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

TIME-OF-FLIGHT ION SCATTERING-RECOIL SPECTROSCOPY

RHEED

ELLIPOSOMETRY
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 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. Consequently, the growth environment for many of these materials is incompatible with conventional surface-analytic methods, which are typically restricted to high- or ultra-high-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^-7-10^-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. 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.K. 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, 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. 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
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The article by T.A. Roberts and K.E. Gray discusses the use of x-ray fluorescence spectroscopy (XRF) 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.

The article by N. Dietz and K.J. Bachmann discusses 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 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.

References
Orlando Auciello, Guest Editor for this issue of the MRS Bulletin, is a senior research scientist at the Microelectronics Center of North Carolina (MCNC) Electronic Technologies Division and is an adjunct professor in the Department of Materials Science at North Carolina State University (NCSU). He received MS and PhD degrees from the Physics Institute "Balseiro," University of Cuyo. Recently, he has focused on coatings for field emitter cathodes. Auciello is a permanent research associate at Argonne National Laboratory and has been a guest scientist at various institutions including Princeton Plasma Physics Laboratory, Argonne, and the University of Wuppertal. His list of publications is extensive, including numerous invited reviews and book chapters, as well as six books. He has been the organizer and director of and a lecturer at NATO Advanced Study Institutes. Auciello recently received the 1994 R. Bunshah Award from the American Vacuum Society, along with Orlando Auciello and J. Albert Schultz, for the work described in their article appearing in this issue. His research interests include the interaction of energetic particles with solid surfaces, sputtering and ionization phenomena, ion and electron emission from surfaces, thin-film deposition, and alloy segregation phenomena. For more information, Auciello can be reached at Argonne National Laboratory, Materials Science and Chemistry Divisions, 9700 South Cass Avenue, Argonne, IL 60439, phone: 708-252-3300, fax: 708-252-9555, e-mail: alan_krauss@anl.gov.

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Jim Eckstein, PhD, is a senior scientist at the Varian Research Center, Palo Alto, where he leads the superconductivity group. His interests are in the use of atomic layer-by-layer molecular beam epitaxy of complex oxides, the structuring of artificial materials, and the study of physics at novel heterointerfaces. Eckstein received his PhD degree in physics from Stanford University where he researched high-resolution laser spectroscopy and nonlinear optics.

Kenneth E. Gray, PhD, is a senior scientist and group leader in the Materials Science Division of Argonne National Laboratory. He received his BS and MS degrees in engineering physics from the University of California—Berkeley and his PhD degree in physics from Cambridge University. His research interests include tunneling and
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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 Implications 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...