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Coating material innovation in conjunction with optimized deposition technologies

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ABSTRACT

Concentrating on physical vapour deposition methods several examples of recently developed coating materials for optical applications were studied for film deposition with optimized coating technologies: mixed evaporation materials for ion assisted deposition with modern plasma ion sources, planar metal and oxide sputter targets for Direct Current (DC) and Mid-Frequency (MF) pulsed sputter deposition and planar and rotatable sputter targets of transparent conductive oxides (TCO) for large-area sputter deposition.
Films from specially designed titania based mixed evaporation materials deposited with new plasma ion sources and possible operation with pure oxygen showed extended ranges of the ratio between refractive index and structural film stress, hence there is an increased potential for the reduction of the total coating stress in High–Low alternating stacks and for coating plastics.
DC and MF-pulsed sputtering of niobium metal and suboxide targets for optical coatings yielded essential benefits of the suboxide targets in a range of practical coating conditions (for absent in-situ post-oxidation ability): higher refractive index and deposition rate, better reproducibility and easier process control, and the potential for co-deposition of several targets.
Technological progress in the manufacture of rotatable indium tin oxide (ITO) targets with regard to higher wall-thickness and density was shown to be reflected in higher material stock and coater up-time, economical deposition rates and stable process behaviour. Both for the rotatable ITO targets and higher-dense aluminum-doped zinc oxide (AZO) planar targets values of film transmittance and resistivity were in the range of the best values industrially achieved for films from the respective planar targets. The results for the rotatable ITO and planar AZO targets point to equally optimized process and film properties for the optimized rotatable AZO targets currently in testing.

1. Mixed evaporation materials for ion assisted deposition with modern plasma ion sources

1.1. Introduction

Optical coating is (still) widely dominated by evaporation technology. Part of the requirements posed to the coatings such as especially adjusted refractive index, small and net compressive film stress, small optical shift and environmental durability has been addressed over the past two decades by the optimization of the process technology including e-beam guns and in-situ monitoring and most recently by the development or optimization of ion and plasma ion sources. To obtain additional ranges of the key film properties and thus to meet many as far unsatisfied requirements, optimization of existing and development of new evaporation starting materials would be required.

This section focuses on the combination of new titania based mixed oxide materials with a variably assisted deposition process involving established and new types of plasma ion sources for assisted deposition. The tests aimed at transparent optical coatings to obtain optimized film properties compared to the pure oxide TiO_2, especially an optimized film stress.

1.2. Experimental details

Ti_3O_5 starting material, mixtures of Ti_3O_5 with an increasing amount of Al_2O_3 ("$Ti_3O_5^{UMICORE}$", UMICORE part. no. 0489455, and DRALO™, part-no. 0484825, [1]) and a mixture of Ti_3O_5 with La_2O_3 (LATI™, UMICORE part.-no. 0701740, [1]) were reactively e-beam evaporated in commercial evaporation coaters BAK 640 (Balzers), CCS II and SYRUS (both Leybold Optics) with and without plasma ion assistance by sources of type MARK (Commonwealth/Veeco), APS and LION (both Leybold Optics).

Evaporation in BAK 640 boxcoaters was done using an ESQ110 e-beam gun with a water-cooled 4-pot Cu crucible with Mo-liners. In CCS II and SYRUS, HPE-6 e-beam guns were employed with a water-cooled 6-pocket Cu crucible with Mo-liners. The materials were premelted with several refilling steps in order to form a homogeneous base melt. Residual vacuum pressure was $\sim 1\times10^{-5}$ mbar. Reactive

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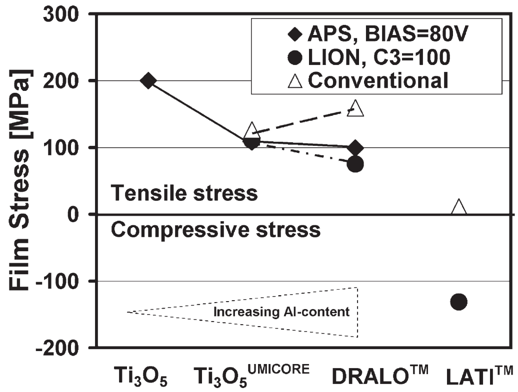

Fig. 1. Achieved average stress values of films deposited from pure Ti_3O_5 and mixed titania films for conventional deposition and weakly assisted deposition with plasma ion sources APS (O_2/Ar) and LION (O_2). Deposition rate 0.25 nm/s. No intentional substrate heating.

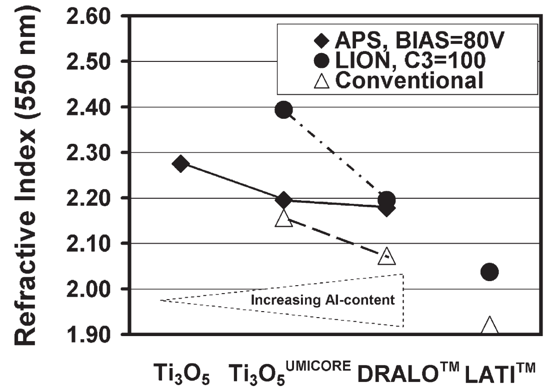

Fig. 3. Achieved average refractive index of films from Fig. 1.

deposition of low-absorbing films ($k<5\times10^{-4}$) occurred at oxygen partial pressures of $2–4\times10^{-4}$ mbar and at physical rates 0.2–0.5 nm/s. Special attention was paid to the refilling schedule and to the quantity of material consumed in each coating run.

The plasma ion sources used the following parameter windows: For MARK sources, an anode voltage of 120 V, an anode current of ~2 A and a neutralisation of ~15% were used. The (pure) Ar-flow through the source was automatically adjusted for the defined anode current and the oxygen was introduced directly into the chamber to give a total pressure of $3–5\times10^{-4}$ mbar. The APS source was operated with two flows of Ar-gas (Ar1: 3–6 sccm; Ar2: 8–12 sccm) and the oxygen was inserted above the anode tube opening through the standard gas ring shower (30–40 sccm) to yield total process pressures ~$2–2.5\times10^{-4}$ mbar. Discharge voltage was ~50 A, total source power ~5 kW and the BIAS was varied in the range 80–120 V using the coil current. The LION source was operated with 15–30 sccm of pure oxygen and with a RF power of ~1.5 kW.

The DC potential was adjusted using the C3 condensor for fixed ratio of condensors C1 and C2.

Deposition of single films was done on several kinds of mineral glasses, plastics (CR39, PC, Zeonex) and Si-wafers. In some cases, full antireflection (AR) coating stacks were deposited using one of the titanium oxide based materials as the high-index (H-index) and SiO_2 as the low-index material.

The films on glass substrates were subject to spectrophotometric measurements of transmittance and reflectance and refractive indices were calculated from these measurements using standard methods. The Si-wafers were used for measurements of the structural (intrinsic) stress measuring and evaluating the waver bow. Thermal stress was derived from the difference of the total stress measured on plastic substrates and the determined structural stress on the Si-wafers. Its values have been reported elsewhere.

1.3. Results and discussion

Titania based films with alumina admixtures showed a decrease and change in sign of the structural film stress for conventional and slightly-assisted deposition in the sequence TiO_2 (from pure Ti_3O_5), TiO_2:Al (from $Ti_3O_5^{UMICORE}$), DRALO™, followed by the mixture of Ti_3O_5 with La_2O_3 (LATI™). Fig. 1 gives the average values of the structural film stress obtained for pure TiO_2 from pure Ti_3O_5 starting material and for the titania mixtures, for deposition with the APS and LION ion sources and weak assistance or with conventional deposition. Fig. 2 shows the observed total ranges of stress for the mixtures and weakly assisted processes using the three different plasma ion sources or conventional deposition.

The refractive index in the Al-doped TiO_2 mixtures decreases with increasing amount of Al_2O_3. The smallest values are obtained for LATI™ (see the observed average values for weak assistance with APS and LION sources or with conventional deposition in Fig. 3 and the obtainable ranges for weakly assisted processes using the three plasma ion sources or conventional deposition in Fig. 4).

Relationship between refractive index and structural stress for films deposited from the titania mixtures with varied degrees of plasma ion assistance and for comparable values of deposition rate and gas pressures is displayed in Fig. 5. Full symbols for $Ti_3O_5^{UMICORE}$ and DRALO™ denote values achieved with the O_2/Ar driven APS source and for LATI™ with the O_2/Ar operated LION source. Open symbols are used for values obtained with conventional deposition or

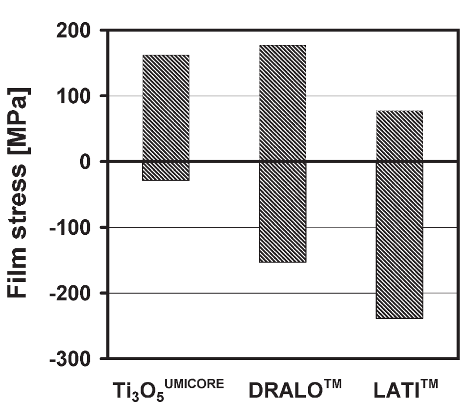

Fig. 2. Obtainable ranges of the film stress for titania based mixtures and weakly assisted deposition with plasma ion sources MARK, APS and LION or conventional deposition (no intentional substrate heating, deposition rate 0.25 nm/s).

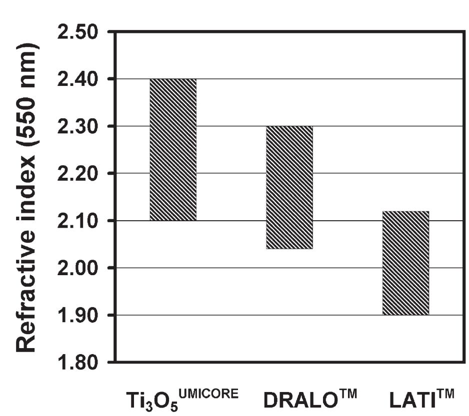

Fig. 4. Obtainable ranges of the refractive index for films from Fig. 2.