

INVESTIGATIONS IN THEORETICAL OPTICS  
AND ELLIPSOMETRY

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P R E F A C E

Part I of the present thesis presents an analysis of three interesting phenomena in atmospheric optics viz. the focusing phenomenon<sup>1</sup> (i.e. the effect of optical stratification on the intensity at a point in the atmosphere), change of colour due to scattering by haze and the effect of atmospheric turbulence on resolution of an imaging instrument. The results obtained by the author in this area have been published in four papers.

The second part of thesis is concerned with the analysis of performance of instruments under realistic operating conditions. The effect of partial coherence (temporal and spatial) on the performance of some instruments has been analysed. A configuration which makes C-T monochromator<sup>2</sup> coma free in other orders except zero, has also been proposed and analysed. The resolution of monochromatic line objects and coloured point objects under realistic viewing conditions has also been investigated. These investigations have resulted in five publications.

A method of making ellipsometric measurements with rapidly changing substrate's surface or rapidly growing film on a stable substrate has been suggested. Further a method to obtain the correct values of  $\Delta$  and  $\psi$  for the reference surface when it is covered with a thin transparent film has

also been suggested. Both the methods have been used by the author for the transient study of gold and chromium electrodes under active environments. The experimental results (both for steady state and transient ellipsometry) along with the mechanisms of film formation and growth are also described in detail. These investigations have been reported in four papers.

The following is the chapterwise summary of the investigations, reported in this thesis.

## PART I

### CHAPTER I: FOCUSING FACTOR IN STRATIFIED MEDIUM

The author has extended the rigorous quantitative theory developed by Sodha et al.<sup>3</sup> to predict the nature and position of the image formed in a stratified medium to include intensity considerations. The following interesting conclusions have emerged from this study:

1. The focusing factor decreases with range.
2. Over-focusing can occur under certain circumstances.
3. The focusing factor is strongly influenced by the directivity of the source.
4. Nature of variation of refractive index with height strongly influences the focusing factor.
5. Effect of the curvature of stratification on focusing factor is negligibly small.

CHAPTER II: COLOUR OF DISTANT LIGHT SOURCES  
SEEN THROUGH HAZY ATMOSPHERE

The intensity scattered in a particular direction is a function of wavelength; when the size of dielectric particles is very small compared to the wavelength of light, Rayleigh scattering is very dominant<sup>4</sup> (i.e.  $I(\theta, \lambda) \propto 1/\lambda^4$ ). However, the scattering law is modified by the size and absorptivity of the particles. Thus the selective spectral regions are lost due to scattering when the beam propagates through a medium containing large number of particles and thus the transmitted light is rich in spectral components which are least scattered. The author in this chapter has investigated the dependence of the colour of transmitted light on the particle density and depth of penetration of the beam in the medium. The particles are assumed to be nonabsorbing, spherical and of identical shape and size. Three different sizes are selected which show predominant scattering in three different regions of the visible spectrum. Although the treatment is quite general but the calculations are made only for the radiations from a black-body and equi-energy sources. It is shown that due to scattering extreme colours in the transmitted light are possible. It is suggested that the knowledge of the colour of transmitted light after a given penetration depth may give an indication to the size and number density of the scattering particles.

CHAPTER III: EFFECT OF ATMOSPHERIC TURBULENCE ON THE SPATIAL COHERENCE OF LIGHT

Because of the inhomogeneities in refractive index of air caused by the turbulence, a coherent light beam propagating through it tends to be partially coherent. The statistical properties of the beam are described by its correlation or structure functions. Assuming a gaussian correlation of the refractive index inhomogeneities, the author has investigated the effect of atmospheric turbulence on the diffraction pattern of a circular aperture and hence the limit of resolution of a telescope. The dependence of limit of resolution on the turbulence parameter and the effective aperture of a telescope is illustrated by a set of graphs. These graphs help to select the maximum effective aperture to achieve useful resolution.

PART II

CHAPTER IV: EFFECT OF TEMPORAL COHERENCE ON THE DIFFRACTION PATTERN OF SLIT-APERTURE

Early investigations on the diffraction at various apertures were confined to monochromatic light. Recently the studies have been extended to include the partially coherent nature of light and the literature on the effect of spatial coherence on the diffraction patterns of various apertures and hence on the imaging properties of the systems is fast growing.<sup>5-9</sup> The effect of temporal coherence on the holographic imaging was shown to lead to a lateral defocusing in the reconstruction.<sup>10</sup> In this chapter the effect of temporal

coherence on the diffraction pattern of an apodised slit aperture has been investigated. To present the results in a general way a non-uniformly illuminated aperture is considered. The amplitude distribution over the aperture leads to the increase in resolution, suppression of the secondary lobes in the diffraction pattern etc. The results indicate that there is no effect of temporal coherence on the imaging properties when the aperture is uniformly illuminated; also when the transmittance of the aperture increases towards the edge from the centre, the difference of the intensity distribution from the ideal case is negligible. However, when the amplitude transmittance is maximum at the centre and decreases towards the edge, the strengths of the secondary maxima is increased and there is also a phase shift in the secondary maxima with respect to the ideal case. Thus the capability of the instrument to resolve two lines of unequal strengths suffers.

CHAPTER V: EFFECT OF NON-MONOCROMATICITY OF LIGHT ON THE VISIBILITY OF FRINGES IN STELLAR INTERFEROMETER

The angular dimensions and intensity distribution of stars and binaries are obtained by the study of phase shift and visibility of the fringes.<sup>11</sup> In optical range, Michelson-Stellar interferometer is used and because of the intensity considerations, the observations are to be made in white light. However, this polychromatic nature of light limits the sensitivity and accuracy of the measurements. In this chapter, the

author has calculated the dependence of visibility on the non-monochromaticity of radiation emitted from a disc star (near star). The problem is analogous to that of considering the effect of temporal coherence on the performance of a stellar interferometer. It turns out that the visibility of fringes decreases with the departure from monochromaticity and the minimum of visibility curve broadens. Thus the precision in making the measurements is lowered.

#### CHAPTER VI: COMA-ELIMINATION IN CZERNY-TURNER MONOCHROMATOR

The symmetrical C-T arrangement<sup>2</sup> consists of two spherical mirrors of equal radii of curvature and a dispersing system, normally a plane grating. The arrangement is symmetrical to the placement of the grating with respect to the entrance and exit apertures. This arrangement is free from comatic aberration only when used in the zeroth order position (no dispersion). Generally spherical aberration is small or negligible at the focal ratios (F/10 or longer) normally used, except for very large systems and astigmatism can be minimised by using curved entrance and exit slits.<sup>12</sup> Thus the only aberration which severely deteriorates the performance of the monochromator is coma. There are, however, many methods (such as use of grating with hyperbolic rulings, compensation by the coma of prism, ellipsoids and paraboloids) to compensate the comatic defect.<sup>13</sup> In this chapter, a new method has been suggested by introducing an asymmetry in the symmetrical arrangement of the monochromator. In this arrangement, the

grating is illuminated by a convergent beam of light and the comatic aberration thus introduced<sup>13</sup> by the grating is compensated by the comatic error due to the unequal widths of the incident and diffracted beams. The disadvantage of this arrangement is that it is coma free only for a single wavelength at a time.

CHAPTER VII: RESOLUTION OF LINE AND COLOURED  
OBJECTS BY A TELESCOPE

Sodha and his collaborators<sup>14-17</sup> have investigated the effect of background intensity, detecting instrument and stage of resolution desired on the resolution of two spectral lines in the emission spectrum; the resolution of two lines of unequal strengths was also subsequently investigated.<sup>18, 19</sup> The study of resolution of two point objects taking above considerations into account, by image forming instruments has also recently been reported.<sup>20, 22</sup>

A study of the resolution of line objects with image forming instruments taking into account the shrinkage effect<sup>16, 17, 19, 23, 24</sup> has been made. The resolution of coloured objects by the image forming instruments has also been studied. The dependence of resolution on colour mismatch against white background has been analysed.

PART IIICHAPTER VIII: INVESTIGATIONS IN ELLIPSOMETRIC TECHNIQUES

Ellipsometry is a very sensitive, precise and convenient tool for measuring the surface and thin film parameters. The measurements obtained with ellipsometry can be interpreted to yield refractive index and absorption coefficient of the substrate and/or thickness, refractive index and absorption coefficient of a film over the substrate. The usual methods of making the measurements<sup>25-27</sup> are steady state and hence cannot be used to study the parameters of rapidly changing surface or the rapidly growing film. In this chapter, a method has been suggested to monitor the refractive index and thickness of a rapidly growing transparent film. While studying the parameters of a film, it is very important to know accurately the parameters of the substrate. In most cases of interest the substrate can be stripped off to its cleanest surface and measurements are made. However, under unfavourable conditions it becomes desirable to obtain film parameters even if the substrate is originally covered with a thin layer of a different film. A technique has been suggested to determine the bare surface optical constants. The measurements are made in environments of different refractive indices and by using simple calculations, reference surface parameters are obtained. These surface parameters can then be used to calculate the film parameters. Both these methods

have been employed in the investigations reported in Chapters IX and X.

#### CHAPTER IX      ELECTROCHEMICAL-ELLIPSOMETRIC STUDY OF GOLD

It is known that the electrochemical oxidation of gold leads to the formation of chemisorbed oxygen<sup>28, 32, 34</sup> or gold oxide.<sup>28-33, 35-37</sup> The thickness of this oxide is reported to be of the order of a monolayer. Later workers<sup>31</sup> observed the inflections in the charging curves and attributed them to the formation of  $\text{Au}_2\text{O}$ ,  $\text{AuO}$  and  $\text{Au}_2\text{O}_3$ . In acidic chloride solutions, passivation is observed with the passivation time dependent on chloride concentration,<sup>38-42</sup> indicating that the passivation occurs when the surface concentration of chloride approaches zero.

An ellipsometric investigation is initiated to confirm the earlier findings, which were observed mainly by the electrochemical means. It is revealed that a sub-oxide is formed in the potential region 0.2-1.1 V vs SCE in acidic solutions with gold oxide formed at more anodic potentials. The thickness of the gold oxide is found to be 10-15 Å while that of the sub-oxide  $\sim 3$  Å. Both the species (sub-oxide and oxide) are light absorbing and probably oxide is semi-conducting. The oxide is identified to be  $\text{Au}_2\text{O}_3$ . At such thicknesses, none of the existing laws<sup>43</sup> (direct and inverse logarithmic) of film growth were found to fit the experimental results and thus it is concluded that either the law of film

growth is different from the generally known or the changes in the surface are sufficient to mask the true kinetic law.

In chloride solutions gold cannot be passivated and hence no measurements could be made. However, in alkaline solutions (even in chloride added) similar species were formed with slightly different optical properties. It is thus concluded that the optical properties of the oxide film depend on the pH and chloride ion concentration.

#### CHAPTER X: AN ELLIPSOMETRIC STUDY OF CHROMIUM PASSIVATION

Chromium exhibits a very low dissolution current when passive and transmits this property to its alloys. Accordingly, numerous investigations into the cause of passivation of chromium have been undertaken; these are well summarised by Gmelin.<sup>44</sup> In a very early application of ellipsometry, Micheli<sup>45</sup> could not detect any difference between the active and passive surfaces of chromium and thus concluded that there was no film present. Andreeva<sup>46</sup> has observed increased thicknesses of the film at chromium with application of either cathodic or anodic polarisation. In this chapter, again a study, using ellipsometry in situ with electrochemical techniques, is initiated to get an insight in the nature of film at chromium. It is found that the film is transparent with refractive index of 2.45 and is identified to be of  $\text{Cr}_2\text{O}_3$ . Film of the order of a monolayer is shown to lead to the passivation and grows only to a thickness of  $\sim 20 \text{ \AA}$  in transient

measurements.

The mechanism of film formation is suggested to be a simultaneous dissolution and precipitation. In steady state measurements quite a thick film ( $100-120 \text{ \AA}$ ) is formed. This film is porous and its growth kinetics does not fit neither the direct nor inverse logarithmic laws.

The work reported in the thesis has resulted in the following publications:

1. Focusing factor in horizontally stratified medium, Brit. J. Appl. Phys., 2, 605 (1969).
2. Focusing in spherically stratified medium, Brit. J. Appl. Phys., 2, 1457 (1969).
3. Effect of fog on the colour of distant light source, Brit. J. Appl. Phys., (In press) (1969).
4. Effect of turbulence on the diffraction pattern of a circular aperture, Brit. J. Appl. Phys., (In press) (1969).
5. Effect of temporal coherence on the Fraunhofer diffraction pattern by non-uniformly illuminated slit aperture, Brit. J. Appl. Phys., 2, 1479 (1969).
6. Effect of non-monochromaticity of light on the visibility of fringes in Stellar interferometer, Optik, 28, 585 (1969).
7. Coma-elimination in C-T monochromator, Optik, 29, 331 (1969).
8. Resolution of line objects seen through a diffraction limited circular aperture, Optik, 29, 437 (1969).
9. Resolution of coloured objects, Optik (accepted)(1969).
10. Monitoring the thin film thickness by ellipsometry, Appl. Opt. (USA), 8, 483 (1969).

11. Determination of metal constants, Brit. J. Appl. Phys., 2, 468 (1969).
12. Electrochemical-ellipsometric study of gold, J. Electrochem. Soc., 116, 910 (1969).
13. Ellipsometric study of chromium, paper presented in the Electrochemical Society Meeting in Montreal held on Oct. 6, (1968), and to appear in J. Electrochem. Soc.

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