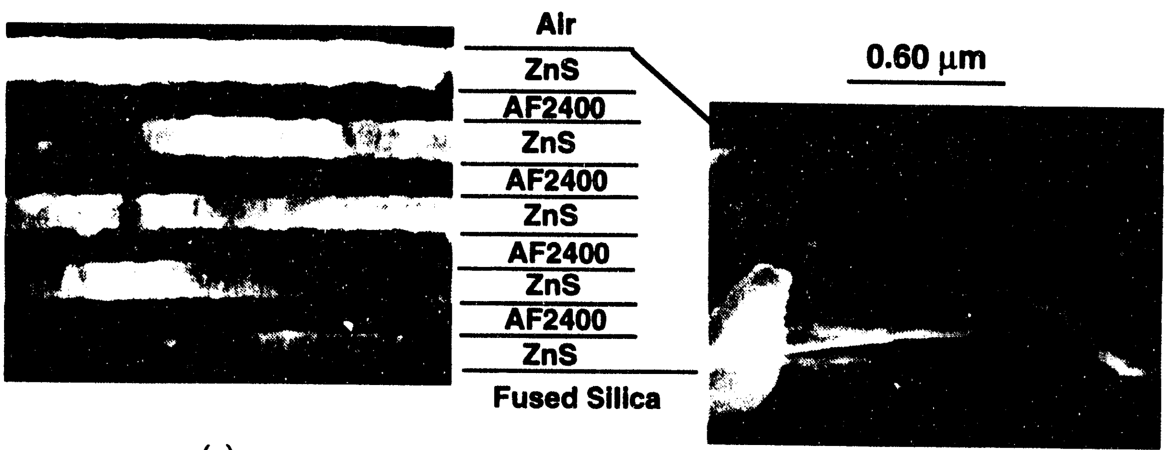
The morphology of this all-organic optical multilayer was rough as shown by the SEM picture in Figure 6a. The predominant defect appeared to be pinholes, in contrast to the defects in the ZnS/AF2400 HR. A cross-section of the organic multilayer is on the right (Figure 6b). As with the ZnS/AF2400 HR, the porosity occurred within the AF2400 layers. The polyethylene layers were relatively compact, but may not have been able to bridge the porous AF2400 as well as the ZnS layers. Higher substrate temperatures, say on the order of 150°C, would also help planarize and smooth the AF2400 layers, but then the polyethylene layers became hazy. The high deposition rates used for both polymers (above 20Å/s) was to minimize the heat load on the organic polymers. Another strategy to alleviate the pinholes would be to reduce only the evaporation rate for AF2400.[9] Slower rates would allow the molecules more time to flow across the surface and not cause self-shadowing effects.

Figure 4. Defects in ZnS/AF2400 multilayered coatings.



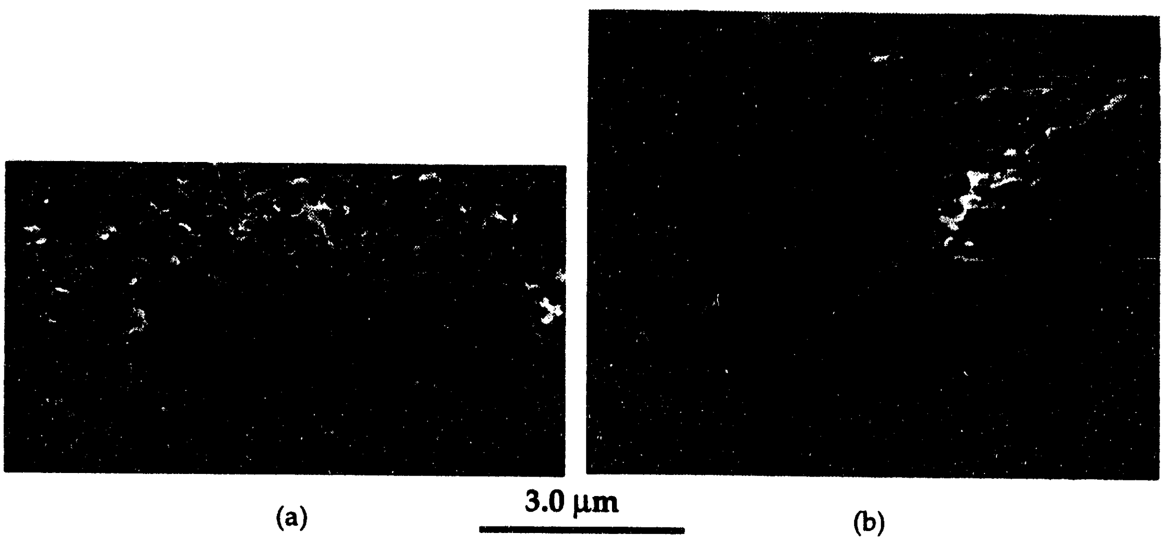
4.3. Thermal sensitivity

The AF2400 layers are sensitive to thermal radiation from an evaporation source. Figure 5 shows two cross-sections of ZnS/AF2400 multilayers. The one on the left (Figure 5a) was made when the ZnS was evaporated from an e-gun. The layers remained intact. The ZnS layers are the brighter bands. The AF2400 layers are gray and the dark spots are pores in the AF2400 layers. The cross-section on the right (Figure 5b) was taken from a ZnS/AF2400 run where a resistance heater was used to evaporate ZnS. The evaporation rates of the ZnS was kept the same in both cases. However, the power required to sustain those rates were 46 watts with an e-gun and 96 watts with a resistance heater. We believe that the heat radiating from the resistance heater caused either the AF2400 layers, or something near to these layers, to go past the melting temperature of AF2400. The AF2400 layers either melted into the ZnS, or if the temperature was high enough, re-evaporated. In either case, the ZnS/AF2400 multilayer collapsed when the ZnS was evaporated from the higher powered source.



(a) (b)

Figure 5. Thermal sensitivity of AF2400 layers. These were scanning electron micrographs cross sections of two ZnS/AF2400 high reflectors. In (a), the ZnS was evaporated from an electron beam gun. In (b), the ZnS was evaporated from a resistively heated Ta boat.



(a) (b)

Figure 6. Morphology of an all-organic reflector. Both pictures were taken with an scanning electron microscope. (a) was the top view (b) was the cross section. The top portion of multilayer was removed during the cleaving procedure.

5. CONCLUSIONS

In conclusion, there were materials that adhered to AF2400 coatings deposited by physical vapor deposition. Functional optical reflectors at 1064 nm were made from ZnS/AF2400 and polyethylene/AF2400. The use of oxides with AF2400 showed multilayer failure by tensile stresses. Organic layers were sensitive to temperature from intentional substrate heating and unintentional thermal radiation from evaporative sources.

6. AUSPICES AND REFERENCES

This work was performed under the auspices of the U. S. Dept. of Energy by Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

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