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Effect of minute's-scale aging on refractive index of chopped and non-chopped optical films

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Abstract. The refractive indices of non-chopped and chopped films of cryolite, MgF_2 and mixed cryolite-MgF_2, which is higher than the bulk value, measured using spectrophotometer, ellipsometer and Abelès method are observed to be higher than corresponding bulk values. Chopped films show a higher refractive index than non-chopped films. The electron diffraction study shows a more amorphous structure for the chopped films. The major part played by chop-time seems to be in increasing the initial minute's-scale aging rather than settling of ad-atoms during chop-time. The observed dispersion curve shows that some unknown material other than water gives an important aging effect.

Keywords. Non-chopped optical films; chopped optical films; refractive index; aging.

1. Introduction

Several workers have found the refractive index (Shklyarevskii *et al* 1972; Kinosita and Nishibori 1969; Heavens 1960) and studied the aging (Ogura *et al* 1975; Koch 1965; Ritter *et al* 1969; Koppelmann *et al* 1961) of optical films and there exists a large variation in the values obtained by them. The technique of chopping the vapour flow during deposition is seen to help in day-scale aging reduction (Vijaya *et al* 1980) as seen from ellipsometer Δ, ψ changes and spectrophotometer transmission coefficient (T) changes.

In this paper we report the refractive index values of both non-chopped and chopped films of cryolite, MgF_2 and mixed cryolite-MgF_2 as measured by spectrophotometer, ellipsometer and Abelès method. The knowledge about the refractive index, rather than Δ, ψ, T, of non-chopped and chopped films will be of great importance in the basic understanding of the aging phenomenon in these films.

2. Experimental details

The films both non-chopped and chopped cryolite, MgF_2 and mixed cryolite-MgF_2 were prepared by vacuum evaporation, using the method reported earlier with alternate chopping (Vijaya *et al* 1980), at a rate of 5 Hz using a circular chopper with a V-shaped cutout (of angle 155°). This gave thickness of about 2 Å during each cycle ensuring sufficient homogeneity in the film for ellipsometric and spectrophotometric measurements. For the mixed co-deposited film study, the two single films (cryolite,

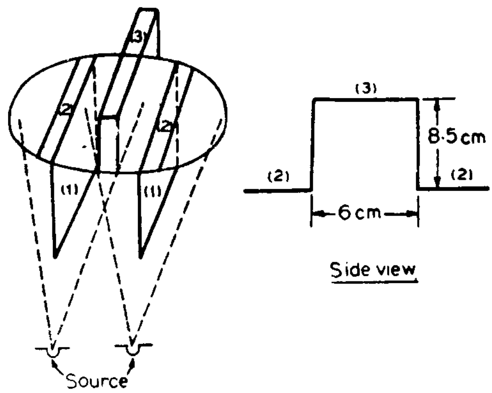

Figure 1. Schematic diagram of the shadowing arrangement for deposition of single and mixed films. (1) Projection for shadowing, (2) Side slots, (3) Central slot.

MgF_2) were deposited at one height and the mixed cryolite-MgF_2 film at a higher level so that the three films were simultaneously obtained and of roughly the same thickness (figure 1). The two sources were kept 22 cm from the substrate holder and were 4 cm apart, suitably shielded from each other. The position of the substrate holder was adjusted such that from the central slot both the filaments could be seen and from the side slots only one filament was seen.

The films were deposited on Belgian glass substrates of suitable size at room temperature. Unground glass was used for spectrophotometric measurements (Type VSU-2P) in the spectral range 4000–6500 Å, whereas glass with one side ground was used for ellipsometer (at 6328 Å) and Abelès method (at 5893 Å) measurements. The transmission data and Δ, ψ ellipsometric data were converted to refractive index using value fitting method by proper computer programs. The films studied were in the thickness range 300–1400 Å in general. The thickness was measured using the Fizeau fringe method and ellipsometer. All the measurements were carried out after removing the film from the vacuum chamber. The error in measurement of refractive index for the spectrophotometer is about $\pm$ 0·1 as compared to $\pm$ 0·002 for the ellipsometer and $\pm$ 0·0001 for Abelès method.

3. Results and discussion

The wavelength dependence of the average (of about 100 films each) initial refractive indices of non-chopped and chopped films, obtained spectrophotometrically, is given in figure 2. Figure 3 gives the average (average of about 140 films each) experimental values of refractive indices and thickness as measured by ellipsometer along with the values of refractive index as obtained by Abelès method. It is evident from these figures that, in general, the values obtained by all the three methods are in sufficiently good agreement with each other for both non-chopped and chopped films. For comparison these data are given in figure 4 along with data obtained by other workers. There are of course many other spot readings (at certain λ) available. It is observed in general that there is a spread in the reported values of refractive index

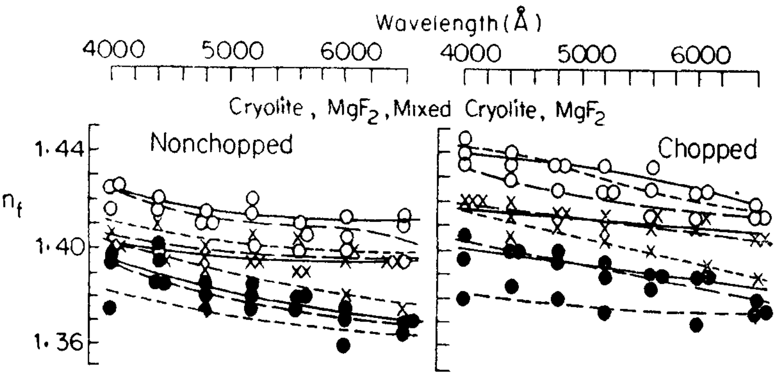

Figure 2. Wavelength dependance of the average, initial refractive index. ● cryolite, O MgF_2, X Mixed cryolite-MgF_2, Thickness: —— ~ 700 Å, — — ~ 900 Å, - - - - ~ 1100 Å Temperature of substrate: Room temperature (27°C).

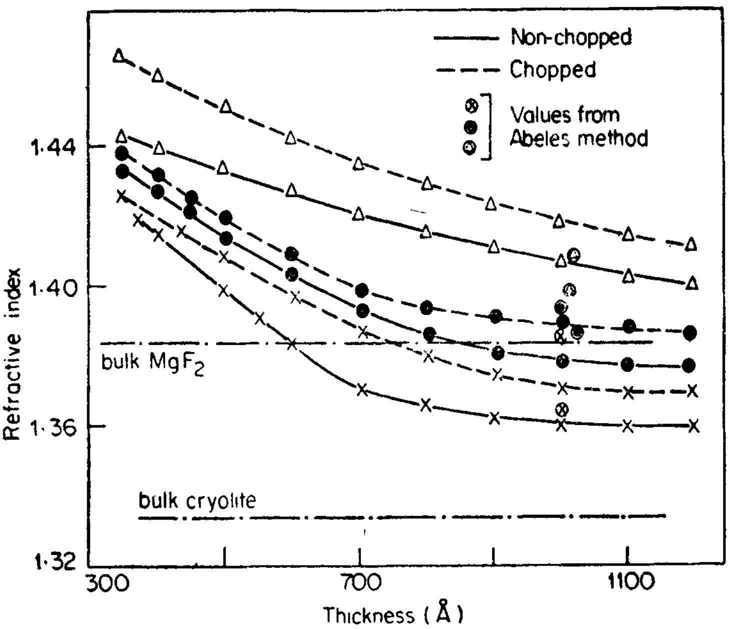

Figure 3. Average initial refractive index versus thickness as measured by ellipsometer at $\lambda = 6328$ Å, X cryolite, Δ MgF_2, ● mixed cryolite-MgF_2. Temperature of substrate: Room temperature (27°C).

(a) from 1·40 to 1·31 for cryolite, (b) 1·41 to 1·34 for MgF_2 at λ of about 6000 Å. Our values lie in the same range.

3.1 *Electron diffraction studies*

The electron diffraction studies (figure 5) show full Debye rings for cryolite, MgF_2 and mixed cryolite-MgF_2 films indicating the polycrystalline nature of the films. It is seen that the rings of non-chopped films are sharper than chopped films. The measured interplanar distance (d_0)-values of non-chopped and chopped films are given in table 1. These were compared with ASTM data for bulk cryolite and MgF_2. All

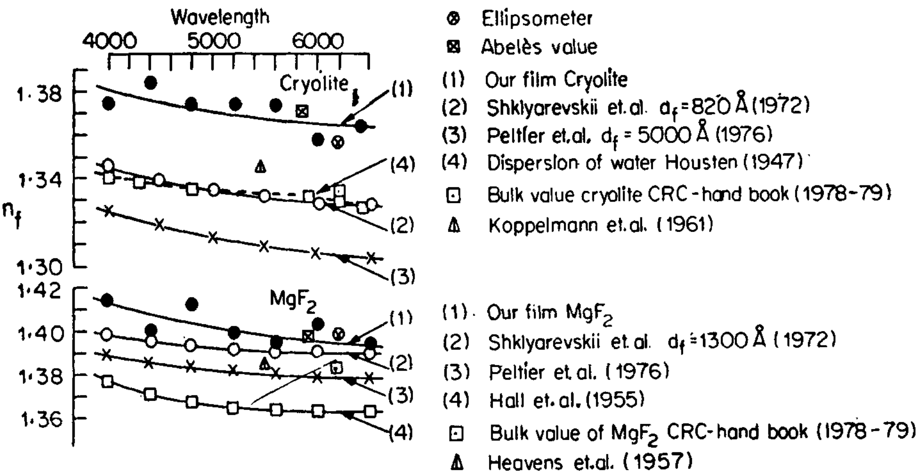

Figure 4. Comparison of reported and our refractive index values.

Table 1. Interplanar distance d_0 values for cryolite, MgF_2, mixed cryolite-MgF_2 films both non-chopped (NC) and chopped (C).

Cryolite		Mixed cryolite-MgF_2		MgF_2	
NC	C	NC	C	NC	C
4·29 (F) (UI)	3·83 (F) (UI)	3·45 (B) (UI)	1·34 (B)	3·32 (F)	...
3·66 (F) (UI)	2·70 (B)	2·52 (B) (UI)	1·14 (F)	3·29 (B)	2·21 (B)
2·74 (B)			1·02 (F)	2·42 (B)	1·82 (F) (UI)
2·28 (F)	2·26 (B)	2·28 (B)	0·93 (B) (UI)	2·10 (F)	1·75 (B)
		2·07 (F)	0·86 (B)	1·84 (F)	1·49 (F)
1·94 (B)	1·87 (F)	1·74 (B)	0·75 (B)	1·73 (B)	1·18 (F)
1·72 (F)	1·68 (F)	1·50 (F)		1·69 (F)	0·99 (F)
1·56 (B)	1·50 (F)	1·35 (F)	0·66 (F) (UI)	1·54 (F)	
1·22 (F)	1·34 (F)	1·23 (F)		1·43 (F)	
		1·13 (F)			

Error ± 0·04 Å; F-faint; B-bright; UI-unidentified.

Besides these, there are a number of very faint lines which are not easily measurable by optical methods.

the bright rings (both chopped and non-chopped) match with the corresponding bulk values indicating that the stoichiometry of the films is being maintained. The table also shows that the mixed cryolite MgF_2 film contains both cryolite and MgF_2 as would be expected. The single and mixed films were deposited in the same cycle. The rings are greater in number in mixed films as compared to single material films. In both single and mixed films there are some very faint lines which are not measurable as well as some lines which are not identifiable with the bulk data (denoted as UI in table 1).

An interesting feature observed in the diffraction pattern is that the d_0-values of non-chopped and chopped films are more often not the same although the film materials deposited are the same. This is shown more drastically in the chopped mixed film where none of the chopped mixed film rings coincide with either chopped or non-chopped single films.

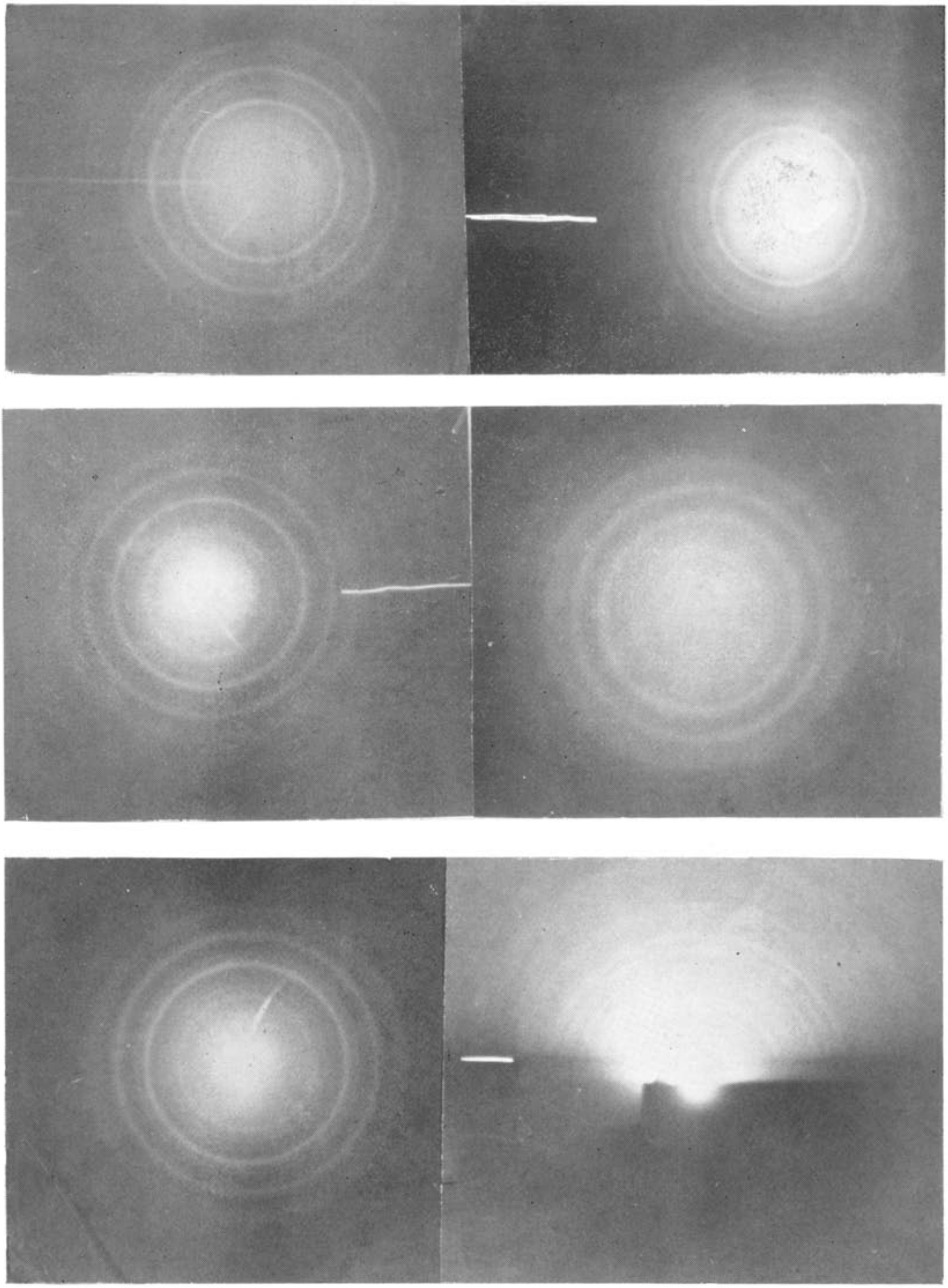

Figure 5. Electron diffraction pattern. a1, b1, c1 Non-chopped cryolite, MgF_2 and mixed cryolite-MgF_2 respectively. a2, b2, c2 chopped cryolite, MgF_2 and mixed cryolite-MgF_2 respectively.

The fact that the diffraction rings of non-chopped films are sharper than those of chopped films suggest a more amorphous (*i.e.* less polycrystalline) film growth for chopped films. But the absence of some of the rings in chopped films as compared to non-chopped films might indicate some reorientation of crystallite due to chopping, whereby the diffraction intensity is reduced, sometimes even to the extent that they are not visible. This effect is seen to be highly predominant in mixed chopped films.

3.2 *Single material films*

From figures 2 and 3, it is evident that the refractive indices of films of single cryolite and MgF_2 taken separately are greater than the corresponding bulk values. It is also seen that for films of cryolite and MgF_2, chopped films have higher refractive index than non-chopped films.

The refractive index of material proper should not change, really, even if its thickness is low (down upto 300 Å). But the film consists of a combination of known and unknown materials, as is reported (Koch 1965; Oliver 1970; Pulkar and Jung 1969; Pulkar and Zaminer 1970) and also as seen from our electron diffraction rings (UI). These materials have their own refractive indices and their own dispersion curves, which will affect the resultant refractive index and dispersion of the film. As the law to be followed is Lorentz-Lorenz theory only, there are three possible major factors (reactions) which may produce the changes in refractive index. (i) replacement *e.g.* vacuum (voids) to H_2O; (ii) conversion *e.g.* MgF_2 to MgO; (iii) addition *e.g.* H_2O layer added. Since the films studied are taken out of vacuum and then measured in air, the *in situ* aging (minute's-scale) is possible which might make the measured refractive index different from bulk values.

The refractive indices of single cryolite and MgF_2 films (see figures 2 and 3) are greater than the bulk values (1·338 and 1·384 respectively) (CRC Handbook 1978–79). This can be due to the presence of oxide material due to conversion reaction taking place, an oxide with higher refractive index than the film being formed due to the reaction with water vapour, present in the vacuum chamber. Another conversion reaction possible is the formation of boundary layer as reported by Oliver (1970). Our single film index is midway between the reported boundary layer and the main film value. Also, as reported by many workers (Kinosita and Nishibori 1969; Ritter and Hoffmann 1969; Ogura *et al* 1975; Macleod and Richmond 1976), moisture absorption increases the refractive index of the film. This sort of replacement and addition reactions can occur during deposition even at the 10^{-5} torr vacuum used by us and also during air inlet into the vacuum chamber.

All these effects seem to be more prominent in thinner films as seen from figure 3 which shows that the refractive index approaches the bulk value for higher thickness films. One would expect such thickness effects, if ' the conversion reaction ' takes place predominantly during deposition and/or during air inlet. These ellipsometric results do give larger spread in measurement at lower thicknesses. This is indicated by the scatter diagram plot (Vijaya 1982) and the values given in table 2 which show more scatter at lower thickness. The chopped films show the same trend and with reduced scatter, indicating reliability of the trends observed in measurements. This, in a way, indicates similarity in 'inhomogeneity' in non-chopped and chopped films (later being more homogeneous as 2 Å layers are produced).

Table 2. Scatter values of refractive index at three thickness for non-chopped (NC) and chopped (C) films.

Thickness Å	Cryolite		Mixed cryolite-MgF_2		MgF_2	
	NC	C	NC	C	NC	C
300	1·46-1·35	1·44-1·38	1·45-1·37	1·46-1·41	1·47-1·40	1·48-1·44
800	1·38-1·34	1·39-1·36	1·41-1·36	1·42-1·37	1·46-1·41	1·46-1·43
1100	1·37-1·35	1·38-1·37	1·39-1·36	1·40-1·38	1·42-1·40	1·42-1·41

The spectral response curve (figure 2) shows that due to the above types of reaction, the effective dispersion of the films is modified, the refractive index being higher throughout the spectral range. In addition, there are some small changes in relative spectral response.

3.3 *Packing fraction analysis*

The packing fraction analysis is the most convenient method for studying the single films. As suggested by many authors (Pulkar and Jung 1969; Guenther and Jung 1976) the films of cryolite and MgF_2 possess columnar crystal growth in a more or less closely packed structure. This means that the films are composed of relatively well-developed crystalline aggregates, grain boundaries and vacant places such as intermediate gaps and pores. Due to the process of chopping these long columnar growth may be quenched during crystal growth, whereby a denser (less-void) structure may be formed leading to the higher refractive index of chopped films as compared to non-chopped films. In our case the non-chopped and chopped films are two extreme limits of chopping speeds giving change in refractive index of about 0·01. The intermediate chopping speeds would show intermediate effects. This quenched crystal growth can be seen as more diffuse rings in the electron diffraction pattern. The growth can still be polycrystalline and somewhat columnar but more randomised (tending towards amorphous) and probably more closely packed due to the chop-time allowing for settling and aging.

Using the columnar model of crystal growth (vertical cylinders) the theoretically predicted packing density as calculated by Pulkar and Jung (1969) is 0·9069. According to Harris *et al* (1979) there exist situations in the columnar model where the packing density can be greater than 0·9069. This can be due to the columns expanding.

Now as the refractive index of the chopped films is higher than non-chopped films, we expect the packing density of the film to be higher than non-chopped films. During chopping of the films, the quenching of crystal growth may tend to produce randomised but somewhat expanding types of columns. This, it is felt, is a possible situation because chop-time aging effects give rise to more sites for adatoms as the film grows. Since we do not have any cross-sectional electron microscope data, we cannot exactly calculate the theoretical packing density of the chopped films. For simplicity, and as a comparison with non-chopped films we have assumed the packing density as 0·9069, also for chopped films. It may be noted that our films are sufficiently homogeneous whether chopped or non-chopped as chopping give 3Å layer if at all.

Assuming this to be the ultimate attainable packing density under ideal conditions, we have tried to calculate the different fractions of the various materials that may be present in our films. The packing density formula given by Koch (1965) can be modified to include the unknown material as follows:

$$\frac{n_f^2 - 1}{n_f^2 + 2} = P_m \frac{n_m^2 - 1}{n_m^2 + 2} + P_u \frac{n_u^2 - 1}{n_u^2 + 2} + P_{H_2O} \frac{n_{H_2O}^2 - 1}{n_{H_2O}^2 + 2}, \tag{1}$$

where, n_f, n_m, n_u, n_{H_2O} are the refractive indices of film, bulk material, unknown material and water respectively, P_m, P_u, P_{H_2O} are the respective packing fractions and $P_m + P_u + P_{H_2O} = 1$.

Due to the growth geometry the films are porous and the pores (1 — 0·9069) can be filled either with vacuum, air or water. We assume that the pores (0·0931) are filled with water and the remaining 0·9069 to be made up of *m* and *u*. Under this assumption we have calculated the different packing densities using data from our single films, which are given in table 3 along with the reported values. We have used the available data of oxides (CRC handbook 1978–79) and boundary layers (Oliver 1970) as the unknown materials. Besides, there are possibilities of other materials like $Mg(OH)_2$ being present, but its refractive index is not known. The fraction of the unknown material indicates to what extent the effective refractive index can change from the bulk value.

Table 3. Value for packing densities obtained from equation (1) for non-chopped (NC) and chopped (C) films of cryolite and MgF_2.

Film	Refractive index n_f* (observed)	n_m (bulk CRC handbook 1978-79)	n_u (assumed)	Packing densities P_m	P_u	P_m date obtained by others
Cryolite	NC 1·360	1·335	1·46 (boundary layer, Oliver 1970)	0·697	0·209	0·84 (Shklyarevskii *et al* 1972)
	C 1·370			0·615	0·291	0·89 (Koppel Mann *et a* 1961, Pulkar *et al* 1969)
MgF_2	NC 1·405	1·385	1·47 (boundary layer, Oliver 1970)	0·606	0·300	0·80 (Ritter *et al* 1969)
	C 1·425			0·366	0·540	0·85 (Koch 1965)
						0·73 (Pulkar *et al* 1969)
	NC 1·405	1·385	1·70 (MgO CRC handbook 1978-79)	0·818	0·088	
	C 1·425			0·748	0·158	

*The refractive index n_f is an average of spectrophotometric, ellipsometer and Abelès values, which are very near each other; $P_{H_2O} = 0{\cdot}0931$; $n_{H_2O} = 1{\cdot}332$.

It is seen from table 3 that the percentage of the unknown material increases, in all the cases, in chopped films. The increase is about 9% for cryolite with reported boundary layer (Oliver 1970). But for MgF_2 the increase with the reported boundary layer (Oliver 1970) is about 24%, much higher than one would expect. It is also *not* shown by the electron diffraction pattern. But assuming MgO as the unknown gives an increase of just 7% which is within the expected limits.

If packing were to be more dense for chopped films reducing P_{H_2O} (0·0931), then the $(m + u)$ fraction will increase, slightly reducing the percentage of u (as refractive index of water is less than the material (m) used). The results thus indicate that chopping may reduce the reported ' day '—scale aging (Vijaya *et al* 1980) by increasing the initial ' minute's '—scale aging (increasing ' surface layer ' packing fraction). The major part played by chop-time seems to be this, rather than settling of adatoms during the chop-time. During the process of chopping about 3 Å of film gets deposited per cycle. Due to the presence of residual gases in the chamber even at 10^{-5} torr vacuum, there is a possibility of some chemisorption/oxidation type of reaction occurring at the individual layers thereby increasing the surface layer packing fraction. Of course the percentage of this type of conversion is very low since it is not noticeable as a strong ring in the electron diffraction pattern.

3.4 *Spectral response tilt comparison*

Though in general the dispersion curve $(n - \lambda)$ can have any shape, for our materials and in the range of λ we have used, the n-values fall practically linearly with λ. Hence, as a simple ' measure ' of dispersion, we have defined here a quantity called the ' tilt ', as $\Delta n_f/\Delta\lambda \; A^{-1}$ where $\Delta\lambda = (6500 - 4000)$ Å, and Δn_f is change in n_f over this $\Delta\lambda$. As seen from figure 4 the dispersion curve obtained by us are quite similar to those by other workers, though there are some variations in the tilts. For convenience we consider MgF_2 films both non-chopped and chopped for discussion. The tilts of our MgF_2 films are: non-chopped 6×10^{-6} (with $\Delta n_f = 0{\cdot}015$), chopped 10×10^{-6} (with $\Delta n_f = 0{\cdot}025$). These are to be compared with that of water with a tilt 4×10^{-6} with $\Delta n_f = 0{\cdot}01$ (The dispersion curve of water is also given in figure 4).

It is seen that the tilts of non-chopped and chopped films are more than that of water and tilt of chopped films is higher than non-chopped films. This difference in tilt indicates that water is not the only additional material in the films. There are unknown materials also present in the films, which gives support to our packing density calculations using equation (1). The tilt of chopped films being higher than that of non-chopped films indicates that the chop-time aging effect which enhances the production of unknown material as seen from table 3.

3.5 *Co-deposited mixed cryolite-MgF_2 films*

As seen in figures 2 and 3, mixed cryolite-MgF_2 films for all thicknesses show a refractive index intermediate to our experimental single cryolite and MgF_2 films and as expected the refractive index of these co-deposited mixed films obeys the Lorentz-Lorenz relation as can be seen from data presented in table 4 for both non-chopped and chopped films. Apparently we can extend the assumption of minute's scale-pre-aging to the mixed films without much harm. There are definite indications of

Table 4. Refractive index of mixed cryolite-MgF_2 films both non-chopped (NC) and chopped (C). Thickness of film 1000 Å.

Method	Type	Refractive index as measured		Mixed cryolite-MgF_2	Mixed value from formula (Yadava *et al* 1973)
		Single cryolite	Single MgF_2		
Spectro-photometer	NC	1·370	1·405	1·395	1·388
6200 Å	C	1·385	1·415	1·405	1·400
Ellipsometer	NC	1·368	1·404	1·378	1·382
6328 Å	C	1·380	1·416	1·401	1·400
Abelès	NC	1·373	1·408	1·378	1·390
5893 Å	C	1·387	1·419	1·397	1·403

additional and different mixed phase boundary layers being formed, which are not observed in single films as indicated by electron diffraction (The d_0 values of chopped mixed films being very much different). The spectral responses of the mixed films show that these films follow the Lorentz-Lorenz relation at all wavelengths (figure 2) for both non-chopped and chopped films indicating that this type of co-deposition technique is successful in producing homogeneous mixed film.

4. Conclusions

This paper reports a special chopping and mixing effects on refractive index of optical coatings. For both chopped and non-chopped films there seems to be a few specific unknown materials present other than the original material which change the effective refractive index and dispersion curve of the films. This change in refractive index as compared to bulk is greater for the thinner films.

The effect of chopping, *i.e.* increase in the refractive index of the chopped film as compared to non-chopped film, tends to increase the initial minute's-scale aging along with the settling of adatoms during the chop-time.

The spectral tilts indicate that water is not the major constituent responsible for minute's-scale aging of the optical films. Identification of such unknown material (whose spectral and other data are not available for comparison) and that too in small quantity, in the matrix of the original material seems to be difficult. Further, the unknown material may decompose easily. Probably IR spectra analysis may lead to some identification.

The refractive index of mixed cryolite-MgF_2 films follow the Lorentz-Lorenz relation at all wavelengths, for both non-chopped and chopped films even using the co-deposition method, indicating homogeneity.

The electron diffraction patterns of non-chopped and chopped cryolite, MgF_2 and mixed cryolite-MgF_2 (obtained by co-deposition) suggest a more amorphous (less polycrystalline) film growth for chopped films and a crystallite reorientation.

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References

CRC 1978-79 *Handbook of chemistry and physics*, 59th ed., (Florida, USA: CRC Press)
Guenther H K and Jung E 1976 *Thin Solid Films* **4** 219
Hall J F and Fergusson W F C 1955 *J. Opt. Soc. Am.* **45** 75
Harris M, Macleod H A, Ogura S, Pelletier E and Vidal B 1979 **57** Thin Solid Films 173
Heavens O S and Smith S D 1957 *J. Opt. Soc. Am.* **47** 471
Heavens O S 1960 *Rep. Prog. Phys.* **23** 1
Housten R A 1947 *A treatise on light* (London: Longmans Green) 7th ed., p. 465
Kinosita K and Nishibori M 1969 *J. Vac. Sci. Technol.* **6** 730
Koch H 1965 *Phys. Status Solidi* **12** 533
Koppelmann G, Krebs K and Leyendecker H 1961 *Z. Phys.* **163** 557
Macleod H A and Richmond D 1976 *Thin Solid Films* **37** 1964
Ogura S, Sugawara N and Hiraga R 1975 *Thin Solid Films* **30** 3
Oliver W R 1970 *Philos. Mag.* **21** 1229
Pelletier E, Roche P and Vidal B 1976 *Nuovo. Rep. Opt.* **7** 353
Pulkar H K and Jung E 1969 *Thin Solid Films* **4** 219
Pulkar H K and Zaminer C 1970 *Thin Solid Films* **5** 421
Ritter E and Hoffmann R 1969 *J. Vac. Sci. Technol.* **6** 733
Shklyarevskii I N, Shazli A F A El and Govoruskehenko A I 1972 *Opt. Spectrosc.* **32** 40
Vijaya K 1982 Ellipsometric study of the changes in optical properties (aging) of non-chopped and chopped films of cryolite, MgF_2, ZnS and their co-deposited mixtures in various ambients Ph.D. thesis, Pune University, Pune
Vijaya K, Puri R K and Karekar R N 1980 *Thin Solid Films* **70** 105
Yadava V N, Sharma S K and Chopra K L 1973 *Thin Solid Films* **17** 243