Scanning photo-induced impedance microscopy—an impedance based imaging technique

Steffi Krause\textsuperscript{a,*}, Habib Talabani\textsuperscript{a}, Ming Xu\textsuperscript{a}, Werner Moritz\textsuperscript{b}, John Griffiths\textsuperscript{c}

\textsuperscript{a} Department of Chemistry, University of Sheffield, Sheffield S3 7HF, UK
\textsuperscript{b} Walther Nernst Institute, Humboldt University, Bunsenstr. 1, 10117 Berlin, Germany
\textsuperscript{c} UNISCAN Instruments, Sigma House, Buxton, SK17 9JB, UK

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Abstract

A.C. impedance spectroscopy is a valuable tool in the characterisation of electrochemical systems and new materials. However, the results obtained using this method are always surface averaged. A new technique, which is suitable for imaging the complex impedance of electrochemical and solid-state systems with good spatial resolution, has been developed. It is based on photocurrent measurements at field effect structures. A semiconductor–insulator structure serves as the substrate for the film under investigation. A pulsed and focused light beam scanned across the sample surface results in photocurrents, which provide information about the local distribution of the dielectric properties of the film. Thin films of poly methyl methacrylate were investigated as a model system. Absolute values of the impedance could be calculated from the photocurrent measurements using a simple calibration procedure. Good spatial resolution was achieved by using a thin epitaxial film of silicon as the semiconductor substrate. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Impedance spectroscopy is a powerful technique for investigating electrochemical systems, processes and new materials. Its main strength lies in its ability to interrogate relaxation phenomena whose time constants range over several orders of magnitude. However, the results obtained using classical a.c. impedance spectroscopy are always averaged across the entire sample area. Lillard et al. developed a method called Local Electrochemical Impedance Spectroscopy (LEIS) \cite{1}. It relies on the fact that a.c. current densities in the solution very near to the working electrode are proportional to the local impedance properties of the electrode. To measure only the component of the a.c. current normal to the surface a two-electrode microprobe was used, which allowed the determination of the a.c. potential drop between planes parallel to the electrode surface. LEIS allows some spatial resolution but is limited to measurements in electrolyte solutions. In this paper, a new technique, scanning photo-induced impedance microscopy (SPIM), suitable for the imaging of the complex impedance of thin films with good resolution will be presented.

1.1. Photoelectrochemistry

Photoelectrochemistry has been used widely to study photo-thermally induced current changes at metal surfaces and to characterise photo-electrochemical reactions at semiconductor | electrolyte interfaces \cite{2–4}. Photo-electrochemical reactions at semiconductor surfaces are usually determined by a competition between charge transfer and recombination of photo-generated electron–hole pairs. These processes can for example be affected by surface-adsorbed species, which act as photo-generated surface states. Particularly useful tools for obtaining recombination and charge transfer rate constants of photo-electrochemical reactions are techniques, which utilise a.c.-perturbation of the illumination.
intensity (intensity modulated photocurrent spectroscopy (IMPS)) or a.c.-perturbation of the potential (photo-electrochemical impedance spectroscopy (PEIS)) [5]. Photo-electrochemical measurements with good spatial resolution have been achieved by focusing light onto the semiconductor or metal surface using a scanning laser microscope (photo-electrochemical microscopy) [4]. A near-field optical microscope employed by Smyrl et al. allows photo-electrochemical imaging with sub-micrometer resolution [6].

1.2. Principle of scanning photo-induced impedance microscopy (SPIM)

The impedance based imaging technique described in this paper is based on the measurement of photocurrents at field-effect structures. In contrast to the photo-electrochemical techniques mentioned above, the semiconductor is, in this case, completely covered by an insulator avoiding any charge transfer at the semiconductor | electrolyte or semiconductor | metal interface. The system under investigation is deposited onto a semiconductor-insulator structure in one of the two arrangements shown in Fig. 1. Investigations can be carried out either in the gas phase with a thin metal film as the gate contact or in electrolyte solutions where the gate voltage is applied through an electrode in the solution. If field-effect structures such as metal–insulator–semiconductor structures [7] or electrolyte–insulator–semiconductor structures [8] are biased by an external voltage, no d.c. current is observed because of the presence of an insulator. The space charge region in the semiconductor can be controlled by the electrical field. Illuminating the structure with light that has energy larger than the band gap results in the generation of electron hole pairs. If the space charge region is in inversion the charge carriers are separated in this field. In the external circuit, a current will be observed which charges the two faces of the insulator. When the light is switched off the insulator will be discharged and the current will flow in the opposite direction. As a consequence, a modulation of the light intensity will lead to an a.c.-current of the modulation frequency. The dependence of this photocurrent on the external voltage is shown in Fig. 2 (curve A). The work function of the metal, charges in the insulator or a potential difference at the electrolyte | insulator (or metal | insulator) interface can depend on the gas or ion concentration leading to a shift of the photocurrent curve on the voltage axis (shift of curve A to B in Fig. 2). This principle has been exploited in so called light-addressable potentiometric sensors (LAPS) first introduced by Hafeman [7] in 1988, who carried out photocurrent measurements at electrolyte insulator semiconductor (EIS) structures with Si3N4 as the sensitive layer.

In contrast to LAPS, we suggest to use differences in the photocurrent in the saturation region of the photocurrent curve for SPIM. If the layer under investigation is deposited on the semiconductor–insulator structure, the photocurrent will be shifted as shown in Fig. 2 (shift of curve A to C). The difference in photocurrent is a function of the complex impedance of the layer added. Photocurrent measurements are advantageous in that charge carriers are only generated where light is injected. Due to the thin insulator (typically some 10 nm) only the field from this area affects the photocurrent. This results in a lateral resolution of photocurrent measurements. Local differences in the impedance can be detected in the scanning mode. An additional variation of the modulation frequency of the light results in a.c.-impedance spectra with lateral resolution.

In this paper, it will be shown that photocurrents can be related to the impedance of a thin polymer film using an appropriate calibration procedure. The results obtained using SPIM will be compared with data generated using classical a.c. impedance spectroscopy. A setup for high-resolution photocurrent measurements will be presented. Two-dimensional photocurrent measurements...
images of model structures will be shown to reflect the impedance of thin polymer films.

2. Experimental

2.1. Sample preparation

For the comparison between a.c.-impedance and SPIM measurements a p-type silicon wafer \((10^{15} \text{ cm}^{-3})\) with a 42 nm thick thermally grown oxide layer was used (obtained from the Microelectronics Centre at Southampton University). Some 20 nm chromium and 100 nm gold film were evaporated onto the silicon to form an Ohmic contact after etching with 10% HF. The structures were then heated to 350 °C for 6 min. Films of Poly methyl methacrylate (PMMA) (MW = 75 000, Aldrich, UK) were spin-coated onto the substrates from 4 to 9% solutions of the polymer in m-xylene (99%, Aldrich, UK) at 5000 rpm for 60 s. The polymer films were baked at 150 °C for 45 min. The thickness of the polymer films (see Section 3) was determined using a DEKTAK 3ST AUTO profiler. Some 20 nm chromium and 200 nm of gold were then evaporated onto the polymer films through a mask by thermal evaporation. The gate area was circular with a 2 mm diameter. For measurements in contact with an electrolyte solution, no gate metal was deposited onto the polymer layer.

For spatially resolved SPIM measurements, a silicon on insulator (SOI) wafer with a 6 μm thick epitaxial layer of p-type silicon and a 40 nm thick thermally grown oxide layer was obtained from the Microelectronics Centre at Southampton University. An ohmic contact was formed as described above. Layers of 1 μm thick positive photoresist were deposited by spin-coating and patterned by photolithography. A thermally evaporated metal layer consisting of 100 nm gold served as the gate contact.

2.2. A.C. impedance measurements

High-frequency capacitance-voltage (HF-CV) and a.c.-impedance measurements were carried out using an Autolab Frequency Response Analyser FRA2 with a potentiostat PGSTAT10 (Windsor Scientific, UK). An a.c. voltage with an amplitude of 10 mV superimposed on a d.c. voltage was applied between gate contact and ohmic backside contact of the field effect structures. A.C. impedance measurements were carried out at a constant d.c.-voltage of −3 V over a frequency range from 100 Hz to 10 kHz.

2.3. Experimental setup for SPIM measurements

The experimental setup for photocurrent measurements (shown in Fig. 3) consisted of an EG&G 7260 lock-in amplifier, an Nd YAG laser \((\lambda = 1064 \text{ nm})\) with a beam diameter of 1.8 mm, a chopper, a 50 × microscope objective (Olympus, SLMPlanFl50) and an XYZ positioning system developed by UNISCAN Instruments. All test structures were mounted onto the positioning system and illuminated from the back of the silicon substrate in order to avoid absorption of light by the polymer layers and reflection of light by the front gate. The positioning system and the lock-in amplifier were controlled using software developed by UNISCAN Instruments for this purpose. It allowed measurement of two-dimensional images of the photocurrent with a positioning accuracy of 1 μm and d.c.-sweeps and frequency sweeps at a single point of the sample.

For a comparison between a.c.-impedance measurements and SPIM, the focusing optics was removed from the setup in order to illuminate the entire gate area. In this case the light was sinusoidally modulated using an acousto-optic modulator (ISOMET 1205C-2) in order to achieve linearity between laser intensity and photocurrent.

Measurements in electrolyte contact were carried out using the custom built cell shown in Fig. 4. An O-ring with an inner diameter of 3 mm determines the area of...
the sample exposed to electrolyte. Measurements were carried out in a 0.1 M KCl solution. A silver wire coated with silver chloride served as the gate electrode. As in the case of gas phase measurements, the back of the semiconductor was illuminated by the laser. In order to illuminate the entire gate area, which in this case was greater than the cross section of the laser beam, the diameter of the laser beam was increased using a beam expander.

3. Results

3.1. Comparison between classical a.c.-impedance measurements and SPIM

The aim of this investigation was to show that the impedance of thin polymer films extracted from photo-current measurements at field effect structures corresponds directly to the impedance obtained by classical a.c.-impedance measurements. Thin films of poly methyl methacrylate were chosen as a first model system since they displayed a simple capacitive behaviour.

Classical a.c.-impedance measurements were carried out at the polymer coated silicon–silicon dioxide structures over a frequency range from 100 Hz to 10 kHz using a frequency response analyser (FRA). The impedance measured \((Z_{\text{FRA}})\) represented the sum of the impedance of the polymer layer and the impedance of the silicon–silicon dioxide base structure (Eq. (1)). Since the structures were biased towards accumulation during these measurements, the impedance of the base structure also corresponded to the impedance of the silicon dioxide layer.

\[
Z_{\text{FRA}} = Z_{\text{polymer}} + Z_{\text{base}}
\]  

where \(Z_{\text{polymer}}\) is the impedance of the polymer layer and \(Z_{\text{base}}\) is the impedance of the base structure Si–SiO\(_2\)–metal. In order to obtain the impedance of the polymer layer, the impedance of the base structure \((Z_{\text{base}})\), Si–SiO\(_2\)–metal, was measured and subtracted from the impedance of the Si–SiO\(_2\)–polymer–metal structures.

Photocurrent spectra were obtained by biasing the structures towards inversion. The change of the photocurrent with the polymer thickness showed the expected trend. The thicker the polymer layer the lower was the photocurrent. The impedance obtained by photocurrent measurements \((Z_{\text{photo}})\) can again be defined as the sum of the impedance of polymer film and base structure (Eq. (2)):

\[
Z_{\text{photo}} = \frac{V_{\text{photo}}}{I_{\text{photo}}} = Z_{\text{polymer}} + Z'_{\text{base}}
\]  

where \(V_{\text{photo}}\) is the photovoltage and \(I_{\text{photo}}\) is the photocurrent.

The impedance of the base structure during the photocurrent measurements \((Z_{\text{base}})\) differed from the impedance measured in accumulation \((Z_{\text{base}})\), since the photocurrent measurements were carried out in inversion, where the capacitance of the space charge region could no longer be neglected.

Two different calibration procedures were used to obtain absolute values of the impedance of the polymer films from photocurrent measurements.

3.1.1. Calibration using known impedance

In the first calibration procedure, only the photocurrent was measured directly of the quantities given in Eq. (2). Rather than measuring the photovoltage, a calibration procedure was developed to determine the photovoltage and the impedance of the structure. The calibration was carried out by introducing known impedance elements into the circuit. A range of resistors was switched in series with the base structure and the photocurrent measured (Fig. 5). For these experiments, the impedance can be defined according to Eq. (3):

\[
Z_{\text{photo}} = \frac{\frac{V_{\text{photo}}}{I_{\text{photo}}}}{Z'_{\text{base}}} = Z_{\text{photo}} + R
\]  

where \(R\) is a known resistor in series with the base structure.

Since the base structure behaved approximately like a pure capacitance, its impedance can be expressed as (Eq. (4)):

\[
Z'_{\text{base}} = \frac{1}{j\omega C_{\text{base}}}
\]  

where \(C_{\text{base}}\) is the capacitance of the base structure during photocurrent measurements, and \(j = \sqrt{-1}\).

For the modulus of \(1/I_{\text{photo}}\) it can then be written (Eq. (5)):

![Fig. 5. Dependence of the photocurrent on the resistance switched in series with silicon–silicon dioxide–metal base structure at 1 kHz (dots). The solid line represents a fit according to Eq. (5).](image-url)
The capacitance of the base structure was determined to be $C_{\text{base}} = 336 \text{ pF}$ from a non-linear fit of Eq. (5) for a fixed frequency of 1 kHz with the fit parameters $C_{\text{base}}$ and $V_{\text{photo}}$. Experimental data and fit result are presented in Fig. 5. Using the impedance (Eq. (4)) and the photocurrent measured at the base structure, the photovoltage was calculated for all frequencies. The impedance of the polymer layer was then calculated using Eqs. (2) and (4).

Both, the impedance of the polymer layer $Z_{\text{polymer}}$ calculated from the photocurrent measurements, and the impedance of the polymer layer, measured using classical a.c. impedance spectroscopy are presented in Fig. 6 for two different polymer thicknesses. The photocurrent derived impedance correlates very well with the classical a.c.-impedance data at frequencies above 100 Hz. Deviations observed at lower frequencies may be related to a lack of linearity between laser intensity and photocurrent.

3.1.2. Calibration by measurement of photocurrent and photovoltage

An alternative method of estimating the absolute impedance of a polymer layer from SPIM data is to measure both, the photocurrent and the photovoltage and calculate the impedance according to Eq. (2). The impedance obtained using this method also correlates well with the thickness of the polymer layer (Fig. 7). A linear relationship between the impedance of the polymer layer and the polymer layer thickness was obtained. The straight line fit slightly deviates from the origin. However, the 95% confidence interval shown in Fig. 7 indicates that this deviation is well within the experimental error.

This calibration procedure is more straightforward than the one described in the previous paragraph, but it requires two measurements in different measurement modes on each point of the surface if an investigation is to be carried out with lateral resolution. Hence, both methods of calibration are currently used in parallel.

3.1.3. SPIM measurements at thin polymer films in contact with an electrolyte solution

As indicated in the introduction, the metal gate contact can be replaced by an electrolyte and thin polymer films be studied directly in contact with an electrolyte solution. As before, thin films of poly methyl methacrylate were used as the model system. To obtain the impedance of the polymer layer by SPIM, photocurrent and photovoltage were measured, and the calibration procedure described in Section 3.1.2 was employed. Fig. 8 shows a comparison of the impedance data of the thin polymer films obtained by SPIM with the impedance derived from SPIM and the impedance obtained by a.c.-impedance spectroscopy. Although the impedance values of the different polymer layers are quite close to each other, a good correlation between the impedance derived from SPIM and the impedance obtained by a.c.-impedance spectroscopy was observed.
3.2. SPIM-imaging

It has been shown that by using a suitable model, impedance data of thin films can be estimated from the photocurrent measurements at field effect structures in inversion. It will now be demonstrated that these photocurrent measurements can also be carried out with good spatial resolution. As reported by Nakao et al., the resolution of photocurrent measurements can be improved by thinning the silicon substrate [9]. Hence, an SOI wafer with a thin epitaxial film of p-type silicon was used as the semiconducting substrate. A layer of patterned photoresist served as the model system (see Fig. 9A). Fig. 9B shows an area scan of the photoresist pattern and Fig. 9C a high-resolution line scan. The pictures clearly demonstrate, that local differences in the photocurrent and, therefore, the impedance can be detected by SPIM with a resolution in the micrometer range. Further improvement of the resolution can be expected by replacing silicon with GaAs as the semiconducting substrates since GaAs was shown to have a considerably shorter diffusion length of the minority charge carriers than Si [10].

4. Conclusions

A new technique, SPIM, suitable for imaging the complex impedance of thin films with good spatial resolution has been developed. The comparison between SPIM and a.c.-impedance measurements has shown that absolute values of the impedance of thin films could be extracted from photocurrent and photovoltage spectra at field-effect structures over a range of frequencies using a suitable calibration procedure. SPIM also has the advantage over other electrochemical and impedance imaging techniques that it can be used to study materials in the gas phase as well as in electrolyte solutions. It is envisaged that SPIM with its current resolution in the micrometer range can potentially be used for the characterisation of multiphase materials such as blockcopolymers, the investigation of the local swelling behaviour of polymers in solutions or the characterisation of biological materials. The materials to be investigated have to be deposited on a semiconductor insulator substrate using standard coating techniques such as spin coating or casting in order to carry out localised photocurrent measurements. In contrast to other electrochemical scanning techniques such as LEIS, no probe is required. The technique can, therefore, be regarded as completely non-invasive.

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