PHYSICS OF THIN FILMS

OPTICAL CHARACTERIZAT ON OF REAL SURFACES AND FILMS

Edited by
Maurice H. Francombe
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VOLUME 19

Physics of Thin Films

Advances in Research and Development

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OPTICAL CHARACTERIZATION OF REAL SURFACES AND FILMS

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Preface

It is well known that *real* thin films of metals, semiconductors and insulators are in general far from homogeneous due to their internal microstructure which is strongly dependent on the preparatory conditions. Consequently the optical properties of the films were seldom reproducible until recently. To cite just one example, Professor Abeles in his extensive review article in this Series on the "Optical Properties of Metallic Films" [*Physics of Thin Films 6*, 151–204 (1971)] confined his attention only to the theoretical aspects and did not discuss the experimental results since "they are more subject to revision and modification in the near future" [*ibid* p. 152]. Further, the assumptions invoked in the interpretation of the experimental data, as for example whether the film is homogeneous or not, etc., also play a dominant role in the final results. This is brought out very clearly in the results of the Round Robin Experiments conducted by the Optical Society of America [Appl. Opt. *23*, 3571–3596 (1984)] in which seven laboratories from around the world were asked to determine the optical constants of Rh metal and Sc_2O_3 using nominally same thin films. It is interesting to observe from Tables 17 and 18 of this article that, in the case of Rh film all the workers assumed the Rh film to be homogeneous, whereas in the case of Sc_2O_3 film only three of the seven groups assumed it to be inhomogeneous. Further even in those three cases, they had to invoke an arbitrary assumption that the inhomogeneity in the film varies linearly with thickness. It is now evident that the assumptions in both the cases are not justified, since (i) the microroughness of the surface was totally ignored and (ii) microstructure and hence the void distribution in the film is seldom linearly dependent on the thickness.

Almost similar statements can be made to the case of surfaces as well. *Real* surfaces are in fact quite different from the ideally perfect surface which corresponds to the plane surface terminating an ideally perfect semi-infinite solid. Even if we ignore the cleavage steps, tear lines, dislocations and damaged regions or the imperfections introduced during the preparatory stage as well as the contaminant overlayer if any on the surface, the abrupt termination of the solid and the presence of the so-called dangling bonds on the outermost layer can cause the symmetry as well as the physical and chemical properties of this layer to be different from those of the bulk specimen.

During the last five to ten years two major breakthroughs have been made in the development of two optical techniques to characterize in real time and *in situ* the films and surfaces respectively. With the first one-Real Time Spectroscopic Ellipsometry (RTSE), we can now nondestructively and noninvasively determine the spectra of the relative changes in both amplitude and the very sensitive "phase" of the reflected light as a function of photon energy in a few milliseconds and thus measure and store such a library of spectra collected during entire film growth in real-time as well. With such a wealth of data we are now able to perform detailed regression analysis of these spectral data first at successive intervals of time and later also globally with the entire data, to finally obtain statistically meaningful results. In other words we are now for the first time able to obtain meaningful and reproducible results on (i) the morphological and/or the microstructural features of the inhomogeneities in the film and (ii) the true optical functions of film-materials. The second optical technique Reflectance Anisotropy (RA) can also nondestructively and noninvasively probe the surface of the growing crystal, to follow (a) the minute variations in the crystallographic symmetry of the growing surface layer during epitaxial film growth and thus (b) in its optical properties. Hence it is now appropriate for us to collect a review of these new optical techniques and the summary of the results obtained thus far, so that the scientists and engineers at large can benefit from this collection of reviews from the pioneers who developed these techniques. At the same time it will also enable us to (i) assess whether the full potentialities of these techniques have been realized or not, (ii) determine their limitations and deficiencies of these techniques and (iii) also point out the areas that need further work and/or development. The present volume in this series on the Physics of Thin Films aims to address these issues.

The first article by Drévillon and Yakovlev provides a critical evaluation of the extensive literature on "reflectance anisotropy" (RA) technique, a field in which Drévillon is one of the pioneers. This is a normal incidence optical probe that uses the reduced symmetry of the surface layer to enhance the typically low sensitivity of reflectance measurements to surface phenomena. Unlike the various electron beam based surface analytical techniques, RA is not limited to ultra high vacuum (uhv) environment and hence has been used successfully to study the growth processes of III-V semiconductors in various deposition conditions ranging from Molecular Beam Epitaxy (MBE) requiring uhv conditions, to metallorganic chemical vapor deposition (MOCVD) under atmospheric pressure H_2 environment. It is shown that in all these cases RA spectroscopy can follow the changes in the various surface reconstructions and also obtain real-time control of the chemical cycles of atomic layer epitaxy (ALE). Further in the case of low pressure MOCVD, RA transient measurements were utilized to control the deposition parameters to optimize the quality of the heterojunctions in GaInP/GaAs superlattice structures.

The second article authored by Collins and his students provides an excellent review of the experimental details, the physics involved and a summary of the results obtained on the growth of technologically important tetrahedrally-bonded films [such as hydrogenated amorphous silicon (a-Si:H), and silicon carbon alloys (a-$Si_{1-x}C_x$:H)] using the Real Time Spectroscopic Ellipsometry (RTSE), a technique pioneered by Collins. It is evident that single wavelength ellipsometry and/or reflectance and absorptance spectroscopy, even with real-time measurements cannot untangle the numerous processes that take part simultaneously during the film growth, such as (i) evolving microstructure (i.e., void volume fraction), (ii) changes in the chemical composition (particularly in the case of alloys), (iii) changes in the crystal structure (particularly in the case of thin metal films) and (iv) surface roughening (or smoothening) effect. On the other hand RTSE is shown to untangle all this and thus provides insights into the monolayer scale surface processes that control the ultimate properties of the material. As a direct result of these studies by RTSE with on line control of the deposition parameters it was possible to control the surface smoothening and obtain improved photoresponse and electronic performance of both these amorphous materials. Similar RTSE studies on the nucleation and growth of diamond films by heated-filament (1950°C) assisted CVD, (i.e., even under the most adverse conditions for any real-time optical studies), have enabled them to identify and overcome numerous problems such as tungsten contamination from the filament at the diamond/substrate interface etc., and grow excellent diamond films by on-line monitoring and control.

The third article by Hien, An and Collins deals with an important problem both from the physics and technological points of view, namely the optical properties of thin metallic films, a satisfactory understanding of which has eluded physicists for well over a century. The development of RTSE has enabled Collins and his group to follow the evolution of the optical function of Aluminum film as a continuous function of thickness throughout the nucleation, coalescence and bulk film regimes. Detailed analyses of their extensive data reveal that at the very early stages of the film growth, the film is composed of partially coalesced disordered particles with a constant electron mean free path λ of 7.5 ± 2 Å even when the film thickness is over the percolation threshold of 45–50 Å. The above value of

λ is found to be the same irrespective of the method of film preparation, or rate of film deposition or the size of the particle. As the film thickness increases to 55–60 Å, there is an abrupt transition when λ increases by an order of magnitude indicating conversion of the defective particles into high quality single-crystalline grains extending through the thickness of the film. For thicknesses above the transition, λ is found to increase gradually with thickness as would be expected for electron scattering at grain boundaries. All the published optical and electrical data in the literature on aluminum, can now be explained for the first time with this picture.

The fourth article in this volume by Chindaudom and Vedam deals with the nondestructive characterization of inhomogeneous transparent optical coatings on transparent substrates with the help of Spectroscopic Ellipsometry (SE). It is shown that the spectral variation of Δ, the relative change in "phase" in the reflected light, contains information on the inhomogeneities in the thin film, while the corresponding spectral variation of Ψ contains information on the optical function of the film material. Hence circularly polarized light was used as the incident beam in a rotating analyzer type SE system, which in turn made it possible to measure the spectral variation of Δ to a high degree of accuracy, even though Δ itself was close to $0°$. Examination of a number of different fluoride and oxide optical coatings (deposited by electron-beam-evaporation) on vitreous silica substrate reveal that *all* these optical coatings were inhomogeneous due to the presence of microrough surface layer and/or a voided interface between substrate and film or inhomogeneous distribution of voids throughout the bulk of the film. Besides depth-profiling the film, SE characterization studies yield also the optical function i.e., the refractive index and its dispersion with wavelength, of the film material. Such data were not available in the literature for some of these materials.

The fifth article in this volume authored by Trolier-McKinstry and her colleagues discusses the characterization of transparent ferroelectric thin films by SE, as well as *in situ* annealing the as-deposited films. All ferroelectric thin films (lead based perovskite films deposited by rf magnetron sputtering, multi-ion-beam sputtering and sol-gel spin-on techniques) studied, display some level of inhomogeneity in the form of low density regions distributed through the thickness of the film and/or surface roughness. It is shown that many of the apparent size effects reported for ferroelectric thin films are probably associated with either poor crystallinity or defective microstructure, rather than intrinsic changes in the ferroelectric properties with film thickness. Results of SE studies on *in situ* annealing of deposited ferroelectric films are also discussed.

The sixth and final article by Parikh and Allara deals with a long outstanding problem in SE that has not been addressed satisfactorily until now, i.e., spectro-ellipsometry of anisotropic materials in its most generalized approach. This includes the material under consideration as optically biaxial, and optically absorbing; and it can be in the form of thin film or act as substrate with lossy overlayers which may or may not be anisotropic. The experimental variables considered are variable angles of incidence, wavelength range varying from 350 nm to 850 nm. Such a problem may appear too esoteric; but it is not far from the case of uniaxial Langmuir-Blodgett films on optically biaxial SbSI substrate. In fact Parikh and Allara have alluded to many such examples in which the effects of anisotropy do arise and play dominant role in ellipsometric measurements. Parikh and Allara have constructed the algorithms for the generalized approach mentioned above, tested the validity of the calculations with the few selected experimental observations and then consider some hypothetical models to generate the spectra of the ellipsometric parameters (Δ, Ψ) in three dimensional [wavelength, angle of incidence, and Δ (or Ψ)] space to gain physical insight into the variety of possible anisotropic effects.

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