Characterization of Optical Coatings for Holographic Applications

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ABSTRACT

Rapid advances in holographic technology have led to a growing requirement for optical thin films such as titanium dioxide and zinc sulphide. These materials have high refractive indices and wide wavelength passbands which makes them important for applications such as filters, reflectors and beam splitters. The characteristics of TiO_2 and ZnS coatings are highly dependent on deposition parameters including substrate temperature, residual gas composition, pressure, condensation rate and reactive ion density. In the present work, electron beam evaporation was used for the deposition of titanium dioxide and zinc sulphide materials. The coatings were deposited onto a polyester film moving at a fixed speed until a total thickness of 50-60nm was reached. The optical and structural characteristics of TiO_2 and ZnS were examined using optical spectrometry and atomic force microscopy. Coatings with 40% reflection in the visible region were achieved.

INTRODUCTION

Over the past few years holograms have grown into a complex business to prevent counterfeiting of security cards, banknote and security labels[1]. The rapid advances in holographic technology have led to the utilization of advanced optical coatings and the development of coating methods to produce holograms at reasonable costs[2,3]. Consequently, this led to an increasing interest in titanium dioxide and zinc sulphide for their high refractive indices and wide wavelength passbands. Oxide coatings such as TiO_2 are inert and can withstand mechanical and chemical attack very well. On the other hand, dielectric materials made of soft coatings such as ZnS are less expensive and can be encapsulated and used in I.D.cards, credit cards and product labels. These coatings can be used as a single layer or in a multilayer AR stack for holographic applications. Magnetron sputtering and ion assisted deposition are the known processes to deposit TiO_2 coating with good optical properties[4,5]. However, film speed remains a problem despite recent development in magnetron sputtering technology. On the other hand, thermal evaporation of ZnS requires a good control of source temperature and evaporation environment to minimize dissociation and reaction with residual vapour molecules. This requires the utilisation of on-line optical system to monitor the optical properties and therefore, the coating thickness across the moving web. The present work investigates the utilization of electron beam evaporation and ion bombardment to deposit stoichiometric TiO_2 and ZnS onto a polyester film moving at a fixed speed. The optical and structural properties of TiO_2 and ZnS coatings were examined using optical spectrometry and atomic force microscopy. Coatings with 40% reflection in the visible region were achieved. This work is part of a programme to investigate the performance of different evaporation sources to deposit high quality optical coatings onto a moving polyester film.

EXPERIMENTAL WORK

The present work was carried out inside a 2m diameter, two zone vacuum web coater. The vacuum chamber contained unwinding/rewinding drives, water-cooled drum, oxygen ion source and four water-cooled electron beam evaporation guns. Figure 1 shows a schematic diagram for the experimental setup.

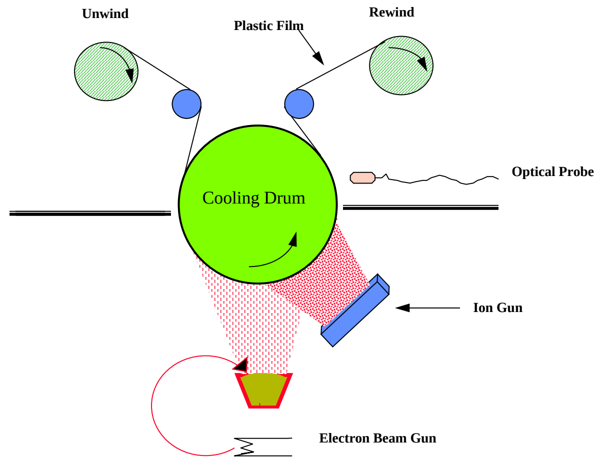

Fig. 1. Schematic diagram of the experimental setup

The chamber was pumped down directly by rotary and diffusion pumps to a base pressure of $5x10^{-5}$ mb. During evaporation and ion bombardment the pressure rose to $3x10^{-4}$mb. The starting material for titanium oxide coating was $TiO_{1.7}$ granules supplied by Merck (Germany). With such a material it is not necessary to perform preheating and vapour deposition can begin after a brief pre-melt phase using a shutter. The starting material was evaporated from an electron beam gun operating at a power of 3.1kW. This power gives an average deposition rate of 60Å/sec as measured by a quartz crystal monitor placed near the substrate surface. The coating reflectivity was monitored using Ocean Optics SQ2000 optical spectrometer in the visible region. The oxygen ion source used for the production of TiO_2 coating consisted of a hollow cathode ion gun capable of producing 2mA/cm^2 at a distance of 15 cm from the source with ions having an average energy of 100eV. During coating, the polyester film was bombarded with ions and electrons escaping from the ion source to prevent charge build up on the film surface. The oxygen gas was fed through the ion source which was close to the moving film. This arrangement reduced crucible poisoning and directed the oxygen ions toward the film to achieve the required stoichiometry. Oxygen flow rate through the ion source was varied between 0 to 100sccm. The ion source voltage was varied between 150-200V; while the source anode current was fixed at 5A. For the deposition of zinc sulphide coating onto a moving polyester film, ZnS granules from Merck were used. In this case the eb guns were operating at a beam power of 2.5-3kW. The final spectral transmittance and reflectance were measured using a Perkin- Elmer Lambda 9 spectrophotometer. From this data the refractive index was calculated from the reflectance using:

$$R = [(n^2/n_s)-1/(n^2/n_s)+1]^2$$

where: n is the refractive index of the coating at a wavelength λ and, n_s is the refractive index of the polyester substrate. R is the reflectance of the coated surface at λ, which is an odd order in the interference pattern. Film thickness was chosen to give high reflectance in the visible region as monitored by the on-line optical spectrometer. Table 1 summarises the evaporation conditions used in this work.

Table I
Deposition parameters of TiO_2 and ZnS coatings on PET

Process parameters	TiO_2	ZnS
Substrate	PET, 25µ	PET, 25µ
Web width	600mm	600mm
Deposition rate	50-60Å/sec	1200Å/sec
Pressure	4x10^{-4}mb	4x10^{-4}mb
Ion gun	Yes	No
Coating thickness	500-600Å	450-550Å
Film speed	1-2m/min	35m/min
EB power	3.1kW	3kW
Starting material	$TiO_{1.7}$	ZnS
Refractive index	2.4-2.5	>2.2
Absorption	<3%	2.8%
Coating tone	no tone/very light yellow	light yellow
Adhesion	excellent	very good
Hardness	hard	soft

RESULTS AND DISCUSSION

1. TiO_2 coating

The deposition rate of TiO_2 coatings and ion gun parameters were optimized in a previous experiment[6]. The variation in optical reflectance as a function of oxygen flow rate through the ion gun is shown in Fig.2. The anode current was kept fixed at 5A. Without oxygen ion bombardment, the deposited titanium oxide coating exhibits a low optical reflectance, a gray metallic finish and a high absorption level. As the oxygen flow rate through the ion gun increases, the spectral reflectance and, consequently, the refractive index increases. The measurement of the refractive index shows a value of 1.9 for coating deposited without ion assisted deposition onto a polyester film moving at a speed of 1m/min.

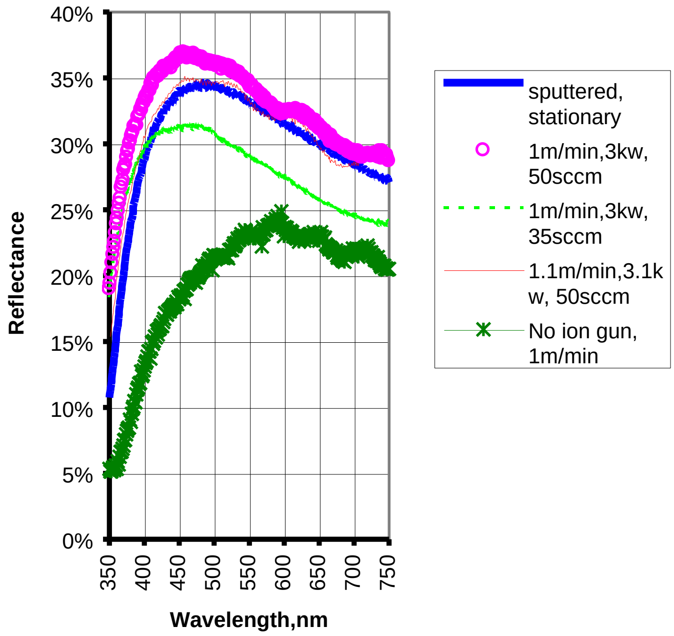

Fig. 2. Effect of oxygen flow on reflectance of TiO_2 on PET

For coating deposited with IAD at an oxygen flow rate of 50sccm the refractive index increases to 2.4. This value is higher than that of a sputtered TiO_2 coating on a stationary glass sample(n=2.3). Coating deposited with IAD at 50sccm oxygen flow rate exhibits a lower absorption than that without IAD. This is due to the formation of stoichiometric coating with full oxidation as a result of enhanced reaction of oxygen ions with the deposited atoms. [7]. For a deposition rate of 60Å/sec the total number of oxide atoms arriving at the substrate is 1.10^{16} atom/cm^2sec. At a web speed of 1m/min and oxygen flow rate of 50sccm, the polyester surface is exposed to the plasma for 9sec. The oxygen ion density near the web surface is 2mA/cm^2 which is equivalent to 1.10^{15} ion/cm^2sec. Therefore, the atom/ion arrival rate at the substrate surface is approximately 10:1. Thus the deposited coating requires a lower number of oxygen ions to obtain a stoichiometric structure onto a moving polyester film at a speed of 1m/min. Fig.2. also show that a good TiO_2 coating can be deposited at a film speed of 1.1m/min. Fig.3. Show AFM picture of the surface morphology of TiO_2 coating deposited onto a polyester film moving at a speed of 1m/min. The coating exhibits a closely packed structure with a smooth finish. On the other hand, coating carried out without IAD exhibit a columnar structure.

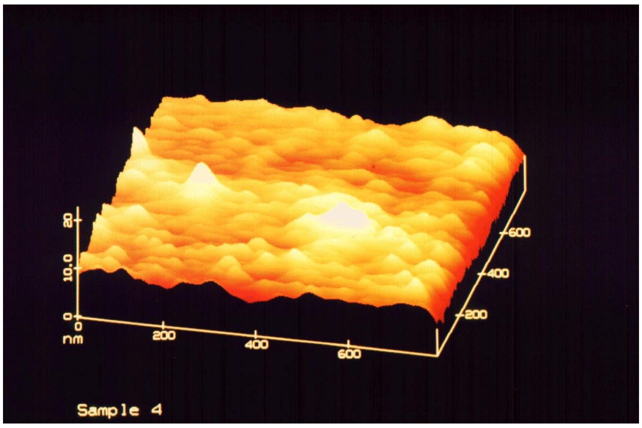

Fig. 3. AFM image of TiO_2 on PET produced by IAD

2. ZnS coating

ZnS coatings were deposited onto a polyester film moving at a speed of 35m/min. The coatings were deposited using four, 3kW EB guns having a rate of 1200 Å/sec each until a total thickness of 450-550Å was achieved. Fig 4 shows the optical reflectance of ZnS coatings onto a Polyester film moving at a speed of 35m/min. The coatings show a maximum reflectance of 35-40% at 450nm. Fig. 4 also exhibits the changes in reflectance due to thickness variation across the 600mm wide polyester film. To achieve uniform deposits it was necessary to place the four EB guns well apart and to control their rates of evaporation carefully. In the present investigation a single on-line optical probe was placed close to the centre of the moving web in the rewind zone to monitor the coating reflectance over the full visible spectrum (350-750nm).

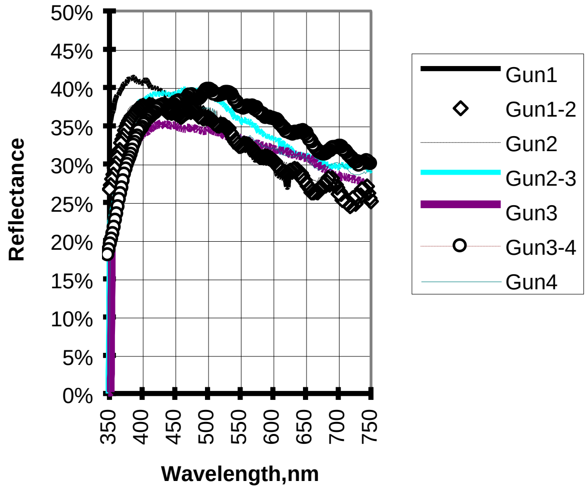

Fig. 4. Uniformity of ZnS across film width

This arrangement resulted in a coating uniformity of ±5% across the film width. The absorption of the deposited ZnS coatings was measured from the transmittance and reflectance data and found to be less than 2.8%. The stress level in ZnS coatings was found to increase as a function of coating thickness. The stress was also influenced by substrate temperature. For this reason, the cooling drum was running at room temperature to reduce the stress level in ZnS coatings. This produced a columnar structure with low stress level as shown in Fig. 5. This effect was also observed by Rufffner et al[8] who reported a change in the ZnS coating structure and stress level as a function of thickness and deposition temperature. It is possible to propose that cold deposition temperatures reduce adatoms mobility and result in a more porous structure with high stress level[9]. Consequently, this would influence the refractive index of the deposited ZnS coatings. It has also been reported that a lower deposition rate could reduce compressive stress in ZnS coatings on stationary substrates[8]. In the present work, the stress level was low in all ZnS coatings deposited at film speeds> 10m/min.

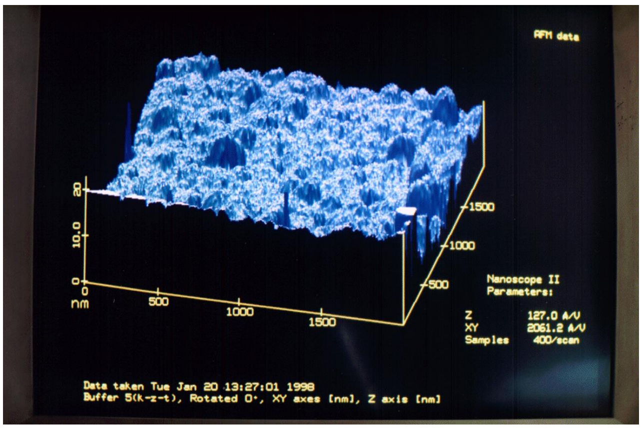

Fig. 5. AFM image of ZnS on PET

CONCLUSIONS

Our investigations have shown that high index optical coatings such as titanium dioxide and zinc sulphide can be deposited onto a polyester film moving at a fixed speed. For the production of stoichiometric TiO_2 coating on a polyester film, oxygen ion bombardment is required. The refractive index is a function of oxygen flow rate through the ion gun at a fixed ion beam current and energy. Coatings obtained at 50sccm oxygen flow rate have a dense structure and a high refractive index with absorption of less than 3%. For the deposition of zinc sulphide coating on a polyester film, there is a correlation between refractive index, stress level and coating thickness. ZnS coatings obtained at film speed of 35m/min exhibit a refractive index >2.2, absorption coefficient of 2.8% and 35-40% reflectance at 450nm wavelength. The coating uniformity across film width is better than ±5%. Vacuum deposited ZnS exhibits a columnar structure. All coatings have a low level of stress and are highly adherent to the substrate. These optical coatings have been successfully utilized for the production of high quality holograms.

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