Molecule-solid interfaces studied with infrared ellipsometry: Ultrathin nitrobenzene films

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This paper aims to demonstrate the high capability of infrared spectroscopic ellipsometry (IRSE) for the characterization of very thin organic films and the organic to inorganic interfaces. It is shown that the detection limit of IRSE facilitates the investigation of ultrathin nitrobenzene (NB) films with monolayer sensitivity. This accounts for substrates from semiconductors to metals. The process of reoxidation of a NB terminated silicon (001) surface is also reflected in the infrared ellipsometric parameters and evidently proceeds despite the organic layer. As a complementary method, x-ray photoelectron spectroscopy (XPS) measurements were performed. © *2005 American Vacuum Society.* [DOI: 10.1116/1.1947801]

I. INTRODUCTION

Controlled deposition of ultrathin organic layers on technologically relevant substrates is likely to become one of the key technologies for nanopatterning of e.g., integrated circuitry devices.

The current research for optimized preparation procedures requires suitable surface and thin film diagnostic tools and the application on the industrial scale will in the long term afford an appropriate process control. We show that IRSE may be well suited for this purpose. The infrared ellipsometric parameters contain the contributions due to the elementary excitation of molecular vibrations and phonons, respectively. The comparatively narrow absorption bands from these elementary excitations facilitate the identification of layers. It has recently been shown that with our in-house built ellipsometric set-ups the detection limit of IRSE enables the investigation of hydrogen and oxygen on semiconducting substrates down to a thickness of less than one atomic layer.[1] In this paper we outline some aspects and benefits that arise from this high sensitivity and spectral contrast of IRSE for the characterization of ultrathin organic layers. We exemplarily show infrared ellipsometric measurements of nitrobenzene (NB) films grafted electrochemically onto silicon, gold, and TiO_2 substrates. Electrochemical techniques were earlier shown to allow well-controlled deposition of organic molecules in the monolayer regime.[2–4] Modification of silicon and TiO_2 surfaces by covalent bonding of organic molecules has been applied, for example, for surface electronic engineering[2,5] and to dye-sensitized solar cells.[6]

The objectives of this work are twofold. Most importantly, it is shown that the infrared ellipsometric parameters can be used to analyze monomolecular layers of nitrobenzene grafted onto different substrates. This includes, to our knowledge, the first IRSE study of an organic film of this scale on a semiconducting substrate. It is furthermore presented, that such an analysis can also be performed on sample areas smaller than 1 mm^2 when infrared radiation from a synchrotron storage ring facility is used.

II. EXPERIMENTAL PROCEDURES

The NB films were deposited in an electrochemical cell onto three different substrates: Si(001), gold/glass, and TiO_2/Ti/glass. The Si(001) wafers were purchased from

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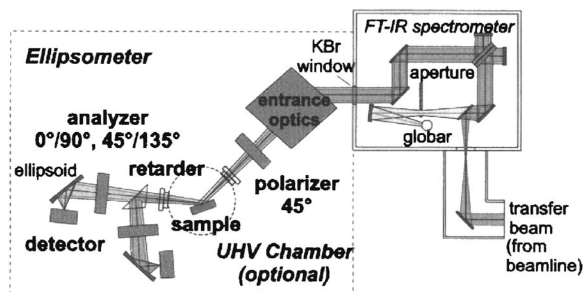

FIG. 1. Ellipsometry set-up at the infrared synchrotron beamline IRIS at the storage ring facility BESSY II. Note that a small, purpose-built, chamber can be implemented into the set-up for measurements under UHV conditions.

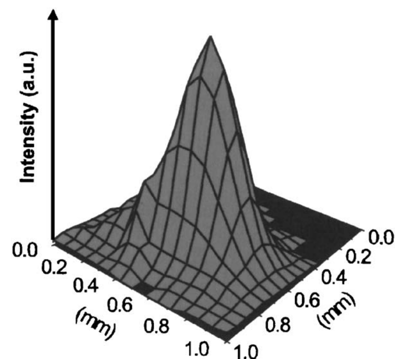

FIG. 2. Focus in the sample plane of the FT-IR synchrotron ellipsometer at ν=5155 cm^{-1}.

Crystal GmbH (Boron doped, resistivity 1–5 Ohm cm). The other substrates were prepared by sputtering of gold onto a glass substrate and by a standard sol-gel process on a Ti-coated glass substrate,[5] respectively.

The electrochemical grafting procedure is in detail described in Ref. 2. Thin organic layers of 4-nitrobenzene on silicon, TiO_2 and gold surfaces were prepared by electrochemical reduction of 4-nitro-benzenediazonium-tetrafluoroborate in acid aqueous solution. It has been proposed that organic molecules are bound covalently to Si and TiO_2 by forming either Si–C≡ (Ref. 7) or Si–O–C≡ (Ref. 8) and Ti–O–C≡ surface bonds,[9] respectively.

Spectroscopic ellipsometry, although typically working in the visible (VIS) to ultraviolet (UV) spectral range, is nowadays a well established method and comprehensive and excellent reviews of the measurement principle are given elsewhere (e.g., Ref. 10). In an ellipsometric experiment one determines the changes of the state of polarization of radiation upon reflection at the sample. Provided that the optical properties of the sample are isotropic within the surface plane of the sample, this state of polarization can (for a given angle of incidence) be characterized by the experimental quantities tan ψ and Δ. Tan $\psi=|r_p|/|r_s|$ represents the ratio of the amplitudes of the complex reflection coefficients r_p and r_s and Δ their relative phase shift. Tan ψ and Δ, in the following referred to as ellipsometric parameters, contain information on those material properties that contribute to the optical response of the sample.

Two different in-house built infrared ellipsometric set-ups, operating with different light sources, have been used in this study. One lab-based ellipsometer attached to a Bruker 55 Fourier Transform spectrometer working with radiation of a globar,[11,12] and a second ellipsometer attached to a Bruker 66 Fourier Transform spectrometer using infrared synchrotron radiation from the IRIS Beamline[13] at BESSY II (see Fig. 1). This set-up is described in detail in Refs. 14 and 15. The much higher brilliance of the synchrotron source enables the investigation of considerably smaller samples or sample areas. The focus in the sample plane is below one 1 mm^2 (see Fig. 2).

Complementary to the infrared ellipsometric analysis, the sample was introduced into an ultrahigh vacuum (UHV) chamber and analyzed by x-ray photoelectron spectroscopy (XPS). The spectrometer system consisted of a nonmonochromized Mg K_α x-ray tube ($h\nu$=1253.6 eV) and a Phoibos 150 electron analyzer (SPECS GmbH, Berlin-Germany). Photoelectron spectra were recorded in normal emission with a total apparatus resolution of 0.8 eV. The energy scale was calibrated with a clean gold foil using a binding energy of 84.0 eV for the Au $4f_{7/2}$ core level. The photoelectron spectra are referenced to the Fermi energy of the sample. The thickness of the organic layer on Si(001) of (2.3±0.7) nm was estimated from the relative intensities of the overlayer C $1s$ and substrate Si $2p$ core-level emissions, in the closed-overlayer-model.[16] This value exceeds the length of a NB molecule (0.7 nm) and therefore indicates that the film does not consist of only one single NB monolayer.

III. RESULTS AND DISCUSSION

A. NB films

Infrared ellipsometric parameters as determined for NB films grafted on Si(001), gold/glass and TiO_2/Ti/glass substrates are shown in Fig. 3. The infrared ellipsometric parameters are in the case of ultrathin films dominated by the optical response of the substrate. The magnitude of the contributions from the organic film is tiny in comparison. Still the sensitivity of our in-house built instruments allows detecting these contributions as can be seen in Fig. 4. The strongest contributions from the NB film are expected between 1300 cm^{-1} and 1650 cm^{-1}. In Fig. 4, the infrared ellipsometric parameters in this spectral range, and referenced against a measurement of the corresponding substrate are shown.

Characteristic bands originating from the grafting of the NB films are observed for all preparations. Comparison to the literature[17,18] allows an assignment of the bands at around 1350 cm^{-1} and 1520 cm^{-1} to the symmetric and asymmetric stretching vibrations of the NO_2 group in the NB molecules. The origin of the band at 1600 cm^{-1} is, in contrast, not as clear. Only this one single feature is observed in the infrared optical response of the electrochemically prepared films, while three bands of comparable amplitudes are observed in spectra of liquid NB (Ref. 18) or frozen solid multilayers on

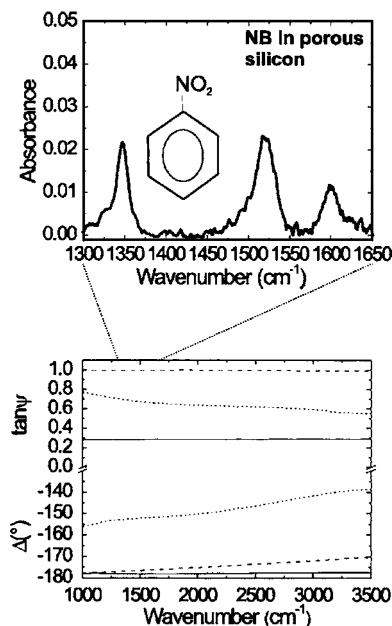

FIG. 3. Infrared ellipsometric parameters tan ψ and Δ of nitrobenzene (NB) films grafted on Si(001) (solid lines), gold/glass (dashed lines), and TiO_2/Ti/glass substrates (dotted lines). The angle of incidence was 65° in all measurements. The spectral region where the strongest contributions from NB molecules are expected is shadowed in grey. The absorbance of NB deposited in a porous silicon matrix is also shown (top panel) for comparison.

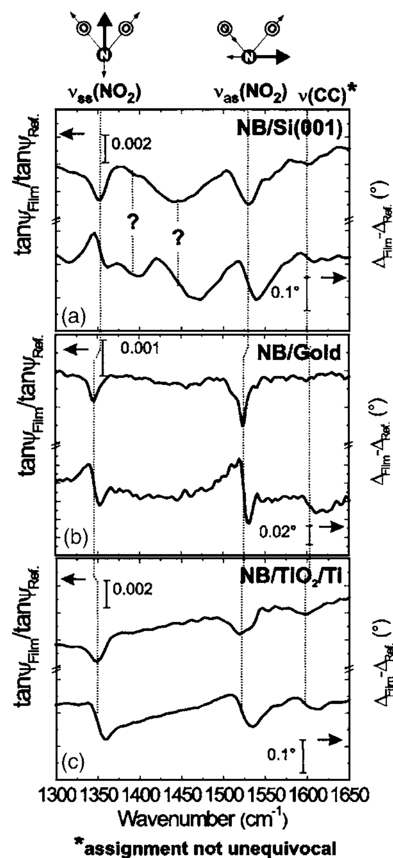

FIG. 4. Relative ellipsometric parameters of NB grafted onto (a) Si(001), (b) gold/glass, and (c) TiO_2/Ti/glass substrates. The angle of incidence was 65° in all measurements.

gold,[17] respectively. It can therefore not safely be decided if this band is due to contributions from C–C ring stretching vibrations or a fermiresonance.

There evidently are further contributions in the preparation on Si(001) shown in Fig. 4(a) that are not expected in pure nitrobenzene films, such as the broad band around 1450 cm^{-1}. Their origin is essentially unknown. Similar bands have been observed earlier in multiple internal reflection spectra of NB films grafted onto Si(111) and were then assigned to not further specified contaminations.[4,19] Interestingly bands in this region are also observed in some measurements of the NB film prepared on gold as can be seen in Fig. 5.

The contributions of the vibrational modes in the referenced infrared ellipsometric parameters in Figs. 4(a)–4(c) vary with respect to their line shape, amplitude and the frequencies where the bands are observed. Clarification, if this is in the individual case due to the bonding to the substrate, molecular orientation or different molecular densities, affords modeling in optical layer models (e.g., see Ref. 22) and is currently under investigation.

There is no direct evidence for covalent bonds between the molecules and the different substrates in the determined infrared ellipsometric parameters. The dominant bands in the spectral range of the presented experiments can be assigned to either molecular vibrations in the film, contaminations or silicon oxide as is shown below. However, special efforts have been meanwhile undertaken to improve the detectivity of the method also in the spectral range below 1000 cm^{-1}, aiming to identify the contribution from Si–C≡ bonds.

B. Reoxidation of NB/Si(001)

It is of high technological relevance whether ultrathin films of organic molecules can also serve to passivate the surfaces and prevent oxidation. IRSE has recently been shown to be an excellent tool to study the initial stages of the process of reoxidation of silicon by monitoring the spectral changes in the range of the ν(Si–O–Si) stretching vibration.[1] In Fig. 6(a) the infrared ellipsometric parameters of the NB/Si(001) sample after exposure to air for one month is shown. Contribution from residual silicon oxide is clearly

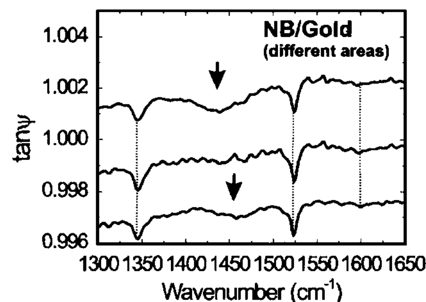

FIG. 5. Tan ψ determined for different areas on the NB/gold sample. The contribution at around 1450 cm^{-1} varies depending on the investigated spot. The angle of incidence was 65° in all measurements. Spectra were slightly shifted for comparison.

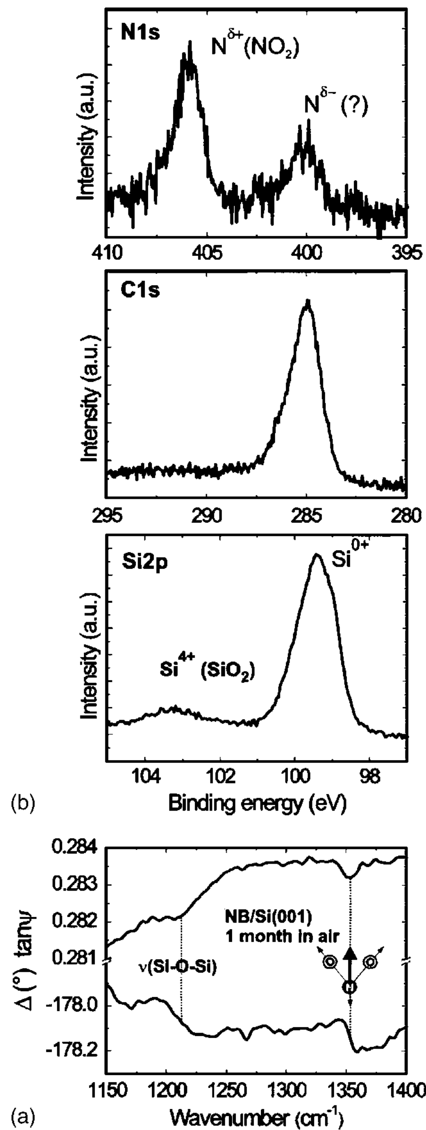

FIG. 6. NB/Si(001) after 1 month in air. (a) Infrared ellipsometric parameters and (b) photoemission from the N 1*s*, C 1*s*, and Si 2*p* core-level. XPS spectra are taken with 1253.6 eV photon energy.

visible in the spectra, while at the same time the presence of NB molecules is confirmed by the contributions of the NO_2 stretching vibrations e.g., the symmetric stretching vibration at around 1350 cm^{-1}.

These findings are supported by the XPS measurements shown in Fig. 6(b). Photoemission from the N 1*s* and C 1*s* core-level proves the presence of NB molecules. The thickness of the NB film of approximately 2 nm is evaluated from the intensity ratio of Si 2*p* and C 1*s*, assuming a closed layer model. The N 1*s* component at 406 eV is characteristic for nitrogen in the NO_2 group.[20] In the Si 2*p* spectrum a second component is observed that is chemically shifted to higher binding energies by 3.6 eV, which can be assigned to fully oxidised Si^{+4} in SiO_2.[20] An observed shifted second component in the N 1*s* core-level spectra at around 400 eV indicates the presence of contaminations or other chemical states in the films. Similar components have been observed earlier in the photoemission of NB films grafted on Si(111) surfaces[3,4] and in studies of NB molecules parasubstituted with $–NH_2$, and $–N(CH_3)$.[21]

IV. CONCLUSIONS

The most important result of this work is that the sensitivity of our IRSE apparatuses allows the identification of contributions from molecular vibrations in ultrathin NB films. This sensitivity can furthermore be achieved with a spatial resolution of below 1 mm^2 when using the FT-IR synchrotron ellipsometer. An obvious benefit of IRSE over ellipsometry in the VIS to UV spectral range is that the derived ellipsometric parameters facilitate a chemical analysis of the organic films by identification of the vibrational eigenmodes. Impurities or modified molecules in NB films on silicon and gold are identified by additional contributions to the infrared ellipsometric parameters. Reoxidation of the Si(001) surface underneath the organic layer is resolved in the IRSE and XPS measurements.

The determined infrared ellipsometric parameters can be used to derive information on the composition of the films. Furthermore, it has been shown that the line shapes in the infrared ellipsometric parameters of thin organic films can be utilized to derive information on the orientation of the molecules from calculation in appropriate optical models.[22]

UHV tight IR viewports have been successfully constructed and an IRSE apparatus is currently adapted to an UHV chamber to enable investigations in a defined vacuum environment. The FT-IR synchrotron ellipsometer furthermore enables mapping experiments on samples with laterally varying properties (e.g., of the composition).

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