ADVANCED EXPERIMENTAL TECHNIQUES IN STRUCTURE ANALYSIS

JAROSLAV FIALA

Photoacoustic spectrometry, diffraction and holography with photoelectrons, confocal and near-field optical microscopy, crystallographic image processing, and atom-probe tomography are discussed in some detail.

1. Introduction

In the limited space available, only a handful of methods will be highlighted that we selected so as to cover as broad and as full range of general conceptual aspects of the multitude of modern techniques for structural analysis as possible.

2. Photoacoustic spectroscopy

Photoacoustic effect is the process of acoustic wave propagation in a sample resulting from the absorption of photons. This process was first invented by Bell, Tyndall, and Röntgen in 1880. Sunlight was focused onto a sample placed in a closed cell containing air that was connected to a listening tube. When the sunlight was repeatedly blocked and unblocked, sound could be heard through the listening tube at the sunlight chopping frequency [1–3]. Spectra are obtained by scanning the wavelength of the light source while monitoring the output of the photoacoustic detector to observe variations in light absorption by the sample [4–6].

Originally, photoacoustic spectroscopy was applied in the ultraviolet-visible spectral region, but later has been extended to the infrared [7] and X-ray [8] spectra. Photoacoustic detection along with the scanning of a focused beam reveals the two-dimensional distribution of components (photoacoustic microscopy) [9, 10]. Furthermore, phase analysis of photoacoustic signals allows us to perform depth profiling, because the signal from the subsurface shows delay in response to the irradiation due to the heat diffusion through the covering layer. This delay time is a function of both the depth of the absorption and the thermal properties (thermal diffusivity) of the sample. This depth profiling potential promises application

Prof. RNDr. J. Fiala, CSc., ŠKODA Research Ltd., 316 00 Plzeň, Czech Republic.

of the photoacoustic method to three-dimensional components analysis (tomography) [11]. Scanning thermoacoustic electron microscopy (scanning electron acoustic microscopy) is another technique for imaging and characterization of thermal and elastic property variations on the scale of a few micrometers: A megahertz--chopped, focused electron beam in a scanning electron microscope generates sound in the sample, and the signal from a transducer attached to the specimen is used to form a scanned image [12, 13].

3. Diffraction and holography with photoelectrons, Auger electrons, and fluorescent X-rays

A photon excites a core photoelectron or an Auger electron from an atom. The outgoing electron wave a_0 is scattered from atoms $1, 2, 3, \ldots$ neighbouring the emitter, producing scattered waves $a_1, a_2, a_3, \ldots$. The interference of the unscattered wave a_0 with the scattered waves $a_1, a_2, a_3, \ldots$ produces the diffraction pattern. This diffraction pattern can then be analyzed at several levels so as to deduce structural information concerning the near-neighbour atoms around a given type of emitter, as well as the atomic composition. The diffraction pattern can be treated as a photoelectron (or Auger electron) hologram, with the unscattered wave a_0 being identified as the reference wave and the scattered waves $a_1, a_2, a_3, \ldots$ being identified as object waves. Or, the deexcitation of a core hole in emitter creates an outgoing fluorescent X-ray, with the unscattered and scattered components of this wave again serving as reference and object in a holographic exposure (X-ray fluorescence holography). The much greater penetration depths of X-rays in matter means that X-ray holography, by contrast with photoelectron (or Auger-electron) holography, can be used to probe nanostructures quite far below a surface [14–18].

4. Confocal and near-field optical microscopy

Confocal optical microscopy is a technique for increasing the contrast of microscopic images, particularly in thick specimens. By restricting the observed volume, the technique keeps overlying or nearby scatterers from contributing to the detected signal. The price for this is that the instrument must observe only one point at a time (in the stage scanning or laser-beam scanning version) or a group of separated points with very little light – in the multiplexed (disc) version. The longitudinal resolution of the confocal microscope is greater than that provided by the standard wide-field microscope. Confocal images appear to be slices of the object because only a thin region of the specimen is viewed at any time. Moving the focal plane yields a series of slice images. In this way, the confocal microscope can be used to digitize a three-dimensional specimen and create a volume data set [19].

Near-field imaging is a method for increasing lateral resolution of the conventional (far-field) microscopy which is limited by a half the wavelength of the light

being used (diffraction limited optics). In the near-field imaging, this limitation is avoided by using a probe with dimensions less than the wavelength to act as a source or detector. It is positioned in very close proximity to the sample, as close as its size, and by scanning the specimen beneath it, an image can be generated at a lateral resolution which depends on the probe size and the probe-to-sample separation rather than wavelength of light. Technically, the resolution of 0.35 nm has been achieved with active light sources based on exciton transport and quenching which occur only inside the source, while the sample is exposed to real evanescent photons [20–22].

5. Crystallographic image processing in HRTEM

Modern transmission electron microscopes for high-resolution work (HRTEM) have a resolution in the range of 200 pm, which is near the interatomic distances in molecules and crystals. Yet, HRTEM images are generally not directly interpretable in terms of atomic arrangement. There are several reasons for this: crystal misalignment, multiple scattering of electrons within the sample and optical distortions (defocus, astigmatism, beam tilt, random noise, etc.) The resolution of electron micrographs can be much improved (to at least 10 pm) by crystallographic image processing. The image processing is based on Fourier analysis of the experimental data in the form of a micrograph: First, the Fourier transform of the micrograph is calculated. Second, crystallographic (both translational and point group symmetry) constraints are imposed on the Fourier transform which is adjusted in this way. Third, inverse Fourier transform yields corrected micrograph [23–27].

6. Atom-probe (micro)tomography

The tomographic atom probe [28] combines an ultrahigh-resolution field-ion microscope with a high-resolution time-of-flight spectrometer [29]. The field-ion microscope is capable of producing images of the surface of a specimen in which each distinct point in the image is an individual atom [30]. The mass spectrometer is used to analyze the specimen chemically with single atom sensitivity for all elements. Use of a multidetection system enables the lateral positions of atoms to be determined for every chemical species [31]. As the depth investigation of the material proceeds, a layer-by-layer reconstruction of the analyzed volume can be undertaken and three-dimensional images of chemical heterogeneities may be produced on a subnanometer scale [32]. Using a laser pulse in place of conventional voltage pulse to remove atoms from the specimen opens the possibility to examine semiconducting materials, too [33]. The capabilities of tomographic atom probe [34] have been illustrated in the studies of grain boundaries [35], early stages of decomposition [36], ordering phenomena [37] or charging, implantation processes, and radiation damage [38].

7. Conclusions

The structure of matter is elaborated on a number of scales. That is why atomic resolution is not the whole truth and the micrographs taken by an atom-probe ought to be supplemented by something like photoacoustic spectra which tell the story of a macroscopic piece of material in terms of its total dynamic response.

REFERENCES

[1] BEL, A. G.: Philos. Mag., *11,* 1881, p. 510.
[2] TYNDALL, J.: Proc. Roy. Soc. London, *31,* 1881, p. 307.
[3] RÖNTGEN, W. C.: Philos. Mag., *11,* 1881, p. 308.
[4] ROSENCWAIG, A.: Photoacoustics and Photoacoustic Spectroscopy. New York, Wiley-Interscience 1980.
[5] KINNEY, J. B.—STALEY, R. H.: Annual Reviews on Mater. Sci., *12,* 1982, p. 295.
[6] RAO, C. N. R.—GANGULY, P.—SOMASUNDARAM, T.: J. Indian Chem. Soc., *63, 1986,* p. 1.
[7] McCLELAND, J. F.: Anal. Chem., *55,* 1983, p. 89A.
[8] MASUJIMA, T.—KAWATA, H.—KATAYOKA, M.—SHIWAKU, H.—YOSHIDA, H.—IMAI, H.—TOYODA, T.—SANO, T.—NOMURA, M.—LIDA, A.—KOBAYASHI, K.—ANDO, M.: Review of Sci. Instruments, *60,* 1989, p. 2522.
[9] ASH, E. A., ed.: Scanned Image Microscopy. New York, Academic Press 1980.
[10] BALK, L. J.: Surface and Interface Analysis, *9,* 1986, p. 47.
[11] MASUJIMA, T.—SHIWAKU, H.—YOSHIDA, H.—SANO, T.—AMEMIYA, Y.—KAWATW, H.—KATAOKA, M.—HOSHI, M.— NAGOSHI, C.—UEHARA, S.—IMAI, H.—ANDO, M.: Review of Sci. Instruments, *60,* 1989, p. 2468.
[12] HOLSTEIN, W. L.: J. Appl. Phys., *58,* 1985, p. 2008.
[13] DAVIES, D. G.: Phil. Trans. R. Soc. London, *A320,* 1986, p. 243.
[14] FADLEY, C. S.: Progress in Surface Science, *54,* 1997, p. 341.
[15] FADLEY, C. S.: Surface Science Reports, *19, 1993,* p. 231.
[16] PATTHEY, L.—BULLOCK, E. L.: J. Electron Spectroscopy and Related Phenomena, *83,* 1997, p. 99.
[17] ZHARNIKOV, M.—WEINELT, M.—ZEBISCH, P.—STEINRÜCK, H. P.: Thin Solid Films, *275,* 1996, p. 266.
[18] GOG, T.—LEN, P. M.—MATERLIK, G.—BAKR, D.—FADLEY, C. S.—SANCHE-ZHANKE, C.: Phys. Rev. Letters, *76,* 1996, p. 3132.
[19] WEBB, R. H.: Rep. Prog. Phys., *59,* 1996, p. 427.
[20] BETZIG, E.—TRAUTMAN, J. K.—HARRIS, T. D.—WEINER, J. S.—KOSTELAK, R. L.: Science, *251,* 1991, p. 1468.
[21] MORRIS, M. D., Ed.: Microscopic and Spectroscopic Imaging of the Chemical State. New York, Marcel Dekker 1993.
[22] WILLIAMSON, R.: Int. Lab. News, *27,* 1997, No. 6A, p. 16.
[23] WANG, D. N.—HOVMÖLLER, S.—KIHLBORG, L.—SUNDBERG, M.: Ultramicroscopy, *25,* 1988, p. 303.
[24] HOVMÖLLER, S.: Microsc. Microanal. Microstruct., *1,* 1990, p. 423.
[25] HOVMÖLLER, S.: Ultramiscroscopy, *41,* 1992, p. 121.
[26] XIAODONG ZOU: Electron Crystallography of Inorganic Structures – Theory and Practice. Chemical Communications of the Stockholm University, No. 5, 1995.
[27] LI, F. H.: Materials Chemistry and Physics, *47,* 1997, p. 118.

[28] BLAVETTE, D.—DECONIHOUT, B.—BOSTEL, A.—SARRAU, J. M.—BONET, M.—MENAND, A.: Review of Sci. Instruments, *64*, 1993, p. 2911.
[29] TSONG, T. T.: Physics Today, *46*, 1993, p. 24.
[30] HAASEN, P.—PILLER, J.: Z. Metallkunde, *78*, 1987, p. 757.
[31] MILLER, M. K.: Surface Science, *246*, 1991, p. 428.
[32] BLAVETTE, D.—DECONIHAUT, B.—BOSTEL, A.—SARRAU, J.—MENAND, A.: Comptes Rendus II, *317*, 1993, p. 1279.
[33] MILLER, M. K.: International Materials Reviews, *32*, 1987, p. 221.
[34] MILLER, M. K.: Vacuum, *45*, 1994, p. 819.
[35] MILLER, M. K.—SMITH, G. D. W.: MRS Bulletin, *19*, 1994, p. 27.
[36] DANOIX, F.—AUGER, P.—CHAMBRELAND, S.—BLAVETTE, D.: Microsc. Microanal. Microstruct., *5*, 1994, p. 121.
[37] BLAVETTE, D.—MENAND, A.: MRS Bulletin, *19*, 1994, p. 21.
[38] AUGER, P.—PAREIGE, P.—AKAMATSU, M.—VAN DUYSEN, J. C.: J. Nuclear Materials, *211*, 1994, p. 194.