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Scanning Photo-Induced Impedance Microscopy—Resolution studies and polymer characterization

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Abstract

Scanning Photo-Induced Impedance Microscopy (SPIM) is an impedance imaging technique that is based on photocurrent measurements at field-effect structures. The material under investigation is deposited onto a semiconductor–insulator substrate. A thin metal film or an electrolyte solution with an immersed electrode serves as the gate contact. A modulated light beam focused into the space charge region of the semiconductor produces a photocurrent, which is directly related to the local impedance of the material. The absolute impedance of a polymer film can be measured by calibrating photocurrents using a known impedance in series with the sample.

Depending on the wavelength of light used, charge carriers are not only generated in the focus but also throughout the bulk of the semiconductor. This can have adverse effects on the lateral resolution. Two-photon experiments were carried out to confine charge carrier generation to the space charge layer. The lateral resolution of SPIM is also limited by the lateral diffusion of charge carriers in the semiconductor. This problem can be solved by using thin silicon layers as semiconductor substrates. A resolution of better than 1 μm was achieved using silicon on sapphire (SOS) substrates with a 1 μm thick silicon layer.
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1. Introduction

Electrochemical impedance spectroscopy as a macroscopic technique has the disadvantage that the data obtained always represents the properties of the structure under investigation averaged across the whole sample area. To investigate the behaviour of heterogeneous systems, impedance measurements with good lateral resolution are desirable. In recent years, different techniques capable of providing information about the local impedance have been proposed. One of the most successful approaches to date is local electrochemical impedance spectroscopy (LEIS). It uses a two-electrode probe to measure the local current density close to the surface of the working electrode [1,2]. Problems associated with the technique are limited miniaturization of the two-electrode probe, that only current densities normal to the surface are considered and that there is no feedback mechanism inherent in the technique that allows positioning of the probe at a defined distance from the surface. Lohrengel et al. developed a technique that provides a very well-defined measurement area [3,4]. Glass capillaries with a silicone rubber gasket at their end (diameter >10 μm) are used to position electrolyte droplets onto the surface of the working electrode. The smallest usable measurement area was estimated to have a diameter of about 6 μm depending on the impedance of the substrate [4]. This technique is particularly useful for the characterization of solid surfaces where information about inclusions, grain boundaries and grain-dependent passivation is sought. Katemann et al. proposed to use an AC scanning electrochem-

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ical microscopy (SECM) setup to image the impedance of a substrate surface [5]. At low electrolyte concentrations and sufficiently high frequency the contribution of the double-layer capacitance of the tip to the total impedance of the system is negligible and the tip current magnitude is strongly associated with the solution resistance and the conductivity of the electrode surface. Compared to LEIS, this technique has potential for improving the spatial resolution by using smaller microelectrodes as scanning probes.

1.1. Scanning Photo-Induced Impedance Microscopy (SPIM)

The localized impedance techniques described above are all based on scanning microelectrode probes. A different approach based on scanning a laser beam across a semiconductor substrate was developed by Krause et al. [6]. The technique, Scanning Photo-Induced Impedance Microscopy, is specifically aimed at the investigation of the local dielectric properties of thin films, membranes and biological materials. A film of the material under investigation is deposited onto a semiconductor/insulator substrate. A gate contact on the material is created by depositing a thin metal layer onto the film or by exposing the material to an electrolyte solution. In the latter case, the circuit would be completed with an electrode immersed in the solution. A bias is applied between the gate electrode and the semiconductor substrate to create an inversion layer at the semiconductor/insulator interface. Light focussed into the space charge layer of the semiconductor generates electron–hole pairs that separate in the field of the inversion layer causing a current to flow in the outer circuit. Electron–hole pairs generated by the light in the bulk of the semiconductor can also contribute to the current if they diffuse into the space charge region. The current is confined to the illuminated area of the semiconductor and provides information about the local impedance of the material deposited onto the structure. Modulation of the light at different frequencies allows measurement of impedance spectra as will be demonstrated using cellulose acetate film as an example (see Section 3.3).

1.1.1. Resolution of SPIM

In terms of experimental approach and substrate materials, SPIM is very closely related to Light Addressable Potentiometric Sensors (LAPS) and the Scanned Light Pulse Technique (SLPT) [7–9]. While SPIM detects photocurrent changes with a metal–insulator–semiconductor (MIS) or an electrolyte–insulator–semiconductor (EIS) structure biased towards inversion (saturation region of the photocurrent–voltage curve) to detect local changes in the impedance, LAPS and SLPT determine shifts of the current–voltage characteristic along the DC voltage axis at a bias near the flat band point to detect local changes in potential. Hence, results obtained regarding the resolution can easily be transferred from one technique to the other.

Factors that can influence the resolution of all three techniques are the quality of the focus in the space charge layer of the semiconductor, the scattering of light within the structure and the diffusion of charge carriers. Electron–hole pairs generated in the bulk of the semiconductor do not only diffuse towards the space charge region in the semiconductor where they produce a current, but they also diffuse laterally, out of the illuminated area, resulting in poor resolution. Two main strategies have been pursued to improve the lateral resolution of SPIM and LAPS. The traditionally used single crystalline silicon can be replaced with semiconductors that have shorter charge carrier life times. Promising results have been obtained using GaAs [10]. The effective diffusion length was determined to be about 3 μm in a 500 μm thick substrate. Unfortunately, the problem of a high quality gate insulator on GaAs with low leakage current has not been solved yet. Another promising material is amorphous silicon [11]. Films of the material with a thickness ranging from 0.3 to 1.3 μm were deposited onto a glass substrate with a thin film of ZnO as the ohmic contact. SiO_2/Si_3N_4 films were deposited as the gate insulator. The effective diffusion length in this arrangement was too short to be measured with the experimental setup used (i.e. < 100 nm). Hence submicrometer resolution of photocurrent measurements is possible using this material if a good quality optical setup is used. However, problems caused by multiple reflections in the multilayer structure used for these experiments have yet to be solved.

Another strategy for improving the resolution involves the use of a thin silicon substrate. Theoretical considerations and experimental results described in the literature suggest that the resolution of photocurrent measurements is closely related to the thickness of the silicon [12,13]. Nakao et al. achieved a resolution of about 10 μm for LAPS using a 20 μm thick silicon substrate [12]. Ito reported a resolution of 5 μm obtained with a 0.5 μm thick silicon layer [14]. However, in this case, the resolution was determined by the size of differently doped islands in the silicon resembling a microelectrode array. Hence, a conclusion about the maximum possible resolution could not be drawn from these experiments.

In this paper, two strategies for improving the resolution were investigated more closely.

1. To carry out SPIM measurements, it is necessary to focus light into the space charge region of the semiconductor from the back of the substrate, i.e. while light is travelling through the semiconductor, charge carriers are produced throughout the bulk of the silicon and not only in the space charge region (Fig. 1A). Two photon experiments have been used in the past to characterise electrical circuits using a technique called two-photon optical beam induced current imaging (TOBIC) [15,16]. In this case, light of energy smaller than the bandgap of silicon is used. Using high intensity illumination by focusing a beam from a high energy pulsed laser delivering femtosecond bursts at high frequencies, two photons can arrive almost simultaneously and combine to generate electron hole

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