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Studies on thin film materials on acrylics for optical applications

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Abstract. Deposition of durable thin film coatings by vacuum evaporation on acrylic substrates for optical applications is a challenging job. Films crack upon deposition due to internal stresses and leads to performance degradation. In this investigation, we report the preparation and characterization of single and multi-layer films of TiO_2, CeO_2, Substance2 (E Merck, Germany), Al_2O_3, SiO_2 and MgF_2 by electron beam evaporation on both glass and PMMA substrates. Optical micrographs taken on single layer films deposited on PMMA substrates did not reveal any cracks. Cracks in films were observed on PMMA substrates when the substrate temperature exceeded 80°C. Antireflection coatings of 3 and 4 layers have been deposited and characterized. Antireflection coatings made on PMMA substrate using Substance2 (H2) and SiO_2 combination showed very fine cracks when observed under microscope. Optical performance of the coatings has been explained with the help of optical micrographs.

Keywords. Coatings on acrylics; dielectric thin films; optical coatings; low temperature coatings; oxide films; antireflection coatings.

1. Introduction

Transparent acrylics (plastics) are extensively used for optical elements like lenses, mirrors, substrates, covers, windows etc in large quantities. Optical thin film coatings are to be deposited on acrylic surfaces to give them the properties such as antireflection, high reflection, transparent conducting coating etc.

Films are also coated on plastics to protect the surfaces against abrasion and moisture penetration. Deposition of thin film coatings on acrylics is a challenging job because they are soft, temperature sensitive, moisture absorbing and desorb in vacuum. Moreover, there is a large gap between thermal expansion coefficient of acrylic substrates and conventional thin film materials. Films deposited on acrylics therefore, suffer from poor adhesion and low abrasion resistance, and are less stable due to high induced thermal stress. As a consequence, the film cracks, blisters and delaminates. The deposition process and the film materials must be compatible to the substrate. Some of the common deposition techniques employed for coating on plastics are vacuum evaporation, magnetron sputtering, plasma polymerization and sol–gel process (John *et al* 1974; Wydeven 1977; Jesse 1992; Chow *et al* 1994; Samson 1996; Szczybrowski *et al* 1997; Diggins 1998). In recent years a number of ion and plasma based deposition techniques have been developed (Allen and Tregunna 1988; Usui *et al* 1995; Baldwin *et al* 1997; Schulz *et al* 1998). The advantage of these techniques is that durable films can be deposited without heating the substrate, which was hitherto not possible. In these techniques, the substrates are bombarded with ions prior to and during deposition. Initially the ions clean the substrate and provides additional energy to the condensing atoms and molecules resulting in hard and dense films. Among these techniques, ion assisted deposition using either end-Hall ion source (Commonwealth Scientific Corporation, USA) or cold cathode source (Denton Vacuum Inc., USA) and plasma assisted evaporation (Leybold Vacuum, Germany) are very useful for coatings on acrylics. However, these techniques are still evolving and the effect of ion bombardment on soft plastic substrates has not been fully studied. Allen and Tregunna (1988) reported that durable and broad band anti reflection coatings on PMMA substrate has been made by ion assisted deposition using Kaufman ion source. A single layer abrasion resistant and antireflection coating has been deposited on poly-carbonate substrate by plasma polymerization (Wydeven 1977). Sol–gel deposition of antireflection coatings looks bright especially for coating on large surfaces and on curved substrates. Some of the problems associated with this technique are high process temperature, reaction of chemicals with acrylics and poor durability of the coatings.

Much of the work, on the deposition of thin films by vacuum evaporation on acrylics is carried out in industries. The process is proprietary and not much published literature is available on the preparation and characterization of films on acrylics. Samson (1996) reported that the inorganic coatings are brittle, easily develop cracks and craze when deposited on soft materials such as acrylics. This is mainly due to the large difference in thermal expansion coefficients that exists between the substrate and thin film coatings. It was also observed that the deposition of organo-siloxane by chemical technique as a glue layer is in practice in industry. This layer is believed to be a matching layer between the acrylic substrate and the inorganic layers, which prevents the cracking of the films. Samson (1996) has also mentioned that as many as eight layers are required to make an antireflection coating for ophthalmic purpose which includes organic layers. Film stress and adhesion are believed to be major factors influencing the durability of coatings on acrylic substrates.

Ion assisted deposition is believed to improve both adhesion and control of stress in the films. MgF_2 films deposited by ion assisted deposition by Baldwin *et al* (1997) had micro cracks not seen by unaided eye but seen with the optical microscope. Hence there is a need for investigations on the formation of thin films by vacuum evaporation on plastic substrates.

In this work, we report the preparation and characterization of single- and multi-layer films of TiO_2, CeO_2, Substance2 (E Merck, Germany), Al_2O_3, SiO_2 and MgF_2 on both glass and PMMA substrates by using conventional electron beam evaporation technique. The prime objective of the present work is to deposit durable antireflection coatings on PMMA substrate by vacuum evaporation.

2. Experimental

Thin films were deposited in a conventional deposition unit (M/s Edwards, England, model-19E4). The base pressure obtained was 5×10^{-6} mbar in 2 h. The materials TiO_2, CeO_2, Al_2O_3, MgF_2 and SiO_2 were obtained from M/s Blazers and Substance2 (H2) from E Merck, Germany and evaporated using electron beam gun (ESV-6, Leybold Heraeus). The films were deposited on fused quartz, clear plate glass and commercial PMMA sheets of 8 mm thickness. Acrylic substrate was degreased by alkali and thoroughly washed in water and then all the substrates were cleaned in laboratory detergent, washed in running water and rinsed in distilled water. Finally the cleaned and dried substrates were subjected to ionic (oxygen) cleaning in vacuum prior to deposition for 10 min. The deposition rate and the thickness were controlled using a quartz crystal monitor. Substrates were mounted on a flat work holder and rotated during deposition to get uniform films. The electron beam source was kept off-centre. The substrates were heated using radiant heater at 50°C prior to deposition. The spectral transmittance of the films in air was recorded using a HITACHI-330 model UV, visible and near IR double beam spectrophotometer. Optical constants and thickness of the films were estimated from the measured spectral data (Swanepoel 1983). The method was based on analysis of the transmittance spectrum of weakly absorbing films on a transparent substrate. Experimentally obtained transmittance spectra were used to read the T_{max} and T_{min} at different wavelengths. These were used in the theoretical relations to arrive at various optical constants of the films. The refractive index and the film thickness were measured to an accuracy of $\pm 0{\cdot}01$ and ± 50 Å, respectively.

3. Results and discussion

3.1 *Single layer studies*

The most useful thin film materials with their characteristics for the preparation of optical coatings are found in the literature (Pulker 1979; E Merck 1998 and Balzers 1995 coating materials catalogues). The important parameter to be noted here is the evaporation temperature as this restricts thin film material to be used for acrylics. As the aim of the present work is to make broad band antireflection coatings, we require three types of materials with high, medium and low refractive indices. Oxide coatings are preferred as they adhere well to the substrates and can easily be deposited through plasma and ion beam techniques.

Substrate temperature and ionic cleaning in vacuum are used to improve durability of the coatings. The influence of these parameters on PMMA substrate has been studied. The transmittance spectra of the substrate alone before and after subjecting it to heating (a) at 50°C for 15 min in vacuum and (b) ionic cleaning for 10 min at 5×10^{-2} mbar are presented in figure 1. It can be seen that the effect of these parameters is marginal on substrate transmittance (90–91%). Hence, ionic cleaning and substrate heating at 50°C have been used prior to the deposition of single and multi-layer films.

Figure 2 shows the measured spectral transmittance characteristics of TiO_2, Substance2, CeO_2 and Al_2O_3 films on fused silica substrates. Well polished quartz substrates were used for the study of optical properties. The deposition conditions are given in table 1. It can be seen from the transmittance spectra that the films are transparent (92% at the wavelengths corresponds to half wave optical thickness) even in the short wavelength region of the visible spectrum. Hence the films are considered as almost absorption free. The refractive index of these films was also estimated as a function of wavelength and the same is presented in figure 3. The refractive index decreases with the increase of wavelength but the variation is comparatively less. This may be due to the fact that the films were prepared at a comparatively lower substrate temperature (< 100°C). The refractive indices of TiO_2, Substance2, CeO_2 and Al_2O_3 are 2·06, 2·03, 1·95 and 1·62, respectively at 550 nm. The values obtained in this work are comparable to those reported in the literature (Ghanshyam Krishna *et al* 1993; Ganesh Shanbhogue *et al* 1997; Mansour *et al* 1992, 1994). The refractive indices of MgF_2 and SiO_2 were also estimated at 550 nm by depositing films on high index glass substrates and these were found to be 1·37 and 1·46, respectively. The extinction coefficient of these films was found to be < 0·0005 at 550 nm. Figure 4 shows the transmission characteristics of single layer MgF_2 and SiO_2 films on PMMA substrate. MgF_2 layer increased the substrate transmittance and this is expected as the MgF_2 material has lower refractive index (1·37 at 550 nm) when compared to PMMA substrate with a refractive index of 1·49 at 550 nm. The transmittance of SiO_2 coated substrate is almost the same as the bare substrate. The optical micrographs (not shown here) taken with 100 magnification for these films coated on PMMA showed no cracks and the surface was very uniform. These studies indicate that the single layer films of MgF_2 and SiO_2 have good optical transmittance on PMMA substrate (comparable to optical characteristics on glass). The coated surfaces are uniform and free from cracks even when observed with optical microscope.

The temperature rise during deposition for these films and film properties are given in table 2 for typical thickness of the films. The TiO_2 film is deposited using TiO_2 as starting material, the temperature of the substrate increased from 76°C to 108°C during a period of 12 min of deposition. The films were quite adherent to PMMA substrate but micro level cracks were observed even with unaided eye. This is mainly due to the rise of substrate temperature beyond 80°C. Alternatively, Substance2 was found to show greater resistance to crack formation because of low temperature deposition. The adhesion of the film to PMMA substrate is also good. The difference in refractive indices between TiO_2 and Substance2 is marginal and therefore Substance2 can be used as high index film material for multi-layer applications. CeO_2 is easy to evaporate by electron beam evaporation, but the refractive index is low and the film had poor adhesion. The Al_2O_3 films are adherent to the PMMA substrate, and the temperature rise of the substrate was only 65°C. Similarly the temperature rise was marginal while deposit-

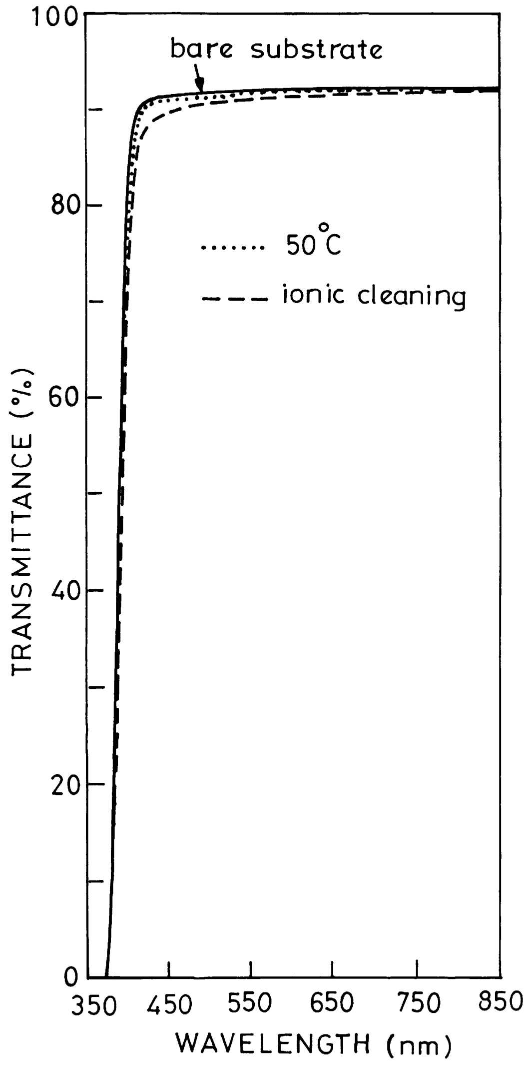

Figure 1. Measured transmittance of a bare PMMA substrate and subjecting it to heating at 50°C in vacuum (. . .) and ionic cleaning for 10 min (– – –).

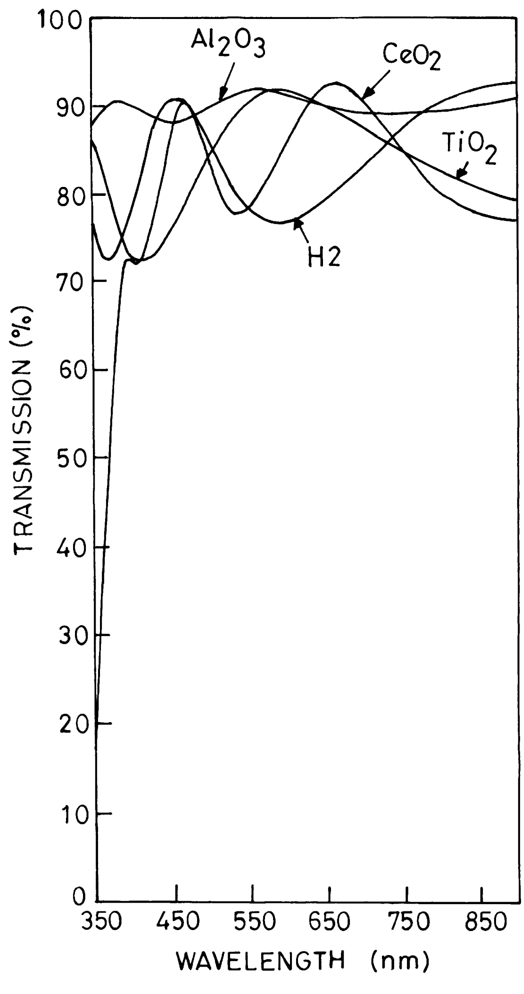

Figure 2. Measured spectral transmittance characteristics of single layer films of TiO_2, Substance2, CeO_2 and Al_2O_3 deposited on well polished fused quartz plates.

ing both MgF_2 and SiO_2 films. The SiO_2 layer adheres well to the substrate.

3.2 *Anti-reflection coatings on glass and PMMA substrate*

After having studied the characteristics of the useful materials in single layers the next stage was to find the suitable film combinations for the development of broad-

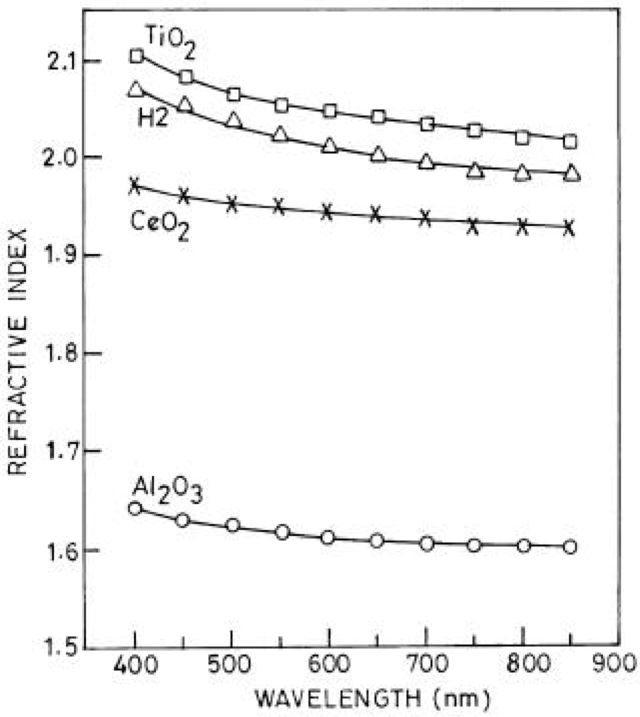

Figure 3. Optical dispersion characteristics of single layer thin films as described in figure 2.

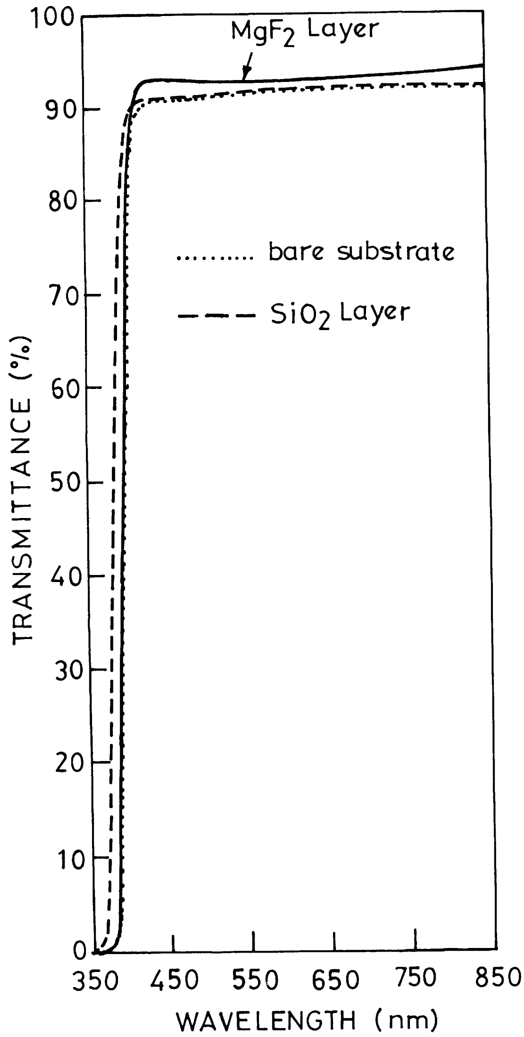

Figure 4. Measured spectral transmittance characteristics of single layer films of MgF_2 and SiO_2 deposited on PMMA substrate.

Table 1. Deposition conditions and characteristics of thin film coatings.

	Deposition conditions			Optical constants		
Material	Pressure (mbar)	Rate (Å/S)	Max. temperature (°C)	'n' at 550 nm	Thickness (Å)	Remarks on film properties
High index						
1. TiO_2	2×10^{-4}	1–2	108	2·06	1500	Films are adherent, durable, micro level cracks observed
2. H_2	2×10^{-4}	2–3	76	2·03	2000	Adheres well to PMMA and refractive index consistent
3. CeO_2	2×10^{-4}	2–3	65	1·95	2500	Tape test failed
Medium index						
Al_2O_3	5×10^{-5}	3–4	65	1·62	2000	Films are adherent to PMMA
Low index						
1. MgF_2	1×10^{-5}	10	30–40	1·37	2500	Uniform coating on PMMA
2. SiO_2	5×10^{-5}	3–4	40–50	1·46	2500	Films are adherent to PMMA

Table 2. Temperature rise during 4-layer antireflection coating for four different depositions.

		Depositions								
		1		2		3		4		
Sl. No.	Layer system	Ti	Tf	Ti	Tf	Ti	Tf	Ti	Tf	Max. temperature
1	H_2	46	51	47	51	48	54	43	49	< 80°C
	SiO_2	48	51	50	50	52	52	47	47	
	H_2	50	72	50	71	53	72	48	66	
	SiO_2	66	68	64	64	67	66	64	62	

Ti, initial temperature in °C; Tf, final temperature in °C.

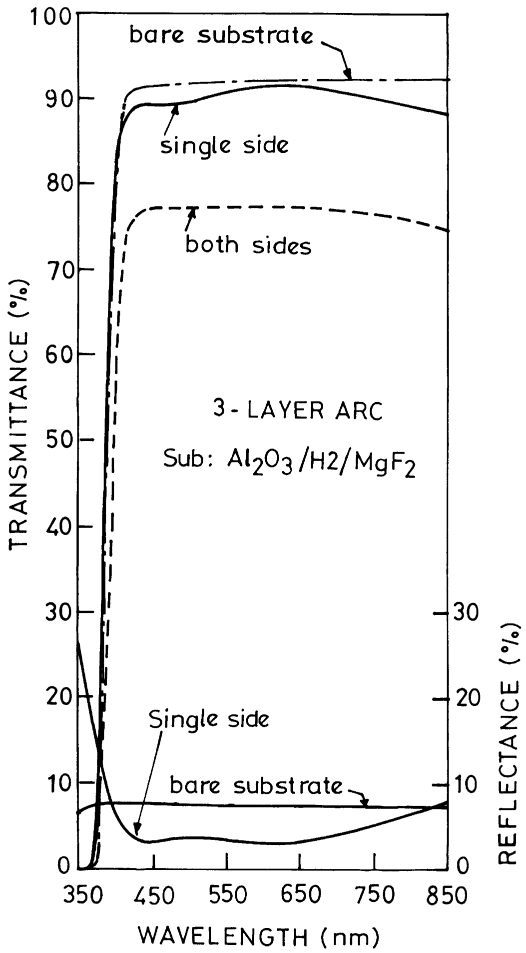

Figure 5. Measured spectral characteristics of 3-layer anti-reflection coatings on PMMA substrates.

band antireflection coatings on typical plastic substrates like PMMA. Initially, a three-layer combination consisting of a quarter wave layer of Al_2O_3, a half wave layer of Substance2 (H2) and a quarter wave layer of MgF_2 was deposited. The temperature of the substrate was below 80°C throughout the coating. Figure 5 shows the measured spectral transmittance characteristics of the 3-layer antireflection coating on PMMA substrate for the single and double side coating. The transmittance of the PMMA substrate was 90% and 78% in the visible region for the single and double side coating, respectively. Optical micrographs taken on these coatings have revealed severe cracking of the film as shown in figure 6. This was taken at 100 magnification. The second side also showed a similar pattern. The severity of cracking is indicated by the width of the crack. Optical micrograph was taken after depositing both sides. The deterioration of transmittance of the coated substrate is mainly due to the severe cracking, which results in scattering of light. The scattering of light in the film deteriorated the transmittance of the films on PMMA substrate.

To circumvent the problem of cracking in 3-layer antireflection coating on PMMA substrate, an alternative combination consisting of Substance2 and SiO_2 has been studied. We tried a 4-layer coating of design, consisting of Sub. 0·24 H 0·404 L 2·16 H 1·04 L AIR. Here, H and L are the one quarter wave optical thickness at 530 nm (0·25 l_0) of high index (Substance2) and low index (SiO_2) materials, respectively. The temperature rise during 4-layer coatings is shown in table 3 for four different depositions. In all the depositions, the temperature always remained < 80°C.

Measured spectral characteristics of a 4-layer anti reflection coating on glass are given in figure 7. The performance of the 4-layer coating on glass is excellent (both in terms of reduction in reflectance (0·5%) and in terms of corresponding increase in transmittance (> 99%)). Figure 8 shows the spectral characteristics of the same coating on PMMA substrate. The transmittance of the single side coated PMMA is satisfactory and comparable to the coating deposited on glass. The reflectance of the single side coated PMMA is less. The reflectance of both sides coated PMMA is observed to be as low as 0·2 to 0·5% in the active region of the visible spectrum (450–650 nm). However, the transmittance of the PMMA substrate after depositing the second side decreased (90%). The surfaces of these coatings were examined and there is no cracking as observed with unaided eye. Optical micrograph (× 100) taken for these surfaces showed very fine cracking of the film which was not as severe as in the earlier 3-layer coating. Figure 9 shows micrograph of the surface of PMMA substrate after deposition of

4-layer antireflection coating. The long straight lines observed in the micrograph is mainly due to the sleeks present in the substrate originally prior to deposition. The deterioration observed in film transmittance after coating both sides is mainly due to cracking of the film. Fine cracks were observed on both sides of the PMMA substrate. The adhesion of the film was tested with scotch tape and found to be good. There was no further deterioration due to aging. The coatings were made on 3″ × 3″ PMMA substrate with uniform characteristics.

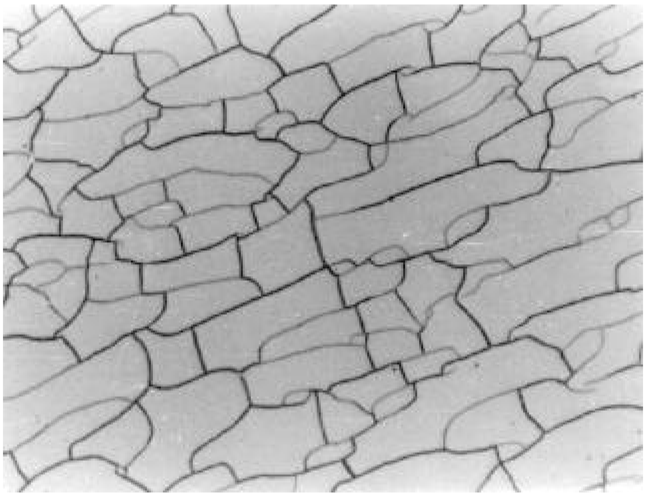

Figure 6. Optical micrograph of PMMA substrate coated with 3-layer antireflection coating.

The following observations can be made from the above investigations. Moderate heating and ion bombardment has no significant effect on optical transmission of the PMMA substrate. Single layer films deposited on PMMA substrates have similar optical characteristics as on glass. However, when the substrate temperature exceeds beyond 80°C, especially in the case of TiO_2 film on PMMA, cracking of the film and in some instances bending of the substrate was also observed. Multi-layer antireflection coatings deposited using 3 layers (Al_2O_3, H_2 and MgF_2) had severe cracking of the film though the final temperature of the substrate never exceeded 80°C. This is mainly due to the residual stresses present in the layer system. The deterioration in the case of 4-layer antireflection coating is not so severe as that of 3-layer coating.

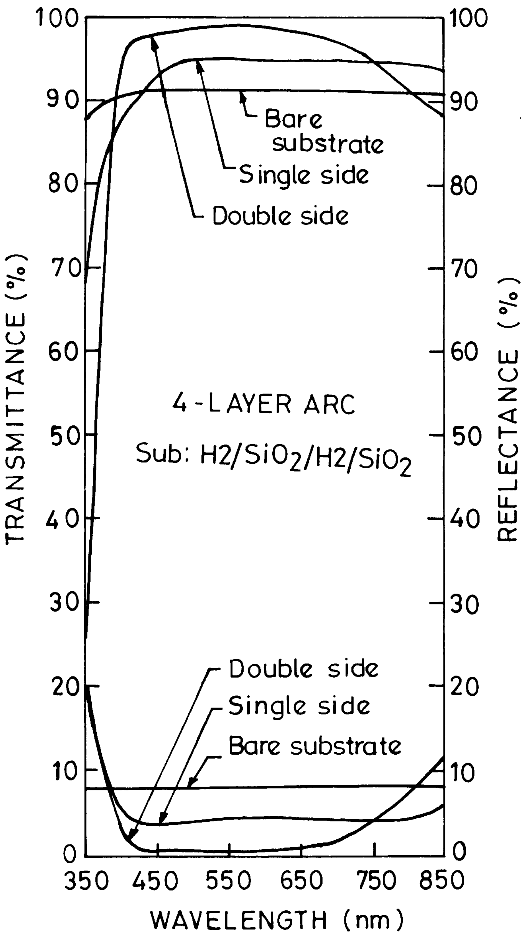

Figure 7. Measured spectral characteristics of 4-layer antireflection coatings deposited on glass.

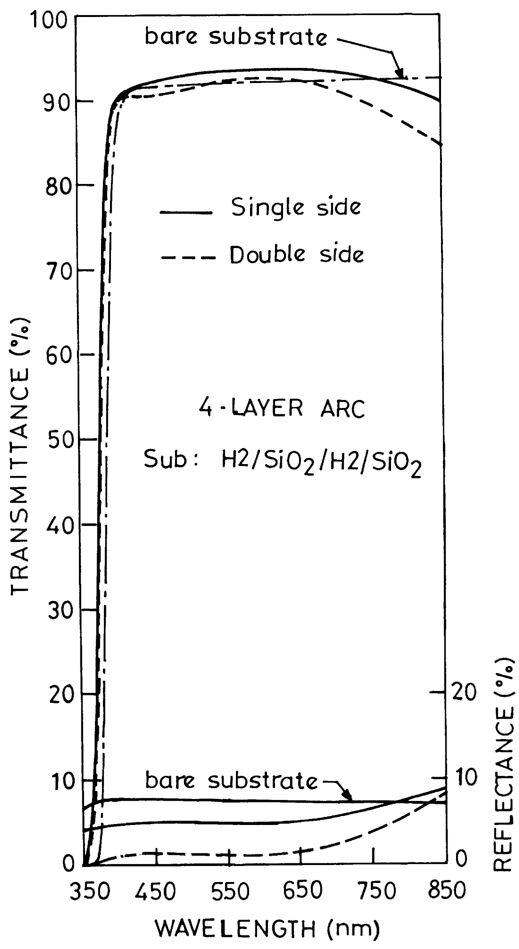

Figure 8. Measured spectral characteristics of 4-layer antireflection coating deposited on PMMA substrate.

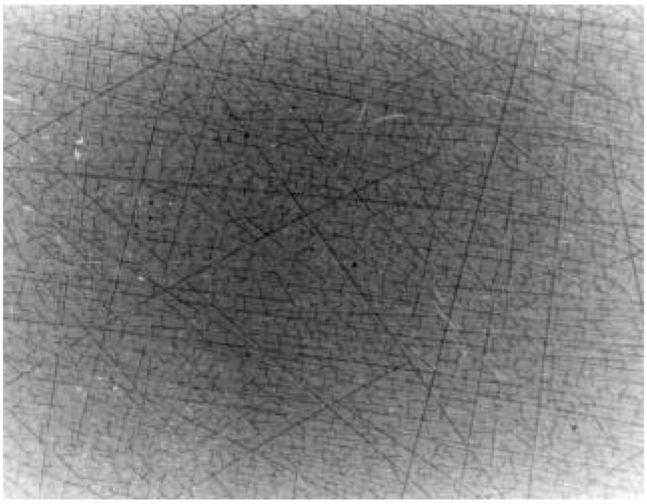

Figure 9. Optical micrograph of PMMA substrate coated with 4-layer antireflection coating.

Optical micrographs best illustrated the microstructure of the coatings. It is to be noted here that the microstructure has been studied after coating both sides of PMMA substrate. This involves breaking of vacuum after deposition and continued the second side coating. There is a possibility of moisture absorption when it is exposed to ambient atmosphere and desorption while re-evacuation. This causes the swelling and shrinkage of PMMA substrate, which might have altered the stress in the films. There is also temperature cycling to the substrate during coating on both sides. This also might have caused the cracking of the film. It should be possible to get better films without any cracks through proper balancing of the process and materials to reduce the residual stresses in multi layer films.

Ion assisted deposition is believed to improve the packing density, adhesion of the films deposited even at ambient temperature. The work in this direction is being pursued currently.

4. Conclusions

The application of vacuum evaporation for the deposition of adherent thin films on acrylics has been shown. Single layer films of TiO_2, Substance2, CeO_2, Al_2O_3, SiO_2 and MgF_2 have been deposited on both glass and PMMA substrates. It is observed that the rise of substrate temperature beyond 80ºC during coating deteriorates the quality of the coatings due to film cracking which was revealed through optical micrographs. Severe cracking has been observed for 3-layer antireflection coating deposited on PMMA substrate. A four-layer antireflection coating has been successfully deposited on PMMA substrate using Substance2 and SiO_2. The spectral characteristics (transmittance) were affected by the cracks present in the films. Further, studies are required to fine tune the deposition parameters to get high quality coatings on plastics by evaporation technique.

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