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Effects of various ambient-aging processes in chopped and non-chopped optical films

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Abstract. The effects of various ambients on the non-chopped and chopped films of cryolite, MgF_2 and mixed cryolite-MgF_2, as measured by ellipsometer, are reported. The moisture decreases the refractive index whereas an increase is observed in air and other ambients. In all the ambient-aging the chopped films show smaller changes (nearly half) in refractive index than non-chopped films. Aging seems to be due to three main processes, a long-term adsorption-like surface reaction and two short-term reactions.

Keywords. Optical films; aging; chopped films.

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1. Introduction

Many workers (Holm and Christensen 1980; Kinoshita and Nishibori 1969; Koch 1965; Koppelmann *et al* 1961; Macleod 1976; Ogura *et al* 1975, 1976; Pulkar 1971) who studied the problem of aging of optical films have found it difficult to provide a solution to the problem on a generalized level. We had earlier reported a new technique of chopping the vapour stream during deposition which reduces the aging of the films in air (Vijaya *et al* 1980). In this paper we report further studies on chopped films.

2. Experimental

The films, both non-chopped and chopped (5–6 rot/sec) of cryolite, MgF_2 and mixed cryolite-MgF_2 obtained (Vijaya *et al* 1980) by vacuum evaporation (vacuum 2×10^{-5} torr, deposition rate 15 Å/sec) were subjected, for few hours (short term aging), to different ambients: (a) air at room temperature, (b) gaseous environment (O_2 and CO_2 separately) for 21 hr, (c) heat to 120°C in air for 3 hr (heat), (d) steam for 3 hr at a flow rate of 0·23 ml/sec along with heating of substrate to 120°C to avoid condensation, (e) saturated humid atmosphere at three temperatures: (1) 12°C low temperature (LTM), (2) 27°C room temperature (RTM), (3) 55°C high temperature (HTM), each for 3 hr.

The effect of repeated (i) RTM exposures (for few hours, but totalling upto about 150 hr) and (ii) RTM heat cycling few hours each, was further studied in greater detail (Vijaya 1982).

About 10 films were deposited per cycle of evaporation for the different ambient aging measurements. The chopped and non-chopped films were deposited in different cycles but under similar conditions. The films were studied over a thickness range 300 Å to 1400 Å. The initial thicknesses, d_f, were found by Fizeau fringe method and also by ellipsometer. For the sake of convenience the thickness was divided into two different ranges: (i) 300–600 Å or thin films (ii) 600–1400 Å or thick films. All these films were kept in normal atmosphere for a few days to see the effect of further "long term" aging.

3. Results

The typical changes (averaged over 30 readings) in refractive index, δn_f, under different conditions for all cryolite films are given in figure 1. The trends of the changes in MgF_2 and mixed cryolite-MgF_2 are similar (see Vijaya 1982 for details). The figure shows that, in general, for all films, the refractive index increases on exposure to air, gases, heat and steam. Next, though the refractive index decreases on exposure to humidity conditions it again increases, on further aging in air after the moisture exposure. One very

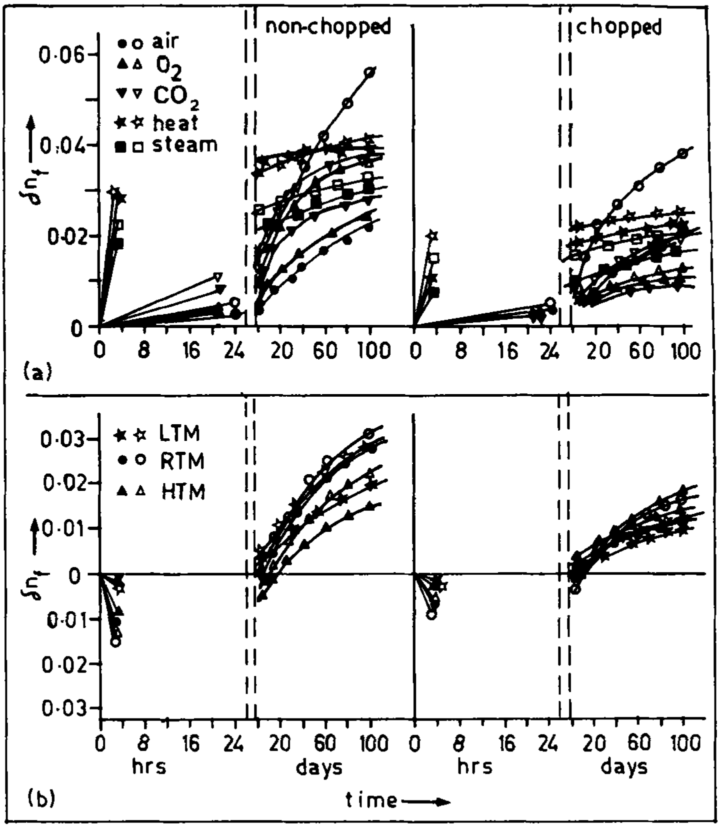

Figure 1. Average aging of cryolite films in different ambients. Open symbols—thin films; closed symbols—thick films.

significant result obtained is that, for all the ambients, the chopped films show lesser changes (almost 50 %) as compared to non-chopped films. Also, chopping reduces the thickness dependence of changes in refractive index. This is prominently seen in the scatter of the full data of the films (instead of averages (Vijaya 1982)).

Next, in almost all ambients there is an increase in film thickness by 50 to 100 Å (Table 1). The increase is greater (~ 100 Å) in MgF_2 and mixed cryolite-MgF_2 exposed to R.T. moisture.

Figure 1 shows that thin films (300–600 Å) show greater aging than thick films (600–1400 Å). Also the change in refractive index, δn_f, due to further air exposure (after pre-exposure to the various ambients), is comparatively smaller than that due to air exposure only.

Amongst the moisture ambients, films exposed to low temperature moisture (LTM), age the least. Exposure to moisture (especially RTM & HTM) tends to produce patches spoiling the films (table 2). About 10 % of films were thus spoiled. But the films exposed to hot moisture produce the highest percentage of spoilt films, probably due to condensation of water on the film. Table 2 also shows that chopping helps to reduce the spoiling in RTM, but in HTM it increases spoiling. HTM is apparently the only ambient where chopping deteriorates the optical films. The mixed films in RTM are not much helped by chopping.

The results with repeated RTM exposures have shown (Vijaya 1982) that after initial decrease of refractive index in about 24 hr, a saturation process is observed to occur on additional exposure. No further decrease occurs even upto 150 hr exposure. But for RTM-heat cycling exposures, it is seen (Vijaya 1982) that on each heating there is an increase in refractive index and on each moisture exposure the refractive index

Table 1. Average values of δd_f (Å) averaged over all thicknesses (error ± 25 Å).

	Average δd_f (Å)					
	Cryolite		MgF_2		Mixed cryolite-MgF_2	
Ambients	NC	C	NC	C	NC	C
Air	50	50	33	16	66	25
Gases	0	0	0	0	0	0
Further air	50	50	50	50	75	50
Heat	33	16	66	33	16	16
Further air	83	33	83	50	33	33
Steam	16	0	16	16	16	16
Further air	16	42	50	33	33	33
LTM	0	0	0	50	75	50
Further air	25	25	75	125	88	125
RTM	0	0	83	83	117	50
Further air	25	50	142	125	158	100
HTM	0	0	50	0	—	—
Further air	50	50	150	50	—	—

NC: Non-chopped, C: Chopped.

Table 2. Spoil data of films under various ambients.

Ambient	Material		Total number of films	Number spoilt and %
RTM	Cryolite	NC	38	10 (33 %)
		C	28	0 (0 %)
	MgF_2	NC	35	5 (14 %)
		C	30	1 (3 %)
	Mixed	NC	35	12 (34 %)
	Cryolite-MgF_2	C	30	8 (26 %)
HTM	Cryolite	NC	8	3 (37 %)
		C	9	6 (66 %)
	MgF_2	NC	11	4 (36 %)
		C	11	6 (54 %)
	Mixed	NC	8	8 (100 %)
	Cryolite MgF_2	C	6	6 (100 %)
All other ambients	All films		About 400	0 (0 %)

NC: Non-chopped, C: Chopped.

decreases. This trend is maintained even for 3–4 cycle (though slightly reduced) indicating that moisture absorption is partly a reversible phenomenon.

4. Discussion

Our results show that reducing the aging of optical films by chopping the vapour stream is advantageous since in most of the ambients the chopped films show lesser δn_f (about 50 %) than non-chopped films. Initially this was thought to be due to quenching of columnar crystal growth (Vijaya *et al* 1980). Our results however indicate that some other more dominant processes may also be operative. The aging phenomenon seems to be made up of two processes: (1) changes in refractive indices and (2) changes in geometrical thickness of the film, the former being normally more dominant.

There seems to be a difference in short-term and long-term aging (i.e. aging in few hours and few days respectively). From δn_f curves (figure 1) it appears that the aging process follows an exponential pattern expected of activation processes. Hence graphs of $\log(n_f)$ versus time were plotted which indicated that different types of processes are involved, given by straight lines with different slopes at different stages of aging. These slope values, under all ambients, have been plotted as scatter diagrams (figure 2), separately for (I) $<$ 24 hr (II) 1 to 5 days and (III) $>$ 5 days.

4.1 *Short-term ambient aging*

For short-term aging ($<$ 24 hr see figure 2(I)) there are three dominant reaction groups for cryolite (figure 2a) and four reaction groups for MgF_2 (figure 2b) and mixed

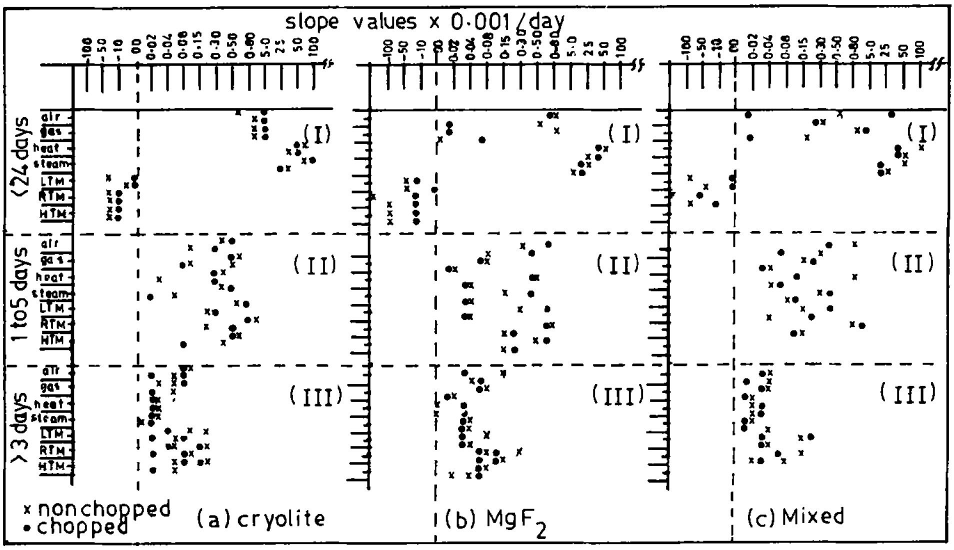

Figure 2. Scatter diagram of slope value for log (n_f) vs time curves, under different ambients (points in upper half are for thin films and those in lower half are for thick films, for each ambient).

cryolite-MgF$_2$ (figure 2c) films. One can distinguish 3 types of reactions: (1) air-dominant (low positive reaction rate $< 4 \times 10^{-3}$ /day); (2) temperature-dominant (high positive reaction rates in range 5×10^{-3}/day to 112×10^{-3}/day; (3) moisture-dominant (negative reaction rates in the range -3×10^{-3}/day to -112×10^{-3}/day).

In the air-dominant process, the adsorption of air/gas seems to be more important than oxidation. It is possible that, in the short time (few hours) allowed for this aging, the surface layer is easily affected (adsorption) which may not be much dependent on type of gas (air, O$_2$, CO$_2$), as in the case of chemical reactions. It can also be seen that for air-dominant process MgF$_2$ chopped films show different reaction rates ($0{\cdot}02 \times 10^{-3}$/day) than non-chopped films ($0{\cdot}7 \times 10^{-3}$/day to 4×10^{-3}/day). The mixed films, as expected, show the processes of both cryolite and MgF$_2$, though chopped mixed films behave more like MgF$_2$.

The process occurring due to heat and steam (large positive δn_f with slopes $> 4 \times 10^{-3}$/day) seem to be purely due to temperature effect. This may result in oxidation of films (or hydroxyl complex formation). There is a possibility of water desorption due to heating but not so for steam ambient.

For purely moisture-dominated process the slopes are negative. It can either be the moisture (a) filling up the pores (absorption) or (b) forming a layer (adsorption), which decreases the effective refractive index or (c) forming some hydroxyl complexes.

In room and high temperature moisture, the reaction seems to be the same, as indicated by slopes (average 37×10^{-3}/day and 38×10^{-3}/day) but in low temperature moisture the slope is lower (12×10^{-3}/day). At lower temperature, complex formation/absorption may be inhibited. But our special recycling experiments with moisture ambients have shown that this short-term moisture-dominant effect is reversible.

The volume percentage of water V present in the film can be found, assuming only water as added material for simplicity, and using the formula of De Rooji *et al* (1977).

$$\frac{(n_f+\delta n_f)^2-1}{(n_f+\delta n_f)^2+2}=\frac{d_f}{d_f+\delta d_f}\cdot\frac{n_f^2-1}{n_f^2+2}\cdot\frac{V n_\omega-1}{n_\omega+2}, \tag{1}$$

where n_ω and n_f are refractive indices of water and film (initial) respectively. Our ellipsometric values n_f (table 3) for cryolite, MgF_2 as well as the reported spectrophotometeric and Abele-method values reported earlier are in the same range and are higher than the bulk values. This is attributed to the effect of immediate aging in the films during deposition and during air inlet into vacuum chamber (Puri *et al* 1983).

Table 3 also gives the water percentage V in film under moisture ambient conditions, calculated using equation (1). For δd_f zero, it is negative indicating that either some material other than water needs to be considered or that the measured thickness changes are not very accurate. As our experimental accuracy of individual thickness measurement is ± 25 Å, we have recalculated V % for $\delta d_f = 25$ Å (instead of zero, as the average value given in table 1 may go up by 25 Å) and the corresponding values are also given in table 3. Next, the maximum of V obtained in both non-chopped and chopped films (13·8 % and 11·5 % respectively) is in RTM for MgF_2. In all cases, it is less in chopped than non-chopped films, indicating that water sorption is not just a top surface phenomenon. Probably crystal quenching reduces the porosity of chopped films, giving lesser sorption of water.

The large sorption capacity of water by MgF_2 film need not only be due to the loose-packed structure (higher porosity) of the film as assumed above but can also be due to the high polarity of MgF_2 valence bonds, whereby the high electronegative fluorine is replaced (Koch 1965). We have indicated the possibility of such complexes being formed in our fresh films from refractive index and electron diffraction data (Puri *et al* 1983).

4.2 *Long-term further aging in air*

For δn_f vs time curves, the observations that (i) films exposed to moisture for a short period, on further exposure to air (figure 1b) change from negative slopes back to positive (as for air only aging figure 1a) and (ii) the cycling experiment gives negative and positive slopes during alternate moisture and heat exposures, indicate that the moisture reaction is reversible and different from air, with a fast reaction rate (-50×10^{-3}/day) compared to air ($0{\cdot}10 \times 10^{-3}$/day). Naturally this reaction will not be observed in long-term aging (figure 2, II & III) and, even if exposed to moisture for longer time, it will give saturation.

The same is also true about the other fast ($+50 \times 10^{-3}$/day), temperature-dominant reaction (oxidation) observed during the first 24 hr. Here the reaction rate R may even be slowed down due to the reduced temperature according to equation

$$R = \mathrm{d}C/\mathrm{d}t = C_0 \exp(-E/kT), \tag{2}$$

where C_0 is the concentration of a reactant. The order of magnitude calculations indicate that R of $\sim 72 \times 10^{-3}$/day at 120°C will reduce to $0{\cdot}08 \times 10^{-3}$/day at 25°C. The latter is just the reaction rate for air-dominant processes ($0{\cdot}10 \times 10^{-3}$/day). This gas adsorption reaction can surely continue to be present in long-term aging. But

Table 3. Volume percentage (V) of water under different moisture conditions for 3 hr exposure (for thin films). Values of V%, in brackets, are calculated assuming thickness to be 25 Å instead of zero.

Material		Initial thick-ness d_f Å	Initial n_f	LTM			RTM			HTM		
				δd_f	δn_f	V	δd_f	δn_f	V	δd_f	δn_f	V
Cryolite	NC	550	1·391	0	−0·003	−0·8 (4·4)	50	−0·015	5·7	50	−0·014	5·9
	C	500	1·401	0	−0·003	−0·8 (4·3)	0	−0·009	−2·3 (3·2)	0	−0·003	−0·8 (4·3)
MgF$_2$	NC	400	1·430	0	−0·015	−3·9 (3·5)	100	−0·042	13·8	50	−0·035	4·6
	C	450	1·463	100	−0·006	2·3	50	−0·008	11·5	0	−0·014	−3·9 (3·5)
Mixed cryolite MgF$_2$	NC	500	1·409	100	−0·022	5·2	100	−0·042	9·1	—	—	—
	C	400	1·433	50	−0·004	1·3	50	−0·029	6·7	—	—	—

NC: Non-chopped, C: Chopped.

figure 2 also shows that this rate decreases progressively with time from (I) 24 hr to (III) > 5 days. This may be due to decrease in effective concentration, because of surface coverage on longer exposure. Apparently the reaction is one and the same, as shown by the smooth variation of the rate.

4.3 *Role of chopping in aging reduction*

It is generally observed in our experiments that the chopping of the vapour flow during deposition, increases the initial refractive index of the films as compared to non-chopped films (Puri *et al* 1983), indicating that chopping may enhance the immediate aging that is taking place within a few minutes of deposition. Our results show that this immediate enhanced aging also helps in reducing the further short-term (in hours) and long-term (in days) aging.

If the columnar growth and corresponding structure with voids (to be filled just by water on exposure, without any other reactions) were the only reasons for the aging of the films, then the chopping would have reduced the aging permanently by quenching the columnar growth, obtained, as shown by electron diffraction pattern (Puri *et al* 1983). But as even the chopped films show changes on short-term ambient aging and further long-term air aging, the additional and dominant reactions, indicated above, seem to be the main reason for aging the optical films. The observed reduction in aging, on chopping, seems to be due to the initially enhanced immediate aging (i) in vacuum system itself due to trapping of air between the chopped layers and (ii) just on opening the vacuum system, which may be due to larger grain boundaries available in chopped films. Such an enhanced aging will reduce the later short- and long-term aging due to slowed reaction rates (equation (2)) because of reduction in concentration (by nonavailability of reactants due to reduced available surface area).

4.4 *Thickness effects on aging*

Figure 2 shows that, in general, the thick films show a slower reaction rate than thin films, prominently so for 0–5 days air-aging. The thin films having more voids compared to thick films, might offer a greater surface area (effective concentration) for reactions to occur.

All the films show an increase in thickness (table 1) on aging. This increase is mainly seen for temperature-ambient and long-term air exposure but the short-term moisture exposure gives very little change in thickness. It may be noted that this process is expected to be reversible as well.

In the case of MgF_2 films, for example, there is a possibility of $Mg(OH)_2$ complex being formed slowly in air or on heating. The molar volume of $Mg(OH)_2$ is higher (24·6) than that of MgF_2 (19·6) and for MgO it is still lesser (11·2). The possibility of formation of hydroxyl compounds, like $Mg(OH)_2$, might be responsible for the increase in thickness. This supports an assumption of slow complex formation rather than oxidation phenomenon.

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