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WHY IN SITU, REAL-TIME CHARACTERIZATION OF THIN FILM GROWTH PROCESSES?

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Editorial

"*In Situ*, Real-Time Characterization of Thin Film Growth Processes," O. Auciello and A. R. Krauss, Guest Editors, MRS Bulletin, XX(5), May 1995

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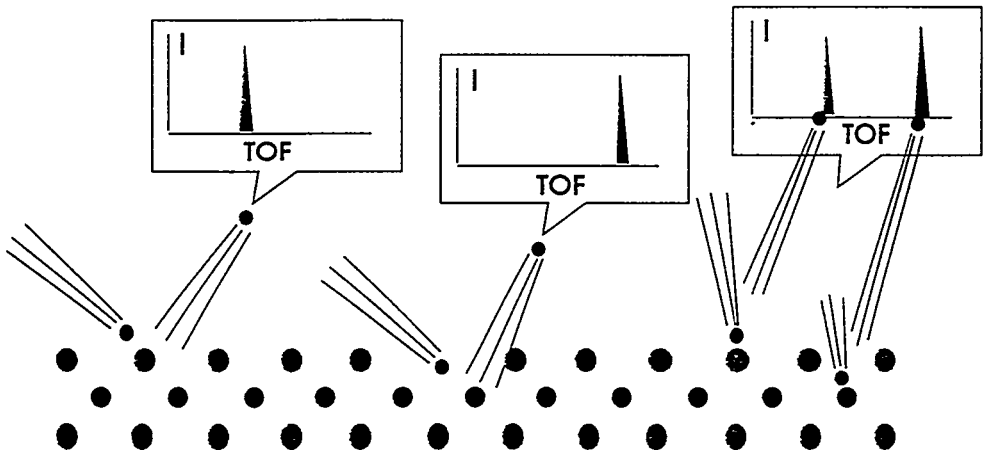
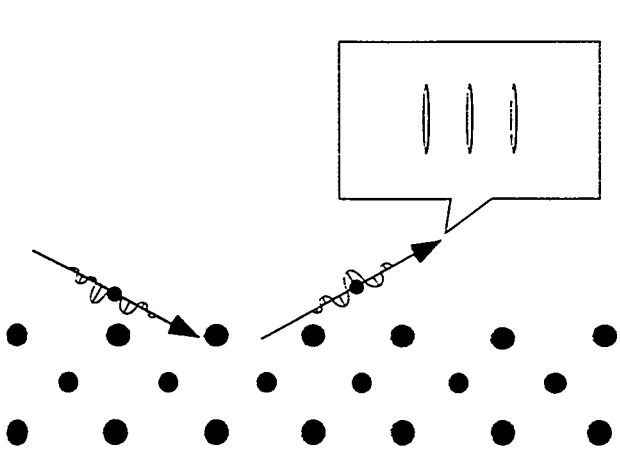
MRS

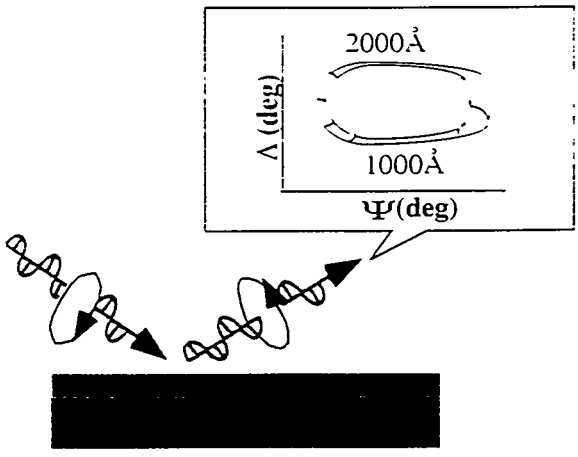
In Situ, Real-Time Characterization of Thin-Film Growth Processes



TIME-OF-FLIGHT ION SCATTERING-RECOIL SPECTROSCOPY



RHEED



ELLIPSOMETRY

Why *In Situ*, Real-Time Characterization of Thin-Film Growth Processes?

Orlando Auciello and Alan R. Krauss,
Guest Editors

It is anticipated that a new generation of advanced electronic and optical devices will involve the synthesis of diverse materials in single or multielement thin-film form, or in layered heterostructures. These devices will most likely involve diverse materials such as high-temperature superconductors, ferroelectric, electrooptic, and optical materials; diamond; nitrides; semiconductors; insulators; and metals[1] in the form of ultrathin layers with sharp interfaces in which the layer thickness may reach atomic dimensions. Therefore, it becomes increasingly important to be able to monitor the deposition process *in situ* and in real time, particularly for complex multicomponent oxides or nitrides, in which the production of the desired phase is a highly sensitive function of the growth conditions, often requiring relatively high-pressure oxygen or nitrogen environments up to several hundred mTorr, and in some cases, several Torr.[1] Consequently, the growth environment for many of these materials is incompatible with conventional surface-analytic methods, which are typically restricted to high- or ultrahigh-vacuum conditions. New deposition and analytical methods, or adaptation of those already established, will be required.

Since thin-film growth occurs at the surface, the analytical methods should be highly surface-specific, although subsurface diffusion and chemical processes also affect film properties. Sampling depth and ambient-gas compatibility are key factors which must be considered when choosing *in situ* probes of thin-film growth phenomena. In most cases, the sampling depth depends on the mean range of the exit species (ion, photon, or electron) in the sample. Techniques such as low energy electron diffraction (LEED), Auger electron spectroscopy (AES), and ultraviolet (UPS) and x-ray photoelectron spectroscopies (XPS) detect 100–2,000 eV electrons which have a typical range of ~5–40 Å in solids. However, electrons also undergo significant gas-phase scattering which degrades the energy information and limits their analytical usefulness to high and ultrahigh-vacuum environments. Reflection high energy electron diffraction (RHEED) employs higher energy electrons (~20 keV) and may be used at pressures up to 10^{-6}–10^{-5} Torr. Low-energy (several keV) ion-beam techniques such as ion scattering spectroscopy (ISS) and direct recoil spectroscopies (DRS) provide perhaps the most surface-specific information of any analysis method, but because they are relatively insensitive to multiple-scattering effects, the quality of the information is not seriously degraded by passage through a region of modest ambient-gas pressure. Methods which detect higher energy (MeV) ions such as Rutherford backscattering spectroscopy (RBS) and elastic recoil detection (ERD) are even less subject to gas-phase scattering, and may be used at pressures up to 1 atm.[2] However the sampling depth increases to 0.5–2 μm. A similar sampling depth is obtained for methods which detect x-ray photons, unless they employ a grazing exit angle to limit the depth of signal origin or grazing incidence to limit the probe depth. Finally, methods which employ visible light such as ellipsometry and interference spectroscopy are not surface-specific, but are useful probes of thin-film growth processes because they determine macroscopic properties such as film thickness, roughness, index of refraction, and growth rate. Methods which detect x-ray or visible photons can typically be used at almost any pressure.

The techniques that are discussed in this issue of the *MRS Bulletin* (see schematics in Figure 1) have been chosen because they may be used for *in situ*, real-time analysis of film-growth phenomena in vacuum and in the presence of ambient gases resulting either from the deposition process or as a requirement for the production of the desired chemical phase. A second criterion for inclusion is that the instrumentation be sufficiently compact and inexpensive to permit use as a dedicated tool in a thin-film deposition system.

The article by A.R. Krauss, O. Auciello, and J.A. Schultz describes the development and application of low-energy (5–15 keV) time-of-flight ion scattering and recoil spectroscopy (TOF-ISARS) methods,[3] which can provide a remarkably wide range of information on surface composition, atomic structure of the first few monolayers, lattice-defect density, trace-element analysis, phonon characteristics, and in some cases, the chemical phase of the growing film in thin-film deposition environments.

The article by E.A. Irene and J.A. Woollam describes spectrometric ellipsometry (SE), a well-established technique that can be used for *in situ*, real-time analysis of growth processes.[4] This method has been extensively used in analysis of semiconductors, and most recently has been applied to study complex high-temperature superconductors and ferroelectric films as examples of complex multicomponent materials. This technique provides information on surface roughness, interface sharpness, and defect density, for example, but interpretation of the data is only possible using a parametric model which requires additional information such as composition, lattice structure, and interface characteristics that can be provided by various techniques, including TOF-ISARS.

The article by C.D. Zuiker, D.M. Gruen, and A.R. Krauss examines the use of optical interference spectroscopy

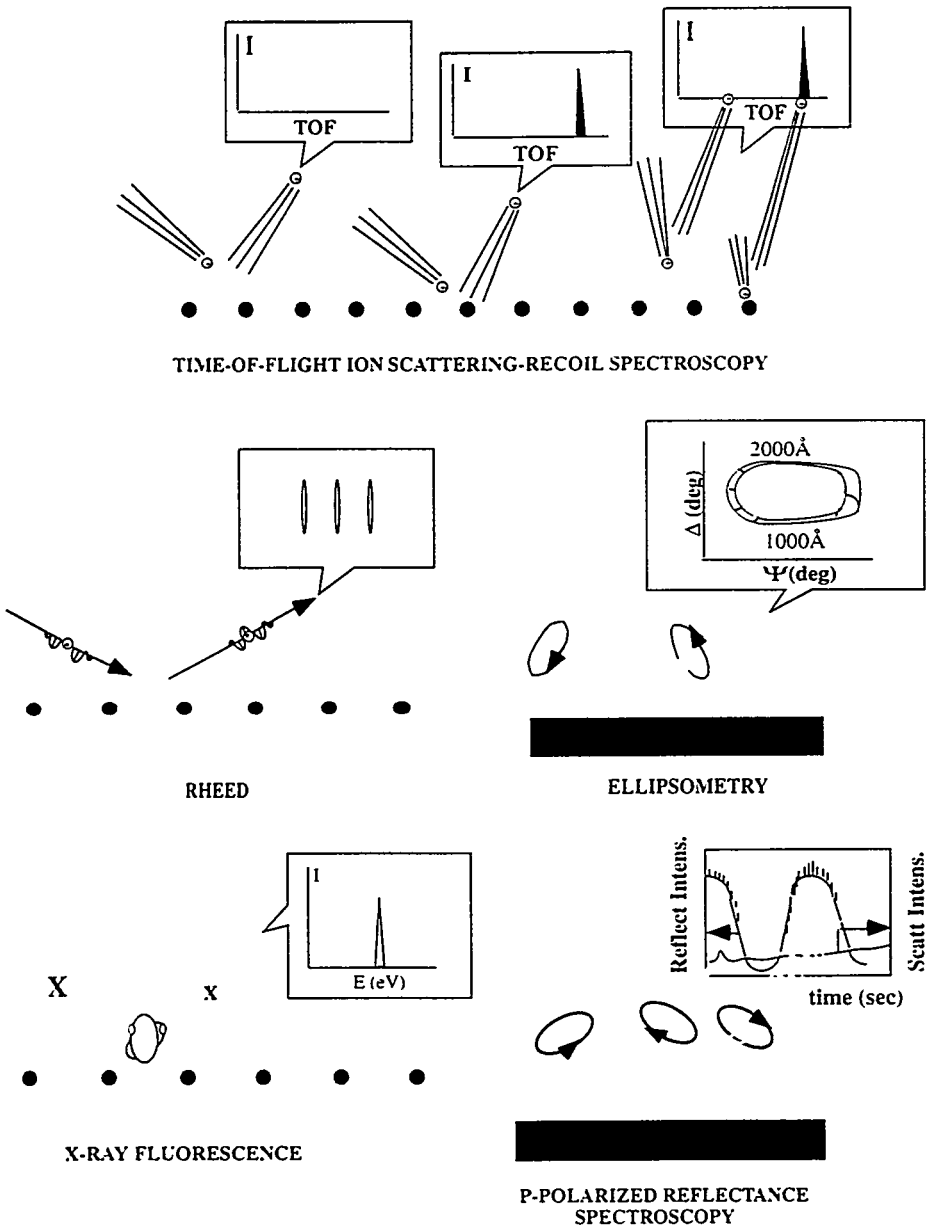


Figure 1. Schematics showing the principle of the in situ, *real-time characterization techniques discussed in this issue.*

as an *in situ* means of measuring film-growth rate and surface roughness on the micron scale. This method has the virtue of simple setup, low cost, and the ability to provide some of the information required for the interpretation of ellipsometric data.

The article by I. Bozovic and J.N. Eckstein focuses on the use of RHEED as a tool for *in situ*, real-time monitoring of growth processes. The diffraction pattern produced by an electron beam impinging on the growing film at a grazing-incidence angle provides a k-space view of the crystallography of the film surface (specifically, the lattice constant and the symmetry), its relation to the underlying layers, and the surface roughness on an atomic scale. RHEED can be used in some cases to determine the nature of the chemical reactions at the surface, and is particularly useful for monitoring transient chemical intermediate states which result from the reactions that occur during the growth of each unit cell.[5]

The article by T.A. Roberts and K.E. Gray discusses the use of x-ray fluorescence spectroscopy (XRFS) for *in situ*, real-time analysis of film-growth processes. X-ray fluorescence induced by x-ray excitation is used to monitor film composition during growth in an ambient background gas. The technique is fairly simple to set up, has a relatively high surface sensitivity, and is nondestructive.[6]

The article by N. Dietz and K.J. Bachmann focuses on a new, inexpensive technique for real-time monitoring of epitaxial growth processes based on the reflection of a parallel-polarized light that impinges onto the surface of the substrate close to the Brewster angle of the material. The method can provide information about optical and dielectric properties of the growing film as well as of growth mechanisms.

The experimental methods described in this issue of the *MRS Bulletin* are not all-inclusive. They present examples of new methods which are being developed or old methods which are being extended to fill the need for better understanding of thin-film growth phenomena in complex multiphase materials and layered heterostructures which utilize these materials for the production of new devices. In addition, the methods were selected on the basis of their potential use as dedicated *in situ* monitors in production facilities.

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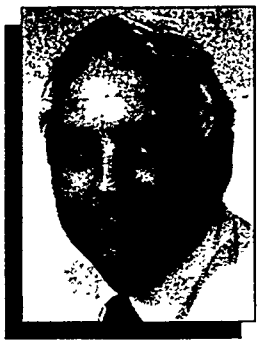

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Ivan Bozovic is a senior scientist at the Varian Research Center, Palo Alto, where he studies synthesis and properties of single-crystal films and heterostructures that include cuprate superconductors and other complex oxides. Previously, he was the head of the Physics Department at the University of Belgrade, a visiting professor at Stanford University and Notre Dame University in Belgium, and a visiting scholar at the University of California—Berkeley and the University of Pennsylvania. His credits include over 120 papers, numerous invited talks, four chaired conferences, the Fulbright Award, and the Belgrade Institute of Physics Prize.

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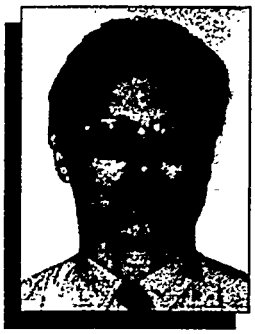

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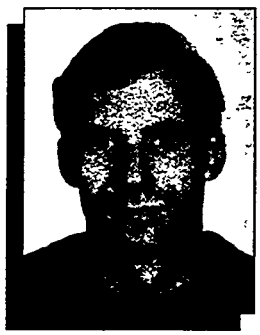

Christopher D. Zuiker

flux flow in superconductors and film deposition. His research has resulted in several patents and RD-100 awards. In 1989, he received the Department of Energy Award for Significant Implication to DOE-Related Technologies in Solid State Physics: "Thin-Film Superconducting Device Concepts and Development."

Dieter M. Gruen is a senior scientist at Argonne National Laboratory and associate director of the Materials Science Division. He received his BS and MS degrees in chemistry at Northwestern University and a PhD degree in chemical physics at the University of Chicago. Gruen has received a number of research awards including the American Institute of Chemists Student Medal, the Department of Energy Materials Science Award, the IR-100 Award, the Inventor of the Year from the Patent Law Association of Chicago, and the University of Chicago Award for Distinguished Performance at Argonne. He has published approximately 300 publications.

Eugene A. Irene received a PhD degree in solid-state chemistry from Rensselaer Polytechnic Institute in 1972. Since 1982 Irene has held a professorship in physical chemistry at the University of North Carolina. Irene's ongoing research includes studies of dielectric films and semiconductor surfaces and interfaces where a combination of optical (ellipsometry, reflectance), chemical (IR, XPS, SIMS, etc.), and electronic methods (C-V, I-V, tunneling) are used to elucidate film-formation mechanisms and properties. Irene received the Callinan award of the Electrochemical Society, and has more than 160 publications in this field. Fifteen PhD degrees have been awarded thus far in his research group.

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Christopher D. Zuiker received his BS degree in nuclear engineering with highest honors, as well as university honors, from the University of Illinois—Urbana. He was awarded a National Science Foundation Fellowship and received his PhD degree in astrophysical sciences from Princeton University with the thesis, "Laser Induced Fluorescence Measurements in an Electron Cyclotron Resonance Plasma Etch Reactor," under the direction of J.L. Cecchi. He is currently working at Argonne National Laboratory in the chemistry and materials science divisions. His research involves plasma-enhanced chemical vapor deposition of diamond films.

UPCOMING IN NEXT MONTH'S MRS BULLETIN:

Theme: Organic Thin Films

Guest Editors: Tisato Kajiyama, Kyushu University; David G. Whitten, University of Rochester; and Toyoki Kunitake, Kyushu University

...including Langmuir-Blodgett films, organic monolayers, lipid bilayers, and other self-assembling structures.