

# PEM<sup>TM</sup>

APPLICATIONS  
NEWS FOR USERS  
OF PHOTOELASTIC  
MODULATORS

## REFLECTANCE ANISOTROPY SPECTROSCOPY

# Sensitivity to atomic monolayers with PEM-based Reflectance Anisotropy Sensors

### ABOUT THE SCIENTIST



Thomas Zettler, Ph.D.,  
Technical University Berlin  
President of LayTec

## *From Surface Science to Semiconductor Production Lines*

*by Thomas Zettler, Ph.D., Technical University Berlin*

Reflectance Anisotropy Spectroscopy (RAS; also called RDS—Reflectance Difference Spectroscopy) is a normal incidence reflectance technique that, by utilizing the anisotropy of reconstructed semiconductor and metal surfaces, has evolved into one of the most useful, new optical surface science techniques. Using a spectroscopic range covering the visible and near-UV part of the spectrum (250 nm to 850 nm), this technique is capable of sensing the stoichiometry and symmetry of the uppermost atomic monolayers of cubic semiconductors and metals. The basic principle of RAS is that the complex reflectance anisotropy  $\Delta r/r$ , caused by the reduced symmetry at the surface of cubic crystals, is measured by a PEM-based optical system acting as a normal-incidence phase-modulated ellipsometer. The signals to be detected are usually of the order of  $|\Delta r/r| < 10^{-3}$  and carry information originating only from the surface region because the bulk beneath is optically isotropic and therefore does not contribute to the measured spectrum.

Interestingly, there are presently two rather different fields where RA spectrometers are used in steadily increasing numbers: basic research in academic solid-state physics departments and growth control in the production lines of the optoelectronics industry. *(continued on page 2)*

Dr. Thomas Zettler received his degree in Physics from the Humboldt University of Berlin (HUB). His thesis was on ZnS:Mn electroluminescent thin-film displays at the Berlin Academy of Science Institute for Electron Physics. After three years at the HUB Physical-Chemistry department he earned his PhD in physics with a thesis on transparent conducting oxides.

As a post-doc he joined the Berlin Academy of Science Institute for Optics & Spectroscopy where he worked in Prof. A. Röseler's group on FTIR ellipsometry. Since 1991 Dr. Zettler has been with the Solid State Physics Institute of the Technical University of Berlin (TUB). There, as a senior scientist in Professor Wolfgang Richter's group, he supervises and coordinates MOCVD and real-time spectroscopy research.

Since 1999, in addition to his duties at TUB, he has been president of LayTec GmbH which he co-founded.

*(Read "About LayTec" on page 6)*

## LOW-LEVEL BIREFRINGENCE

# Hinds Instruments Introduces Exicor<sup>TM</sup> *A Low-level Birefringence Measuring System for Characterizing Optical Materials*

Driven by the semiconductor industry's accelerating demand for higher quality optical components for DUV optical systems, Hinds Instruments has developed an innovative low-level birefringence measurement system, Exicor. As the long established leader in photoelastic modulator (PEM) technology, we have developed a new technology based on the PEM that offers unparalleled sensitivity in birefringence measurement.

*(continued on page 4)*



Figure 1: MOCVD reactor for III-V semiconductor growth (Aix-200, AIXTRON, Germany) equipped with a RAS real-time sensor (LayTec, Germany) at Hahn-Meitner-Institut, Berlin, Germany.

## Sensitivity to atomic monolayers with PEM based Reflectance Anisotropy Sensors...

(continued from page 1)

The motivation among those in the 'basic research' camp to use RAS in their surface science studies is obvious: "watching" the atoms on surfaces with light that, as opposed to electrons, can penetrate gaseous and liquid ambient, opens a completely new 'playground' that extends beyond the traditional study of clean surfaces in an ultra-high vacuum. On the other hand, major suppliers of industrial metal-organic chemical vapor disposition (MOCVD) systems equip their reactors for large-scale optoelectronics and communication electronics production with RAS sensors. They are capitalizing on this technique's demonstrated ability to measure growth rates, compositions, doping levels, interface formation and surface reactions.

### The basic optical principles of RAS

RAS measures the difference  $\Delta r$  in the normal-incidence reflectances  $r_x$  and  $r_y$  for light that is linearly polarized parallel and perpendicular, respectively, to a chosen in-surface-plane axis  $x$  of a sample [1]. Usually it is given as  $\Delta r/r$ , i.e., normalized to the averaged reflectance  $r$ :

$$\frac{\Delta r}{r} = \frac{r_x - r_y}{(r_x + r_y)/2} \quad 1$$

For the most important case of an anisotropic surface on an isotropic bulk material, the complex surface dielectric anisotropy  $\Delta\epsilon_s^*d$  ( $d$  refers to the 'thickness' of the surface and usually is of the order of 1nm) can be directly derived from the complex dielectric anisotropy by:

$$\frac{\Delta r}{r} = \frac{4\pi i}{\lambda(\epsilon_b - 1)} \cdot \Delta\epsilon_s^*d \quad 2$$

Consequently, with the bulk dielectric function  $\epsilon_b$  known, the surface dielectric function  $\Delta\epsilon_s^*d$  can be derived straightforwardly from the measured RAS spectrum (Fig.2). The spectrum of  $\Delta\epsilon_s^*d$  is, in contrast to the as-measured  $\Delta r/r$  spectrum, a unique property of the reconstructed surface and as such is directly related to only the respective surface band structure and the corresponding surface transition matrix elements involved. This is where the surface science potential of RAS originates. On the other hand, tiny changes in surface stoichiometry can have a major impact on the surface dielectric anisotropy. When measured in real-time, RAS gives the key to industrial growth monitoring and growth control on a sub-monolayer level.

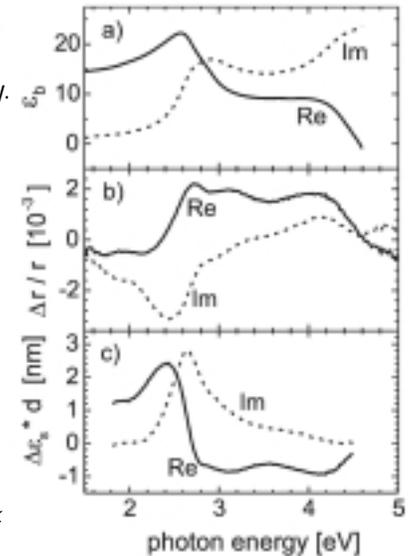


Figure 2: GaAs (001) (2x4) surface dielectric function (c) as calculated from the measured RAS spectrum (b) and the respective GaAs bulk dielectric function (a).

A typical set-up for RAS is shown in Fig. 3. The light from a Xe arc-lamp source is focused through a polarizer prism on a sample close to normal incidence (typically  $\sim 5^\circ$ ). The reflected light is, after having traveled through a photoelastic modulator (PEM) and an analyzer prism, refocused on the entrance slit of a monochromator and finally detected by, e.g., a photomultiplier. With both the polarizer axis and the PEM axis oriented parallel with respect to each other, only an anisotropic sample with its optical axis oriented along  $45^\circ$  gives maximum modulation through the PEM and therefore maximum modulation in the detector output.

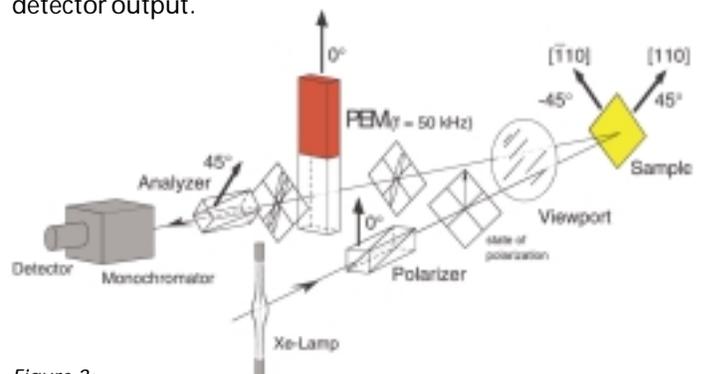


Figure 3: Optical set-up for RAS according to [2]. The diagram is from [3].

The PEM imposes on the light that is impinging on the detector a well-defined phase shift that oscillates with a modulation frequency  $\omega$  and having an amplitude  $\delta_{PEM}$ . The RAS signal is determined by normalizing the ac components  $I_{1\omega}$  and  $I_{2\omega}$  of the detector output to the respective dc component  $I_0$ :

$$\frac{I(t)}{I_0} = 1 + \operatorname{Re}\left(\frac{\Delta r}{r}\right) 2J_2(\delta_{PEM}) \cos 2\omega t + \operatorname{Im}\left(\frac{\Delta r}{r}\right) 2J_1(\delta_{PEM}) \sin \omega t \quad 3$$

$J_1$  and  $J_2$  in Eq. 3 are the Bessel functions of the first and second kind, respectively.

### Optical surface science applications

Ten years ago, the direct correlation between RAS spectra and surface reconstruction was first verified [4]. RAS was then predominantly considered as an optical surface science technique that allows for the transfer of UHV-borne knowledge about surface reconstructions and surface electronic states into the field of surface studies in gas phase environments. This has become an important issue, because traditional electron based UHV surface science techniques such as low-energy electron diffraction (LEED) and Auger electron spectroscopy cannot be applied in a gas phase. However, with the emergence of more sophisticated ab-initio theoretical approaches to the surface optical properties [5] in conjunction with recent advances in computational power, a very detailed agreement between experimental RAS data and its respective ab-initio calculated counterparts has been found. In Fig. 4 an InP (001) mixed dimer (In and P atoms) reconstruction serves as an example. The detailed geometry of this reconstruction (Fig. 4a) has been shown by RAS, scanning tunneling microscope (STM), and X-ray photo-emission spectroscopy (XPS) experimental work combined and directly compared to ab-initio theoretical calculations [5]. The various peaks in the experimental data (Fig. 4b), which have been measured at 25K in order to minimize thermal broadening of the RAS signatures [6], are present in all details as well as in the theoretical calculation. It is from the anisotropy in the electronic wave functions and transition matrix elements of the surface atom's valence electrons that these spectra originate.

### Epitaxial growth monitoring by combined RAS/Reflectance sensors

Before one could make use of the enormous surface sensitivity of RAS for process monitoring and control in semiconductor production-line environments several problems had to be solved. In basic research laboratories, experimenters study tiny, carefully treated and positioned pieces of crystal. However, for the production of optoelectronic and telecommunication devices the conditions are quite different: MOCVD reactors will hold typically 5-10 large wafers in a high temperature environment. The wafers move on a gas-foil that rotates with varying frequency and a considerable wobble. The growth of course takes place at the surface being assessed by the RAS sensor, but because semiconductor devices usually consist of many layers, the optical signals from the surface are modified by Fabry-Perot interferences. Therefore, it took several technical inventions (including the PEM-based RAS set-up [2]) and the direct combination of RAS and reflectance measurements through sophisticated software algorithms [7] to solve these problems.

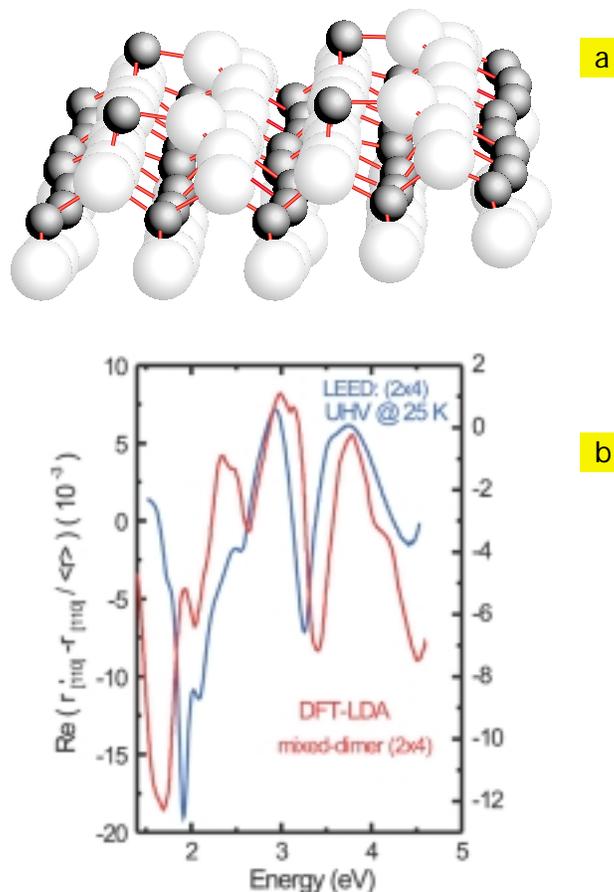


Figure 4: RAS on InP (001):  
 (a) Stick and ball model of the InP (001)-(2x4) surface [8];  
 (b) measured (blue) and calculated (red) spectra [5,6].



(continued from page 4)

Details of the system are described in "Review of Scientific Instruments," October 1999 (Wang & Oakberg, vol. 70, p. 3847), with the first commercial version, **Exicor 150AT**, delivered in January 2000. Preliminary results of photomask blank measurements were reported at the symposium on Photomask Technology in September 1999 (Wang & Troccoli, SPIE vol. 3873, p. 544). The significance of birefringence measurements relating to semiconductor photolithography was reported in the February 2000 issue of "Solid State Technology" (Wang, vol. 43(2), p. 77). In the short period of time since product introduction, 75% of the leading edge semiconductor stepper manufacturers (directly or through their supply chain) and over half of the major calcium fluoride and fused silica manufacturers have adopted Exicor technology. The technological innovation provided by Exicor was recognized at CLEO 2000 with a *New Product Award*.

### Birefringence Measurement Technology

PEMs are a specialized type of polarization modulator used to analyze polarization states when very high sensitivity and/or speed are required. These PEMs use a variety of optical materials such as fused silica for their optical elements. If there is birefringence in these optical elements, they may induce artifacts in polarization measurements made with PEMs. As a result Hinds Instruments has historically had a strong interest in the measurement and control of low levels of birefringence in optical materials.

Linear birefringence is a property of optical materials that creates a difference in the speed of light for two perpendicular polarizations of light passing through the sample. The birefringence produces a relative phase shift between these two polarizations. The degree of phase shift is called retardation and is measured in nanometers. Birefringence can either occur naturally or it can be artificially produced (stress birefringence).

Traditional methods of measuring the magnitude of retardation due to birefringence include viewing the optical sample between crossed polarizers. This method has poor sensitivity for low levels of retardation. An improvement on this measurement uses a rotating quarter-waveplate sandwiched with the sample between the polarizers. This method is tedious and still limited to a sensitivity of 1-2 nanometers.

Further improvement can be made using an electro-optical system with a continuously rotating waveplate, sandwiched with the sample between polarizers. Better sensitivity can be obtained, but the method is still limited by problems such as the uniformity of the waveplate and noise generated by operating rotating mechanisms.

Much higher sensitivity can be achieved by replacing the rotating waveplate with a photoelastic modulator. The signals produced are similar to those of the rotating waveplate, but an advantage of the PEM is that it produces a polarization modulation of the light beam having extremely

high accuracy and quality (i.e. modulation purity) with no mechanically moving parts. This is due to the resonant character of the PEM device. Another advantage is that the modulation is much faster, typically 50 kHz as opposed to (at most) a few hundred Hz for a rotating waveplate. The use of phase sensitive detection (lock-in amplifiers) produces repeatable sensitivities as high as  $\pm 0.005$  nanometers of retardation.

### The Exicor Product Line

The first model of this new low-level birefringence measurement instrument was the **Exicor 150AT** shown in the photo (page 4). The inaugural commercial prototype was delivered in January of this year. The 150AT meets the requirement for characterizing small optical materials, including photomask blanks, with very high sensitivity and repeatability. The sample stage accommodates optical materials as large as 150 mm x 150 mm and weighing up to 7 kg.

Another important application for Exicor is characterizing very large optical blanks used to manufacture precision optics in DUV photolithography. For this the **Exicor 350AT** was developed—accommodating sample sizes as large as 350 mm x 350 mm x 300 mm, weighing up to 25 kg. The first system was delivered a few months ago to an optics manufacturer in Japan. An **Exicor 450AT** for even larger optical blanks is now in development.

Certain customers have unique sample requirements which are not met by either the 150AT or the 350AT. Some want to integrate Exicor's birefringence measurement technology with their own translation system or custom software. Others do not need automatic scanning because of very small samples. To meet these needs we produced the **Exicor MT**. This is a modular version of the instrument which consists of a source module, a detector module, and an electronic control unit. A computer system and minimal software can also be provided.

These products and their specifications can be viewed on our Exicor web site, [www.exicor.com](http://www.exicor.com). Also much of our literature can be downloaded from the site.

Low-level birefringence characterization has suddenly become a critical requirement for high-end optical glass manufacturers. A technical representative from one of the leading European lithography optical system manufacturers drove several hours to discuss his Exicor requirements with us at an unrelated chemistry show, Analytica 2000. His unsolicited observation was that where as two years ago birefringence measurement was not a concern,—now it has suddenly become critical.

More than ever before, the optics industries require a means of measuring low levels of birefringence to qualify optical components and materials. Exicor represents a major technological breakthrough to meet this requirement with high sensitivity, speed, and repeatability as well as comprehensive data analysis capabilities.



Address correction requested.

PHONE: 503/690.2000  
FAX: 503/690.3000  
TOLL FREE: 1.800/688.4463  
EMAIL: info@hindspem.com  
WEB SITES: www.hindspem.com  
www.exicor.com

## INSIDE PEM

Reflectance Anisotropy Spectroscopy

Low-level Birefringence

© 2000, Hinds Instruments, Inc.  
Printed in USA. BB/5M/10-00

## ABOUT LayTec

(continued from page 1)

LayTec is a spin-off company from the Technical University of Berlin, specializing in real-time and in-line sensors for semiconductor epitaxy. With its EpiRAS™ sensors LayTec recently became the exclusive vendor of combined reflectance/RAS sensors for AIXTRON, the world's leading manufacturers of MOCVD systems. For LayTec's customized RAS/RDS spectrometers, ellipsometry software and other products, please see the company's internet site [www.laytec.de](http://www.laytec.de).

## UPCOMING TRADE SHOWS

DATE	EXHIBIT/CONF	LOCATION
Jan 23-25, 2001	Photonics West 2001	San Jose, CA
Feb 27-28, 2001	Micro lithography 2001	Santa Clara, CA
Mar 5-8, 2001	PITTCO 2001	New Orleans, LA
May 8-10, 2001	CLEO 2001	Baltimore, MD
Jun 18-22, 2001	LASER 2001	Munich, Germany
Jul 31-Aug 3, 2001	SPIE 2001	San Diego, CA

## Reflectance Anisotropy Spectroscopy...

(continued from page 4)

### Acknowledgements

Dave Aspnes, who invented the RAS/RDS technique and helped us with countless discussions, is thanked. Wolfgang Richter's permanent support is appreciated. He probably was the very first who fully recognized the vast potential RAS has for MOCVD. Many thanks also to all the diploma students and PhD students at TUB who have contributed with their work to today's level of expertise on RAS.

### Bibliography

1. J.-T. Zettler, Progress in Crystal Growth and Characterization of Materials 35, p. 27-98 (1997).
2. D.E. Aspnes, J.P. Harbison, A.A. Studna, L.T. Florez, and M.K. Kelly, J. Vac. Sci. Technol. **A 6**, 1327 (1988).
3. J. Zettler, W. Richter, K. Ploska, M. Zorn, J. Rumberg, C. Meyne, M. Pristovsek, Int. Workshop on Semiconductor Characterization, Washington, USA 1995, American Institute of Physics, p. 537 (1996).
4. I. Kamiya, D.E. Aspnes, H. Tanaka, L.T. Florez, J.P. Harbison, and R. Bhat, J. Vac. Sci. Technol. **B 10**, 1716 (1992).
5. W.G. Schmidt, E.L. Briggs, J. Bernholc, and F. Bechstedt, Phys. Rev. **B 59**, 2234 (1999).
6. T. Hannappel, S. Visbeck, M. Zorn, J.-T. Zettler, F. Willig, J. Cryst. Growth, in press; W.G. Schmidt, N. Esser, A. M. Frisch, P. Vogt, J. Bernholc, F. Bechstedt, M. Zorn, Th. Hannappel, S. Visbeck, F. Willig, W. Richter, Phys. Rev. **B 6**, 24 (2000).
7. J.-T. Zettler, K. Haberland, M. Zorn, M. Pristovsek, W. Richter, P. Kurpas, and M. Weyers, J. Crystal Growth, **195**, 151 (1999).
8. K. Lüdge, priv. comm.