Thin Solid Films xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Infrared ellipsometry for improved laterally resolved analysis of thin films

Karsten Hinrichs [a,*], Andreas Furchner [a], Guoguang Sun [a], Michael Gensch [b], Jörg Rappich [c], Thomas W.H. Oates [a]

[a] Leibniz-Institut für Analytische Wissenschaften – ISAS – e.V., Department Berlin, Albert-Einstein-Straße 9, 12489 Berlin, Germany
[b] Helmholtz-Zentrum Dresden-Rossendorf, Institut für Strahlenphysik/Institut für Ionenstrahlphysik und Materialforschung, Bautzner Landstr. 400, D-01328 Dresden, Germany
[c] Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Insitut für Si-Photovoltaik, Kekuléstr. 5, 12489 Berlin, Germany

ARTICLE INFO

Available online xxxx

Keywords:
FTIR-microscopy
Infrared spectroscopic ellipsometry
Molecular orientation
Thickness
Polymer film
Silicon oxide
Homogeneity

ABSTRACT

In the present article we discuss developments towards increasing the spatial resolution of infrared ellipsometry and ellipsometric microscopy for the study of thin films. Relevant aspects in the interpretation of observed peaks in the infrared (ellipsometric) spectra are discussed. In particular anisotropic effects in dependence of molecular orientations in organic films and the excitation of a macroscopic wave, the Berreman mode, in thin silicon oxide films are addressed. For correct interpretation of measured data optical simulations are essential to avoid incorrect conclusions on band frequency and assignments.

1. Introduction

Key points in the development of infrared (IR) ellipsometry in recent years are the extension of the spectral range to the Far Infrared–Terahertz regime [1–9], improved spatial resolution [10–13], adaption to measurements of solid–liquid interfaces [14–16] as well as improved temporal resolution. All these developments were essential for the comprehensive characterization of metamaterials, hybrid materials, thin films and interfaces as well as interaction and preparation processes. A particularly important role in the improvement of lateral resolution has been played by synchrotron ellipsometers at the NSLS in Brookhaven [5], ANKA in Karlsruhe [7], MAX-lab in Lund [9] and BESSY in Berlin [12]. The high brilliance of the 3rd generation light sources in standard mode of operation has enabled ellipsometric measurements of small samples or sample areas with lateral resolutions down to a few hundred micrometers at defined optical conditions and with high optical throughput [17–23]. Recently, time-resolved measurements up to the femto/picosecond range are foreseen [24] either using the time structure of the 4th generation light sources such as free-electron-lasers or laser-based time-domain ellipsometry [1,2,4]. Fig. 1 shows a schematic for the range of potential lateral resolutions in various schemes of infrared spectroscopic ellipsometry.

Using standard IR lab sources with low numerical aperture focusing optics, the typical lateral resolution is a few mm^2 for thin film sensitivity. Only for certain samples with a particularly strong response (e.g. strong oscillator or/and resonance band) sub-mm resolution may be achieved. Using brilliant sources such as lasers or storage rings the lateral resolution may be increased down to a few 100 μm. On the other hand small spot sizes can be also reached at larger opening angles using lab sources (e.g. globar) and a focusing optic with higher numerical aperture [10,11]. Recently the possibility of far field ellipsometric microscopy using a standard Fourier transform infrared spectroscopy (FTIR) microscope has been demonstrated [10] reaching a 40 μm lateral resolution for thin silicon oxide and polyimide films (Fig. 2). Using scanning and imaging microscopic concepts in the far field and brilliant light source measurements down to the diffraction limit in the range of a few μm [25,26] may be performed. Further improvement down to a few 10 nm lateral resolution is in principle possible by employing near-field concepts [27,28]. With the different types of far field ellipsometry the application of optical models is well established [29–34]. The required measurement concepts are dependent on the complexity of the sample and the depolarization and cross-polarization terms. They range from amplitude measurements in polarization dependent measurement schemes [33,34] to generalized and 4 × 4 Mueller-Matrix ellipsometry [3,6,29–32]. However, in all cases the application of optical modeling is essential when interpreting optical spectra of thin films. In the examples presented below, the critical role of optical modeling for the determination of correct resonance frequencies and average tilt angles of molecules will be shown.

2. Experimental and simulation details

2.1. Lab based infrared spectroscopic ellipsometry (IRSE)

The IR ellipsometric measurements were performed with a photometric rotating polarizer ellipsometer [33,35], externally attached to a

* Corresponding author.
E-mail address: karsten.hinrichs@isas.de (K. Hinrichs).

http://dx.doi.org/10.1016/j.tsf.2014.02.006
0040-6090/

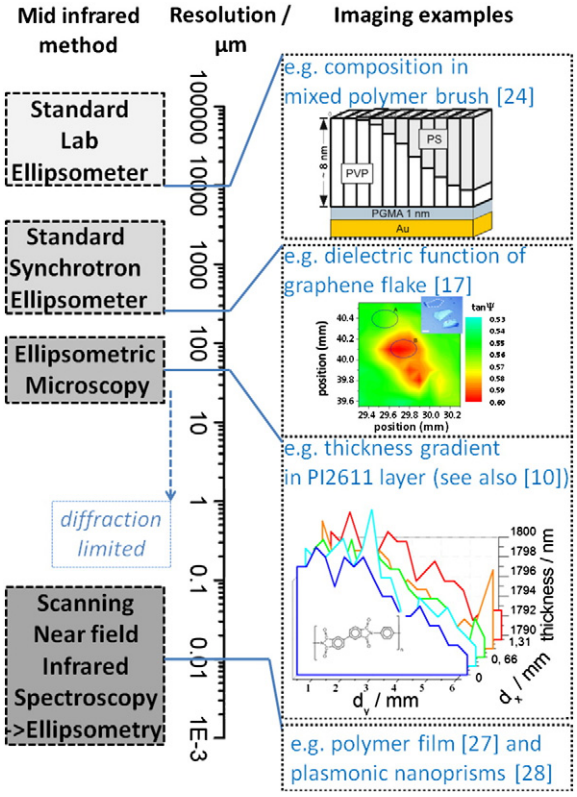

Fig. 1. Potential lateral resolutions in various infrared ellipsometric set-ups. On the right selected imaging examples are shown from top to bottom for lab ellipsometry with a few mm^2 lateral resolution (modified sketch, reprinted with permission from [24]. Copyright {2005} American Chemical Society.), synchrotron ellipsometry with a 175 × 245 μm^2 lateral resolution [This figure from [17], reprinted with permission from [17]. Copyright [2011], AIP Publishing LLC.], ellipsometric microscopy with a possible 40 × 40 μm^2 lateral resolution [for details see Ref. [10]] (mapping example with polarization dependent spectroscopy with 328 µm resolution is shown) towards 10 × 10 nm^2 with scanning near field techniques [27,28].

BRUKER 55 Fourier transform spectrometer. The experimental quantities are $\tan\Psi = |r_p| / |r_s|$ representing the ratio of the amplitudes of the p- and s-polarized complex reflection coefficients r_p and r_s (p: parallel, s: perpendicular to the incidence plane), and Δ, which is the phase shift between them. The probed spot on the surface was approximately 40 mm^2 at 65° incidence angle.

2.2. Synchrotron based IRSE

The IR ellipsometric measurements were performed with a photometric rotating analyzer ellipsometer [12,22] with microfocus and mapping option, externally attached to a BRUKER 66 FTIR spectrometer at the IRIS synchrotron beamline at BESSY. The probed spot on the surface is dependent on the size of the used micro-aperture about 175 × 245 μm^2 or larger at 65° incidence angle.

2.3. Lab based ellipsometric microscopy

The ellipsometric microscopy set-up (Fig. 2b) is in detail described in Ref. [10]. The lateral resolutions were in the range of 40 to 160 µm at 16° angle of incidence. For the ellipsometric FTIR microscopy measurements a Bruker Hyperion 3000 FTIR microscope with a Cassegrain objective (15×) with a numerical aperture of 0.4 was used. An optical plane aperture (OPA) was introduced which has the function to define an optical plane for the incident and reflected beam. A range of incident angles is defined by the numerical aperture and the central mirror of the objective (CM). A possible position for a retarder (Ret) as a phase shifting optical device for complete ellipsometric measurements is marked. By using a retarder the extension of the developed procedure towards generalized ellipsometric infrared microscopy is principally outlined. This approach is in general interesting for mapping of thicknesses and anisotropic properties of thin films or e.g. plasmonic, oxide, biofunctional, hybrid and metamaterials with high lateral resolution.

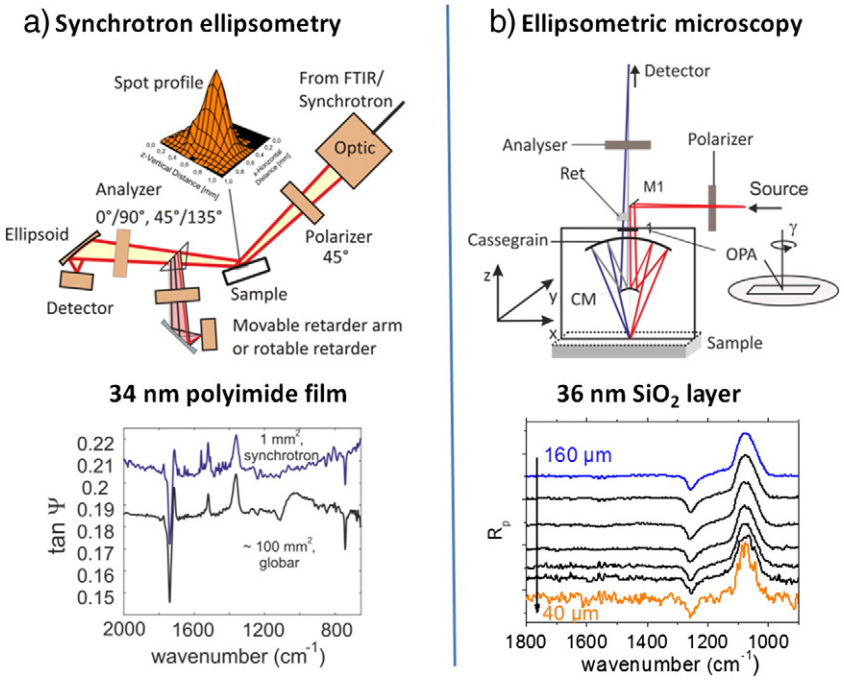

Fig. 2. Set-ups for a) synchrotron infrared ellipsometry and b) ellipsometric infrared microscopy (scheme modified from Ref. [10]). On the bottom left the lateral resolution limit is motivated for thin film studies: here an ellipsometric spectrum of a 34 nm polyimide film on a 1 mm^2 silicon substrate [modified spectrum from [13]. Reprinted with permission from the Society for Applied Spectroscopy is shown in comparison using a globar and a synchrotron source.]; on the bottom right p-polarized reflection spectra taken with the FTIR microscope in dependence of the lateral resolution are shown. Data from [10], reprinted with permission from [10]. Copyright {2013} American Chemical Society.

Please cite this article as: K. Hinrichs, et al., Thin Solid Films (2014), http://dx.doi.org/10.1016/j.tsf.2014.02.006