CHAPTER IV

DISCUSSION

4.1 INTRODUCTION:

As already mentioned in chapter -I, Art. (1.4) very less work has been done on the properties of cerium oxide films deposited by thermal evaporation and very few references are available on the adhesion, stress and optical properties and aging aspects of these films.

From the results of the previous chapter it is seen that the chopping technique[65,66] has been immensely successful in increasing the adhesion of cerium oxide films and decreasing the stress. Also the changes in (Δ) and (Ψ) i.e. optical properties due to ambient aging has reduced by chopping. This chapter discusses the various results reported in chapter-III and gives possible tentative explanations.

4.2 ADHESION AND STRESS OF CERIUM OXIDE FILMS AND EFFECT OF CHOPPING.

From chapter III it is seen that chopping increases the adhesion and decreases the stress of cerium oxide films. The increase in adhesion is sufficiently higher than the error limit $\pm$ 9.8 KgF/cm^2 of measurement set up to emphatically state that chopping does improve the adhesion considerably. The fact that adhesion increases considerably due to chopping (fig - 3.3.2 (1))indicates that the intrinsic stress in the film is reduced. Generation of internal stress is closely connected with the adhesion.

This fact is proved from the experimental results also (fig.3.3.2 (2)).

The bonding between the cerium cxide film and substrate (glass) which is also an oxide may be a combination of monolayer on monolayer, chemical bonding interface layers, occurring simultaneously.Since the films are deposited by thermal evaporation the average kinetic energy of the vapour particles on evaporation is 0.1 to 0.2 ev. The bonding process can only be through a weak boundary layer or adhesion layer through chemical bonding.

Most of the dielectric films are known to grow in a columnar structure, since the growing columns or grain do not know how tall it should become, it also cannot know how large it should get in diameter. If there is continuous flow of impinging atoms the individual adatoms or admoleoule is literally frozen into the site where it initially arrived.[76] This yields films which have a highly disordered microstructure with long columns of material interspersed with voids extending through out the thickness of the film During the initial stages the growth of the film is heterogeneous and as thickness increases nucleation becomes homogeneous. It has been reported,[76] that nodules which are conical in shape are formed during heterogeneous nucleation which also created voids in the film. The presence of voids in the film decreases the adhesion of the film. The intrinsic mechanical stress depends upon the microstructure of thin films. The stress displayed can be explained qualitatively by the insufficient filling of the available space in the columnar microstructure by the coating material.

Stresses are also generated in the lattice due to the freezing of a large number of defects. The freezing occurs due to the lesser mobility of adatoms. The voids being a sort of defect in the film. It has been reported[69] that the columnar growth in which the packing density is greater than 0.906 expand in cross-section as the film grows, this expansion is restrained by other columns leading to a compressive stress. For packing density less than 0.906 the columns shrink in cross-section towards the outersurface and this behaviour gives the tensile stress. Our cerium oxide films shows tensile stress indicating that the packing density might be less than 0.906. Fig. 4.2 gives the structural model[69].

High adhesion is promoted by low concentration of flaws, non planer defects, presence of fracture blunting features, low stresses, and stress gradient, intrinsic stress of the film add to the applied stress during adhesion measurement.

The process of chopping the vapour flow during deposition (chopping rate 5-6 rot/sec.) gives the thickness of about 2Å layer of film during each chopping cycle ensuring sufficient homogeneity of the film but quenching the crystal growth[66]. Due to this process the columns are

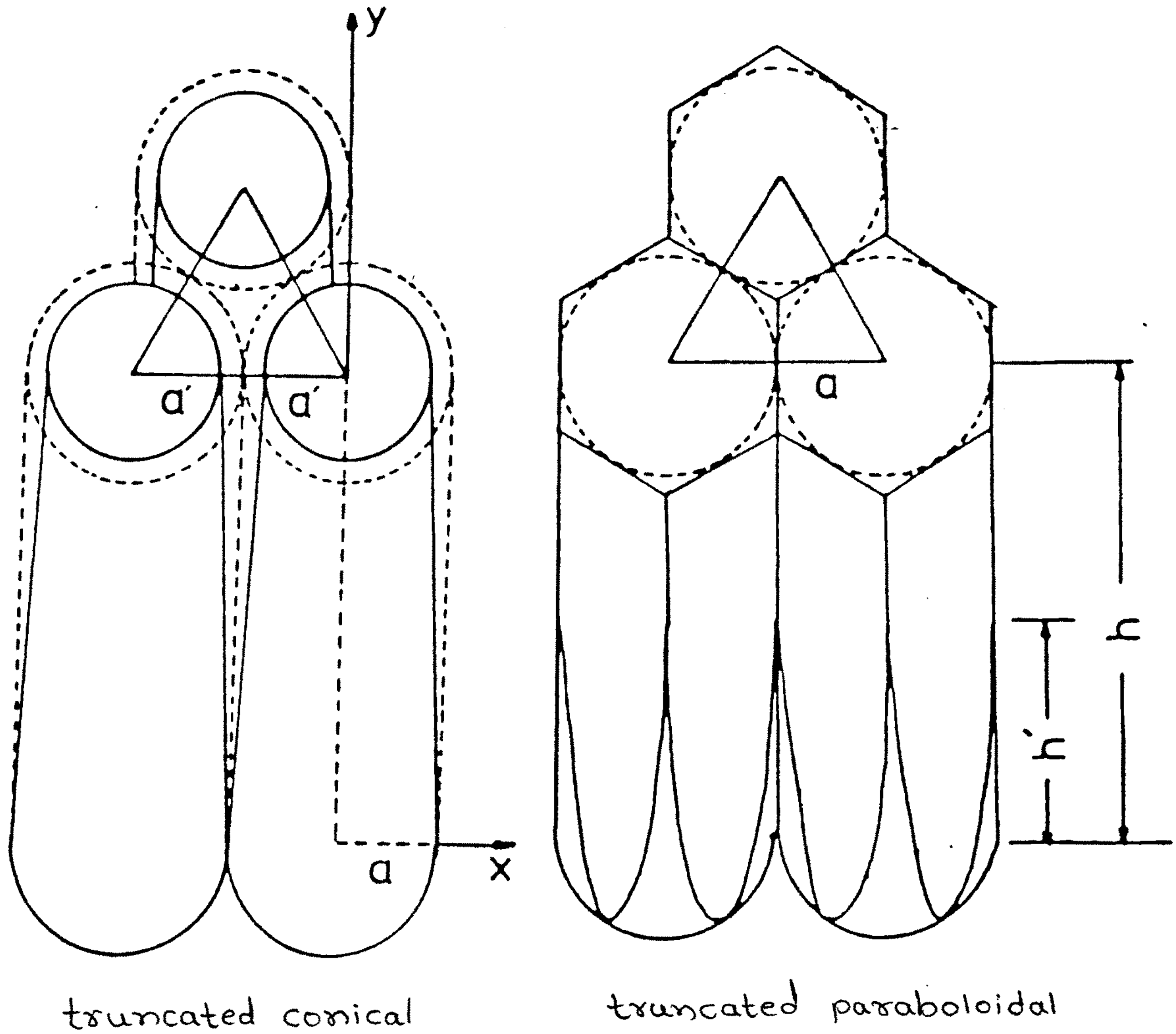


Fig 4·2 Structure models

not allowed to grow tall or wide reducing the columns formation.

During the chopping process there is chance of existence of pseudo boundaries within individual layers changing the structure of the layers. This type of pseudo boundaries have been reported by Ogura[69], when there is a discontinuity in the rate of deposition. The chopping process can also be regarded as a sort of discontinuity producing phenomenon.

The intermittant deposition during chopping also enhances the surface mobility of the incident adatoms reducing the columnar microstructure considerably. Chopping also increases the number of nucleation sites, by allowing the adatoms more time to settle. Another effect of chopping might be a sort of stirring effects on the films which tend to prevent large crystallite growth.

The overall effect of all these process is the decrease in the number. of voids due to lateral surface diffusion of the depositing particles in the film and hence increase in packing density and decrease in grain size. Another effect of increase in surface mobility is that the defects are not frozen and hence a comparatively defect free film is obtained.

When defects are less and grain size is smaller, fractures cannot propagate for long distances. This results in enhanced adhesion and lower stress of chopped films compared to non-chopped films. The enhanced adhesion and decreased stress due to increased mobilities of adatoms and decreased void density due to lateral surface diffusion have been reported[129] for deposition on heated substrate.

Quenching of crystal growth due to chopping results in the changes in morphology of the columnar structure. This also helps in relaxation of internal stress. This type of relaxation of internal stress due to morphology changes have been reported by Jacobs etal.[25]

Chopping also seems to assist the affinity of adatoms to oxygen, whereby strengthening the bonding layer between substrate and film.[130] Laugier[37] has reported the decrease in stress due to excess oxygen content in the film. Electron diffraction[65] data for MgF_2 and cryolite films and ESCA for MgF_2 films (unpublished results) show the presence of more oxygen in chopped films. This type of effect can be assumed to be present even in chopped cerium oxide films also, giving higher adhesion and lesser stress as compared to non-chopped films. It seems a combination of various processes are responsible for the enhanced adhesion and decreased stress for chopped films.

4.2.1 EFFECT OF VARIOUS AMBIENTS ON ADHESION.

From the results shown in (Table 3.3.3.4) it is observed that adhesion decreases on exposure to moisture ambient and increases on heating.

The changes being lesser in chopped films than non-chopped films. It has been reported[83] that the adsorption of polar molecules like water in porous films causes substantial tensile stress through the mutual electrostatic repulsion of the adsorbed molecule dipole. This results in an increased intrinsic stress resulting in decreased adhesion. This might be the main reason why CeO_2 films show lesser adhesion on exposure to moisture ambients. It is expected that stress will increase on exposure to moisture (This part of experimentation could not be done during the course of experimental work.) Ennos[46] has reported that moisture plays a important role in variation in film stress and adhesion. The H_2o molecule may be chemically reacting with the film material and produce some irreversible chemical changes which causes the stress to increase. This will result in decrease in adhesion, since voids and defects are lesser in chopped films, these factors are likely to affect the chopped films to a lesser extent. The low temperature moisture doesnot change the adhesion much, indicating that, the low temperature might in some way inhibit moisture adsorption or chemisorption.

The addition of salt (Nacl) to the humid atmosphere does not seem to have an any special effect on the adhesion as these films also behave similar to room temperature moisture exposed films. Though these films show more oscillatory behaviour as compared to room temperature moisture exposed films. The reason for this oscillatory behaviour is not known (alternate higher and lower adhesion) Fig.3.3.3.2 (1).

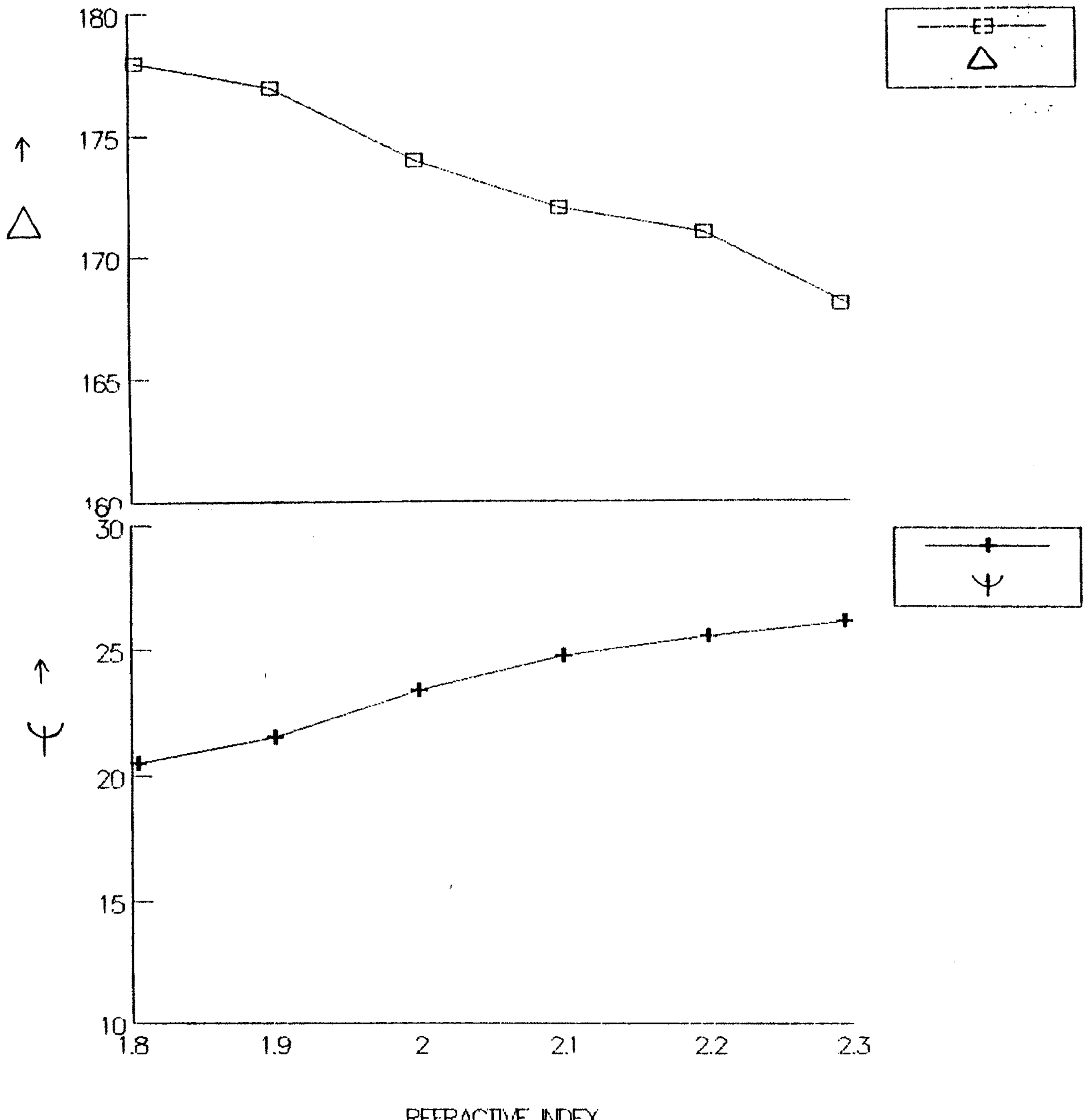
This type of oscillatory behaviour is not seen in chopped films. Indicating that the process of chopping somehow alters the microstructure of the films. Whereby decreasing the randomness in behaviour.

As expected the heating improves the adhesion, this type of effect for dielectric films have been reported by other authors,[23,85,88] Due to heating the adatoms mobility increases and relief of strain energy takes place, due to this stress relief, the long range order in films decreases whereby increasing the adhesion of the film. Also heating removes partially the moisture adsorbed in the film during deposition, during air inlet. It is expected that stress will also decreases due to heating.

4.3 DISCUSSION ON ELLIPSOMETRIC PARAMETERS.

The refractive index is the basic optical constant of the optical coatings. This study reports only the changes in (Δ) and (Ψ) as function of thickness and time. Since at the time of writing the thesis, the pc compatible computer program for determining refractive index from (Δ) and (Ψ) values was not ready.

Fig.4.3 gives the theoretical plot[65] for (Δ) and (Ψ) Vs the optical properties for a 1000 Å thick dielectric film on glass substrate. From the value of (Δ), (Ψ) the approximate value of refractive index can be



g-4·3 THEORETICAL PLOT OF Δ, Ψ Vs REFRACTIVE INDEX FOR 1000 Å THICKNESS.

estimated if the thickness of the film is known to a sufficient accuracy. Since both (Δ) and (Ψ) change with thickness this method of estimation is not very accurate but, one can at least know the approximate value of refractive index. With this in view the discussion has been made on the basis of whether, there is any increase or decrease in refractive index. Corresponding to changes in (Δ), (Ψ) (mainly Ψ) and not exact values of refractive index.

4.3.1 <u>DISCUSSION ON FRESH FILMS.</u>

The property of cerium oxide are largely dependent on the deposition conditions, the refractive index of values from 1.9 to 2.5 have been reported.[102-106] This indicates the large variation in (Δ), (Ψ) values which are the actual experimental parameters. This variability is shown in the large scatter of (Δ) and (Ψ) for various thickness. Fig.- 3.3.1 (2).

The (Δ) of chopped films are lower than that of non-chopped films where as (Ψ) of chopped films are higher than that of nonchopped films indicating the possibility of refractive index of chopped cerium oxide films being higher than nonchoppped films.

Macleod[54] has reported that cerium oxide tends to form inhomogeneous layers. Also Hass et al[131] have found that cerium oxide reacts with the molybdenum crucible. These might be the reasons for the large variation observed in our (Δ), (Ψ) values. At this stage no definite conclusion can be made due to the lack of refractive index data of our films. The value of refractive index of bulk cerium oxide is around 2.48. For a refractive index of 2.48 from fig. 4.3 the (Ψ) value should be around 27 and (Δ) should be around 165. Our value of (Ψ) is very low compared to the theoretical value indicating that refractive index of our films are between 1.7 and 1.8.

The refractive index measured by Abele's method (work of co-worker)[128] gives the value of 1.9 for a film of 1200 Å thickness, indicating that our estimation of refractive index value from (Δ),(Ψ) value is quite correct.

The refractive index of material proper should not change even if thickness is very low. The deposited thin films consist of combination of unknown materials as is reported.[61,63] These unknown materials have their own refractive index which will affect the refractive index of the film. Flourides, sulphides probably have oxide impurities but the nature of impurities in oxide film is unknown. Lange et al[132] have reported oxide dependent differences in thin film properties as opposed to bulk properties due to structural or chemical complexities not accounted for. Another reason for lower refractive index of the film, might be due to the presence of voids in the film due to the coloumnour growth of the films. These voids will get filled with moisture, a process which begins to occur immediately as the films are exposed to the atmosphere.(minutes - scale aging.) It has been observed[69] that approximately 8 to 10% of the film is filled with water during and after deposition before air inlet.

As already mentioned in article 4.2 the chopping process results in a more closed packed structure with lesser voids and lesser defects. This might be the reason why chopped films shows higher refractive index (higher Ψ) than nonchopped films.

The process of chopping produces smaller grain size. Bradford et al[133] have reported that for oxides like CeO_2, Al_2O_3, MgO there is a increase in refractive index with increasing grain size. But our chopped films show higher refractive index as compared to nonchopped films indicating that decrease of grain size is not a dominant factor in the determination of refractive index. Other process are more dominant in increasing the refractive index.

4.3.2 EFFECT OF AMBIENTS ON (Δ), (Ψ). [REFRACTIVE INDEX.]

Our results in table 3.3.3.4 shows that chopping of the vapour flow is successful in reducing the changes in (Δ) and (Ψ) in all the ambients studied.

In air the rapid changes in (Δ) and (Ψ) during the initial few days especially decrease in (Ψ) indicates rapid decrease in refractive index. The aging process seems to stabilize after six-days resulting in no further change. It is felt that some permanent chemical reaction takes place in air initially. Similar chemical changes have been suggested by Ennos[46] due to atmospheric moisture.

On exposure to moisture (Δ) decreases and (Ψ) increases indicating an increase in refractive index of the film due to moisture ambient. If water were to just fill the pores of the film one would expect the refractive index to decrease, since the refractive index of water is 1.33. But all our films show increase in (Ψ) (increase in refractive index) due to moisture ambient indicating that the process of aging is not due to just filling of voids with water. When these films are kept in air and measurements taken after 180 day's. The value of (Δ) decreases and (Ψ) also decreases drastically. Moisture seems to have enhanced the long term aging phenomenon. This suggest the presence of low refractive index material in the film due to long term aging of the film. The changes being more in non-chopped films than in chopped films. It seems that water is not the major constituent responsible for minute scale aging of cerium oxide films. Identification of the unknown material (Data of which is not available) that too in small quantities in the matrix of the original material seems to be difficult. ESCA and IR spectra analysis may lead to some identification.

The changes in cold moisture are lesser than that of room temperature moisture, indicating that low temperature inhibits moisture interaction.

On heating one would expect an increase in refractive index similar to that observed in flouride and sulphide films.[67] But our films show decrease in (Ψ) on heating, this might be a purely oxide dependent thin film property with chemical complexities not accounted for. After 180 days exposure to air (Ψ) increases again, becoming more than the fresh film value for nonchopped films and same as fresh film value for chopped films. On heating a sort of annealing and recrystallization process might be occurring which enhances the long term aging process. Heating may also help in progressive crystallization due to diffusion of vacancies to produce a more ordered crystal lattice and the more crystalline structure resulting in a increased refractive index.[62] It has been suggested by Pulker[57] that densification where by an increase in refractive index can be brought about through a decrease in vacancy by suitable heat treatment. All these explanations are valid for both chopped and nonchopped films.

Time did not permit extending the scope of this work, to study the effect of ambient on stress and include other oxides.

4.4 CONCLUSION.

The work described in this thesis is an attempt at studying the mechanical and optical properties of non-chopped and chopped cerium oxide films, which are used as high refractive index material in optical coatings. The study of the effect of various ambients on the adhesion and optical properties is of great technological value.

Direct pull - off method for adhesion measurement, using the adhesion tester fabricated in our lab has proved to be a very simple and accurate technique for comparison of adhesion of chopped and nonchopped films giving quantitative results.

The interferometric technique for measuring stress has also proved to be very useful in our measurements. Ellipsometry seems to be a very simple, but powerful technique for aging studies once the computer program is available. The information obtained by using ellipsometry can be valuable considering the very low cost of ellipsometer, fastness and ease of its operation.

A very significant success obtained from this work is that, the use of chopping technique has increased the adhesion of the film to a great extent, lowered the intrinsic stress considerably and produced films with lesser aging.

The following are the important conclusion obtained from this work.

1) Chopped cerium oxide films show higher adhesion than nonchopped films.
2) Chopping decreases the intrinsic stress of the films

considerably.

3) Chopped films have higher refractive index than nonchopped films.

4) Ambient aging effects are lesser in chopped films than in nonchopped films.

5) Quenching of crystal growth, decrease in voids, enhancement of surface mobility are some of the main effect of chopping which reduces column formation and improves the properties.

6) Chopped films might have higher packing density and smaller grain size.

7) Chopping produces a comparatively defect free film leading to lesser stress and higher adhesion.

8) Chopping also seems to assist oxygen affinity to adatoms giving rise to higher adhesion and lower stress and higher refractive index.

The work on chopped films indicates that it has a considerable potential for improved optical layer deposition compared to other costlier techniques like Electron - beam evaporation, sputtering, ionassisted deposition etc. The use of chopping process is a very simple and cost effective method for producing good adherent coatings.

4.5 SCOPE OF FUTURE WORK.

Plastics are increasingly replacing glass in various optical applications due to their light weight. For obtaining hard coatings on them chopping might prove to be a very good method for film deposition without resorting to heating of substrate or bombardment with high energy particles.

For more detailed interpretation of phenomenon of chopping, nondestructive characterization / XPS of interface should be carried out to find out the exact nature of adhesion process.

For a detailed interpretation of chopping in aging reduction, different rates of chopping has to be tried on different types of flourides, sulphides, oxides and their mixtures. We feel that there might be some critical chopping rate for particular film combination which gives films with almost no aging, very less stress and very high adhesion.

With the detail knowledge of single films and mixed films it will be possible to go for multilayer films using these chopped films. Multilayer films have great scope in optical technology especially in the field of filters and the optical waveguides.

Spectral study using ellipsometer with different light sources, along with spectrophotometric data may give more accurate method for characterizing optical films.