Ion Assisted Deposition of TiO_2 on Moving Web Using Oxygen Ions

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ABSTRACT

Ion Assisted Deposition technique (IAD) has become an established process for the production of optical coatings. The continuous bombardment of the substrate with energetic inert or reactive gas ions produces a highly dense, stoichiometric coating with excellent adhesion to the substrate. This process offers many advantages over the conventional method of vacuum evaporation onto heated substrates which produces coatings with poorer optical and mechanical properties. Furthermore, the conventional method of using a heated substrate is not suitable for thermally sensitive substrates such as plastics.

In the present work a polyester film moving at a speed of 0.5m/min was bombarded with oxygen ions during the deposition of titanium dioxide film. This process produced a transparent TiO_2 coating with a refractive index of 2.4.

INTRODUCTION

Recent trends in vacuum metallizing have concentrated on coating plastic films with transparent optical materials such as SiO_2 and TiO_2 for gas barrier and optical properties [1-3]. To make the process more cost effective in the packaging industry thin oxide coatings have to be deposited on to a moving web at a particular speed. For such applications various methods have been employed including reactive sputtering, reactive evaporation and ion vapor deposition in the presence of reactive gas [4,5]. Optical properties are usually influenced by many of the deposition parameters, including working pressure, evaporation and deposition rates, substrate temperature, mobility of adatoms on the substrate surface and the starting material in the crucible [6,7]. Optimization of the different parameters should give coatings with the required optical and mechanical properties. However, optical coatings deposited by vacuum evaporation have an open columnar grain structure with a packing density of less than unity. This can result in water absorption through open pores leading to a variation in the refractive index of the film[8]. Another problem with vacuum evaporation is the abrupt interface between the coating and the substrate with little or no interdiffusion. If interdiffusion occurs after deposition, then severe shifts in the optical properties would occur [9]. Heating the substrate to about 300°C may resolve some of these problems, but some coating/substrate combinations may require temperatures of more than 300°C to achieve the improvement required. Furthermore, heat sensitive materials such as plastics must be kept close to ambient temperatures during coating to prevent thermal damage. An alternative approach to heating is ion bombardment during formation which adds activation energy to the growing coating, thus disrupting the columnar growth. Ion bombardment with reactive ion species can enhance the reaction to produce stoichiometric chemical compounds without substrate heating [10].

In the present work, a moving polyester web was bombarded with oxygen ions during the evaporation of Ti_2O_3 to deposit a titanium dioxide coating. Stable films with high refractive index were produced for ion-to-atom arrival rate ratio of 1:4.

ION ASSISTED DEPOSITION PROCESS

In this process the substrate is continuously bombarded with energetic ions during the evaporation of a coating material to produce a coating with superior properties than those produced by only vacuum evaporation. In the ion assisted deposition technique different types of ion sources are used to bombard the substrate with ions with various flux and energy levels. Energetic ions employed can be either inert ions to influence the nucleation and growth, reactive ion species to produce stoichiometric chemical compounds or a combination of the two. Consequently, the early stages of film growth on the substrate are controlled by a complex mixture of processes involving collision, penetration and entrapment of high energy particles. Knock-on sputtering effects in which surface atoms are knocked into rather than out of the substrate may also be important, even though the penetration depth is very small [6]. Ion implantation plays only a comparatively minor role in the actual material growth, due to the small amount of energy involved (10-1000eV). Thus the deposition energy

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(the transfer of energy from energetic ions and neutrals to the film and substrate atoms) and the associated mixing process represent the major contributions of the energetic particles. Figure 1 shows the effect of ion-solid interactions on various coating characteristics during the ion assisted deposition process.

The simultaneous ion bombardment of the growing coating can result in Pseudo-diffusion interfaces created by mixing coating material with the substrate. This can produce a graded interface resulting in enhanced adhesion. In reactive coating reactive ion species are used to replace the lost constituent elements such as oxygen which tend to dissociate at high temperature during evaporation. The fundamental effects of ion bombardment on film formation are summarized in Table I.

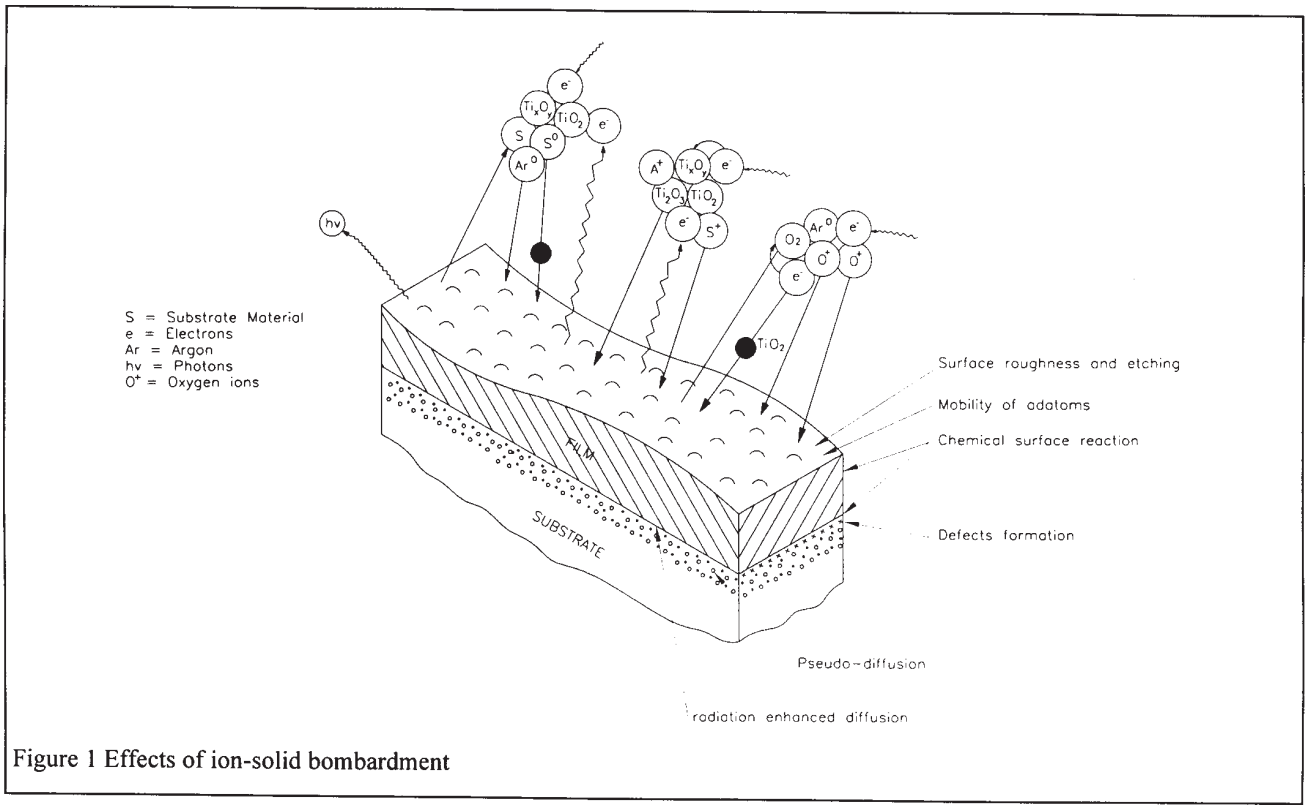

Figure 1 Effects of ion-solid bombardment

Table I
Fundamental effects of ion bombardment on film formation

Process	Effect
Defect formation	Nucleation sites, interfacial layer, increased bonding
Coating-substrate mixing	Interface formation
Surface cleaning	Adhesion improvement, removal of oxides, chemical reaction
Deep etching	Mechanical bonding
Ion species	Chemical reaction, removal of
Surface diffusion	contaminants
Continuous bombardment	Change in morphology, epitaxial film
Ion implantation	Change in morphology, nucleation growth, heating effects
	Interface formation

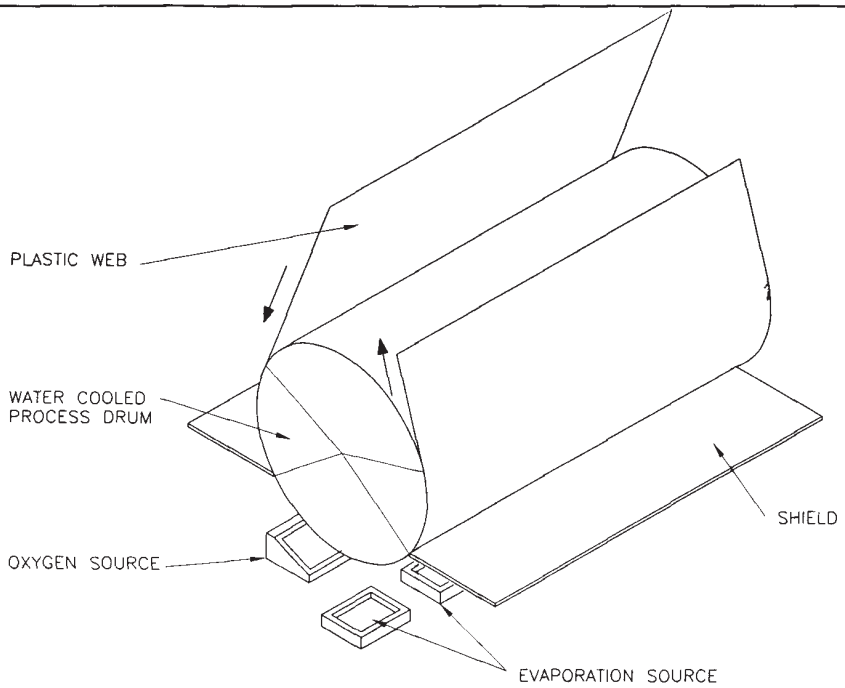

Figure 2 Schematic of the titanium dioxide deposition process inside the vacuum web coater

HEAT LOAD ON THE WEB DURING OXIDE DEPOSITION

When plastic film is metallised, the heat load on the film is determined from the net balance of the heat generated during the coating process and heat transference into the drum. In reactive coating heat load on the web is generated by the following mechanisms[11,12];

1. Heat radiation from the source.

2. Heat of condensation of the deposited coating on the plastic film.

3. Heat of reaction to form the chemical compound.

The heat radiated from an evaporation boat or EB crucible can be approximated given its temperature, emissivity and exposed surface area. The heat of condensation is the heat liberated by the condensing vapor on the substrate surface during coating formation. This can be quantified fairly accurately given the latent heat of vaporization, latent heat of fusion, mean specific heat capacity, evaporation temperature and thickness of the coating material. The heat of reaction is the heat of formation of the chemical compound and occurs when the reactive ion species react with the dissociated evaporant which has lost some of its elements during evaporation. This can be calculated by assuming a partial dissociation and recombination of the evaporant near or on the substrate surface. Electron beam evaporators and ion guns can also generate some heat load on the web although by careful design this can be reduced substantially.

EXPERIMENTAL WORK

The present work was carried out inside a 2m diameter, two zone vacuum web coater. The vacuum chamber, pumped down directly by rotary and diffusion pumps, contained unwind/rewind drives, water-cooled drum, oxygen ion source and water-cooled evaporation source. Figure 2 shows a schematic diagram of the experimental setup.

The oxygen ion source used in this work was capable of producing 1mA/cm² at a distance of 30 cm from the source with ions having an average energy of 100eV. The plastic web was bombarded with ions and electrons escaping from the ion source to prevent charge build up on the 50 µm polyester film. Prior to the evaporation and ion bombardment the chamber was pumped down to a base pressure of 1×10^{-5} mbar. During evaporation and ion bombardment the pressure was raised to 3×10^{-4}mbar. Oxygen flow rate through the ion source was fixed at 100sccm. Table II summarizes the evaporation conditions used in this work.

The evaporants used in the present work were TiO and Ti_2O_3. However, it was found that the latter had a better evaporation rate than TiO. Furthermore, the evaporated TiO

coating on the polyester film showed a darker finish than that of the evaporated Ti_2O_3 and this was probably due to the dissociation of the oxygen atoms and the formation of metallic rather than sub-oxide film on the web. As a result, the experimental work continued with only Ti_2O_3 as the evaporant.

RESULTS AND DISCUSSION

Before activating the oxygen ion source, the evaporation rate of the Ti_2O_3 was first optimized to achieve a uniform coating on the polyester web at a line speed of 0.5m/min. The polyester was then coated for 5-10 minutes before activating the ion source. The deposition rate in the present work was fixed at 1260 Å/min for a web speed of 0.5m/min and a source-to-substrate distance of 33cm. The final thickness of the titanium dioxide coating on the polyester was 400 Å. Upon activating the oxygen ion source the colour of the coated polyester web changed from transparent light gray to colourless indicating a change in the refractive index of the film. Refractive indices of the ion assisted and un-assisted titanium oxide coatings were measured using a conventional spectrophotometer. The measurements indicated that the refractive index changed from 2.25 for the un-assisted coating to 2.4 for the ion assisted coating. Table III shows the typical process parameters used for oxygen ion bombardment near the web surface.

The total heat load on the polyester web at a line speed of 0.5 m/min was calculated and found to not exceed 1 W/cm² as shown in Table IV. The most significant heat load is generated by heat radiation from the source. In the present work the process drum was not chilled and no thermal damage was observed on the polyester film during coating and ion bombardment.

Table II
Evaporation parameters for titanium oxide coating

Evaporated material	Density g/cc	Evap. temp. °C	Web speed m/min	Evap rate g/s	Specific Evapor. rate g/m²s	Vapour press. Pa	Mean free path cm	Particle density part./m³
Ti_2O_3	4.6	1800	0.5	0.00092	0.47	0.41	7.5	1.4×10^{19}
TiO	4.9	1700	0.5	0.00098	0.5	0.63	4.6	2.3×10^{19}

Table III
Process parameters for oxygen ion bombardment

Evaporant	Web speed m/min	Deposition rate Å/s	No.of TiOx atoms arriving at the web at/cm²s	O^+ ions bombardment rate ion/cm²s
Ti_2O_3	0.5	21	4×10^{15}	1×10^{15}

Table IV
Thermal load on polyester film
during evaporation of Ti_2O_3

Source of heat load	Heat load on web W/cm²	Comment
Film condensation	0.004	Deposition rate =2.1 nm/s Web speed =0.5 m/s
Chemical reaction	0.0014	Assuming 10% dissociation rate
Heat radiation	0.76	Assuming ε=0.5, γ =0.15, T= 1840°C Ion energy= 100 eV Ion current density = 2 mA/cm² Maximum temperature difference on web = 96°C (assuming heat transfer coefficient = 100 W/m²K)
Oxygen ion bombardment	0.2	

For a deposition rate of 21 Å/sec the total number of oxide atoms arriving at the substrate was 4×10^{15} atom/cm² sec [Table 3]. At a line speed of 0.5m/minute the polyester surface was exposed to the plasma for a period of 18sec. The oxygen ion density near the web surface was 1mA/cm² which is equivalent to 1×10^{15} ion/cm²sec. Thus, the deposited coating required a lower number of oxygen ions than expected [7] to obtain a stoichiometric structure with a refractive index of 2.4 when Ti_2O_3 was used.

It is possible therefore, to speculate that when TiO is used as a starting material more oxygen ions would be required to replace the dissociated atoms and to obtain a refractive index of 2.4. This would require an ion gun with a higher current density or the gun could be located closer to the web. However, this may generate more heat and cause damage to the plastic web.

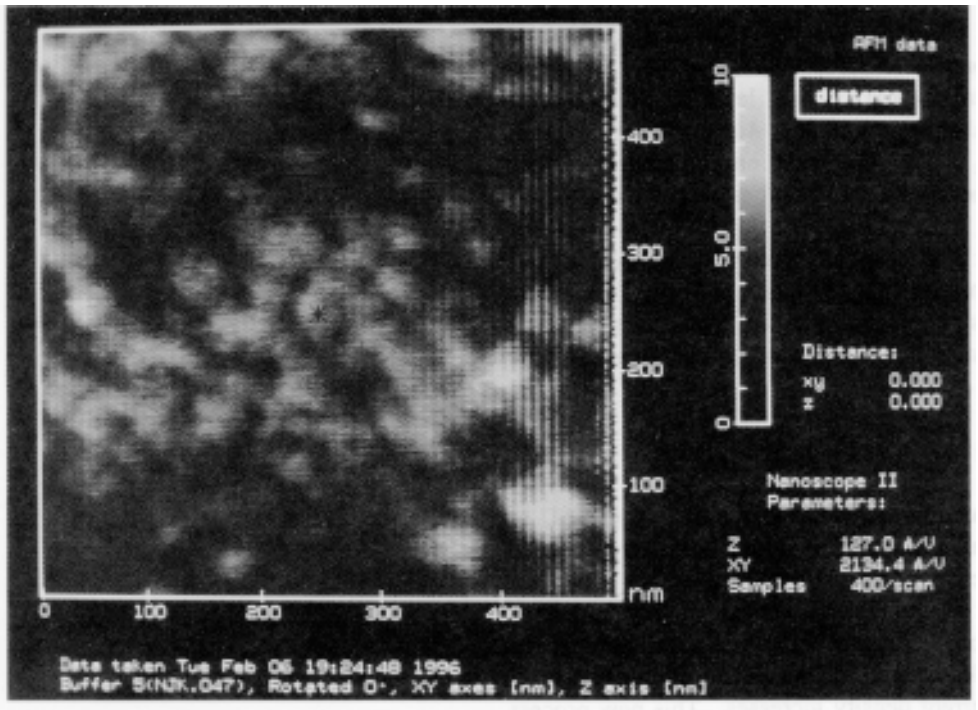

Figure 3. AFM pictures of titanium oxide films deposited on polyester at oxygen current density of 0.3 mA/cm²

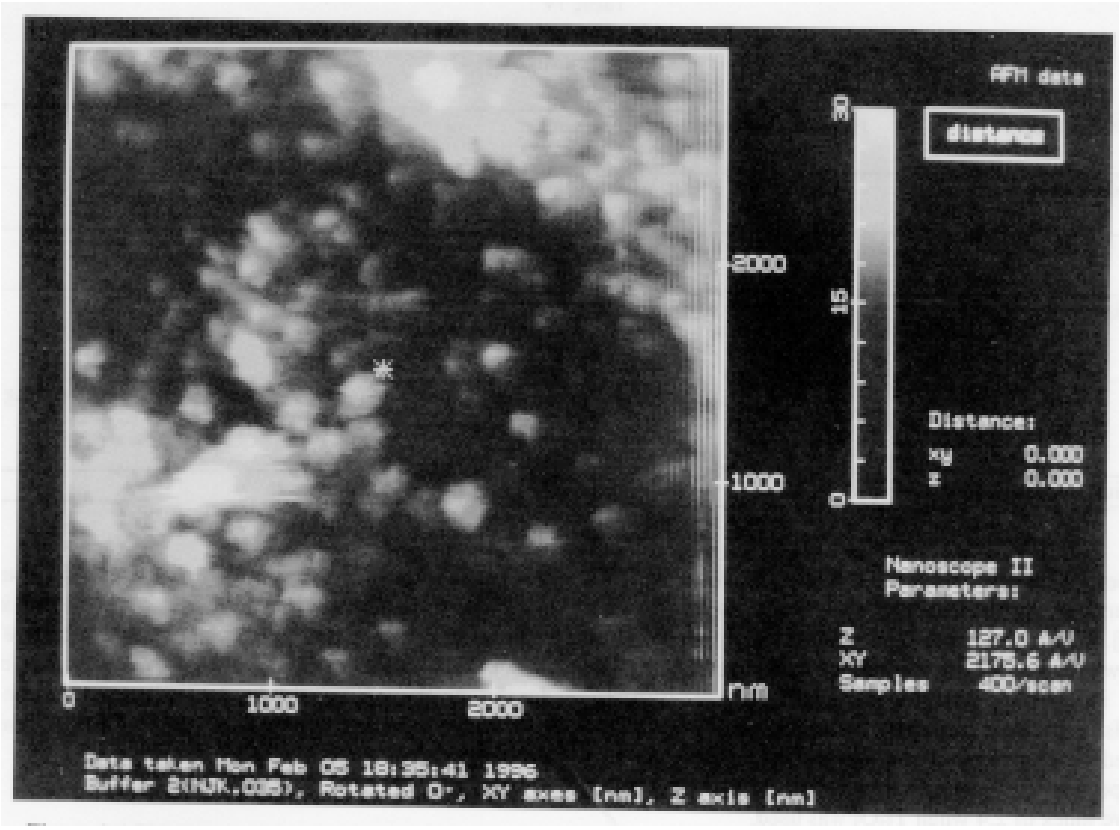

Figure 4. AFM pictures of titanium oxide films deposited on polyester at oxygen current density of 1 mA/cm²

The structure of the thin deposited film was investigated using Atomic Force Microscopy (AFM). This technique allows observation at a microscopic level of the surface of insulating materials [13]. Figures 3 & 4 show the structure of 400 Å thick TiO_2 coating deposited on polyester at oxygen ion current densities of 0.3 and 1mA/cm² respectively.

It can be seen that as the oxygen ion current density increases from 0.3m to 1 mA/cm², the grain size increases from 30nm to 200nm. This may be due to the formation of polycrystalline film as a result of ion bombardment at higher current density.

CONCLUSIONS

The results presented in this work show that oxygen IAD of thermally evaporated titanium oxide on polyester produced films with a refractive index of 2.4. When Ti_2O_3 is used as a starting material a relatively lower number of oxygen ions to the number of deposited atoms is required. Furthermore, the grain size of the deposited titanium dioxide film increases as the oxygen ion current density increases. This new process can safely produce optical coatings on temperature sensitive substrates such as plastic films.

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