

# Optimized PVD materials for coatings on plastics

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New or optimized-mixed evaporation materials of PIZOLIN, ALVIRIT, ROMA, and TiO53<sup>[1]</sup> on the basis of high-index pure substances of TiO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub>, CeO<sub>2</sub>, ZrO<sub>2</sub>, and Ta<sub>2</sub>O<sub>5</sub> are developed with the aim of identifying dielectric materials with specific refractive indices, reduced film stress, better wear or humidity resistance, and improved ultraviolet (UV) blockage compared to pure substances. Materials are tested in conventional and slightly ion-assisted deposition using process windows typical for coating polymeric substrates. Films with refractive indices in the range of 2.08–2.40, as well as tunable film stress below values for pure substances, are observed. In some cases, the admixture leads to a shift in absorption edge or improvement in moisture resistance of films. Individual results based on the new formulation on film materials with blue colour in transmission (OLIVIN P) in metal and metal oxide mixtures are presented.

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Thin film physical vapor deposition (PVD) coatings on plastics, such as those used for ophthalmic, display, instrumentation, and precision optical applications, currently face a number of challenges. As such, apart from their primary optical function, additional features in terms of low mechanical stress, ultraviolet (UV) blockage, environmental resistance, and antistatic properties were increasingly addressed. Optical coatings on high-index optical plastics partly require materials that could adjust refractive indices. The use of new types of high-index plastics is currently restricted in terms of chemical tintability, which partly requires especially designed coloured PVD coatings that can be used for coating materials.

Mixtures of transition metals or metal ions embedded in oxide or oxyfluoride matrices address such need to develop coloured PVD coatings for high-index plastics. Films of material mixtures like OLIVIN P (blue-coloured), MALBUNIT and MELDINA (brown-coloured), GREY (grey-coloured), ROSE (pink-coloured), and OLIVIN C2 (yellow-coloured) were adjusted to accommodate the plastic materials, and were tunable in their properties<sup>[1]</sup>.

Mixed oxide materials for deposition were developed and tested using the electron beam (e-beam) evaporation onto plastic substrates in terms of their process capability and obtainable film properties. These investigations comprised a.o. materials like ALVIRIT, ROMA, and TiO53<sup>[2]</sup>. ALVIRIT and TiO53 in the form of granules at 0.7–3.5 mm were first melted under several steps to form a base-melt. For each deposition run, a required quantity of granules was added and then subjected to a pre-melting procedure under closed shutter. Evaporation deposition was conducted at a.o. in boxcoaters of type BAK640 with e-beam gun ESQ110 out of a Cu-crucible with Mo-liner. ROMA, in the form of tablets, did not require the preparation or preconditioning procedures and was directly evaporated from a Cu-crucible with or without Mo-liner. Since the ESQ110 e-beam gun did not allow temporary variations in beam pattern, the crucible was rotated. It was assumed that this relative motion

could be omitted using commercially available beam pattern technologies.

Evaporation for all oxide materials was reactive (i.e., a certain amount of oxygen backfilling occurred either directly in the chamber, or through the employed ion or plasma ion source). Deposition was carried out conventionally onto unheated substrates (and for reference purposes, onto heated substrates with temperatures ~300 °C), as well as ion or plasma ion assistance using a.o. the MARK II source operated with Ar or O<sub>2</sub> gases. Deposition rates and the employed plasma ion assistance were in ranges that are typical found in the deposition of plastics, for instance, in ophthalmics.

The resulting coated substrates were in the form of

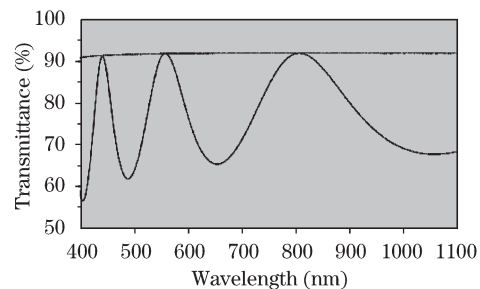


Fig. 1. Optical spectrum for ALVIRIT film over UV and VIS spectral ranges. Also shown is the spectrum for uncoated substrate C1737F.

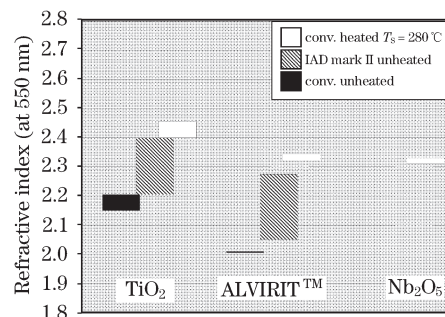


Fig. 2. Obtainable ranges of refractive index at 550 nm for

ALVIRIT films under different coating conditions in relation to pure  $\text{TiO}_2$  or  $\text{Nb}_2\text{O}_5$ .

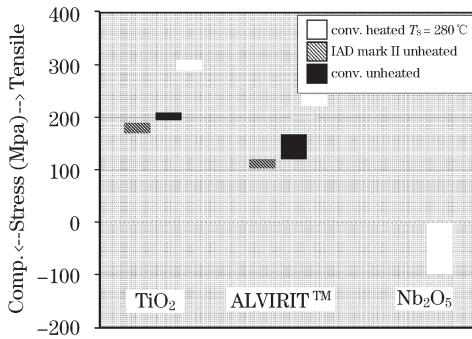


Fig. 3. Observed ranges of structural stress for ALVIRIT films for different coating conditions in relation to pure  $\text{TiO}_2$  or  $\text{Nb}_2\text{O}_5$ .

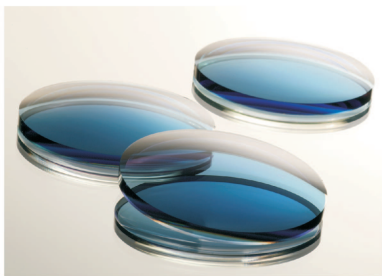


Fig. 4. Plastic lenses of CR39 with OLIVIN P coating on the concave side. The convex side was not antiglared.

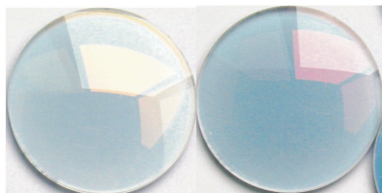


Fig. 5. Variation of reflective colour of convex side for OLIVIN P coating.

mineral glasses (C1737F, fused silica), silicon wafers, and polymeric lenses of CR39. Measurements were conducted according to optical spectral photometry (UV-ranges), determination of film stress, and in part, environmental

testing according to military specification (MIL) standards.

OLIVIN P (transition metal-metal oxide proprietary mixture), in the form of tablets, was deposited a.o. in a BAK640 boxcoater from a Cu-crucible with or without Mo-liner using an e-beam gun ESQ110. In the absence of available beam pattern, the crucible was rotated under a standing beam. Deposition onto unheated mineral (C1737F), polymeric (CR39) and silicon substrates was accompanied by ion assistance and by using MARK II operated with pure Ar gas. The deposition did not require premelting or preconditioning steps other than ramping up power to its final value at rates of 1–2 nm/s. The employed process conditions are compliant with requirements for coatings on plastic substrates in ophthalmics.

ALVIRIT melt and evaporated congruently with respect to the proportions of  $\text{TiO}_x/\text{NbO}_x$  in the vapour phase to yield optically homogeneous films, as shown in Fig. 1. layers with the thicknesses at  $\sim 300\text{--}400$  nm show the refractive indices at 550 nm of 2.02–2.28 (Fig. 2) and structural stress of tensile type with values of 100–170 MPa (Fig. 3) for deposition with conditions compatible to plastic substrates. The absorption at 550 nm was below spectrophotometrically detectable limit ( $\sim 8 \times 10^{-4}$  for the extinction coefficient). Oxidation problems for cold deposition of  $\text{Nb}_2\text{O}_5$  with no or limited plasma ion assistance were resolved using ALVIRIT. In terms of process conditions, refractive index and structural film stress for ALVIRIT were smaller than in pure  $\text{TiO}_2$  films deposited from  $\text{Ti}_3\text{O}_5$ . These properties can be advantageous when using ALVIRIT as a high-index material in BBAR coatings for plastic substrates.

The obtained OLIVIN P films are of blue colour in terms of transmission (Fig. 4), which could be tuned by film thickness and deposition parameters. Reflective colour could be adjusted partly and independently vis-à-vis the degree of blue colour (Fig. 5). Structural film stress is near zero.

## References

1. OLIVIN C1, OLIVIN C2, OLIVIN P, MALBUNIT, MELDINA, GREY, ROSE are proprietary metal-oxide or metal - oxyfluoride mixtures of UMICORE THIN FILM PRODUCTS
2. PIZOLIN, ALVIRIT, ROMA, TiO53 are proprietary oxide mixtures of UMICORE THIN FILM PRODUCTS