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Linköping University Post Print

N.B.: When citing this work, cite the original article.

Original Publication:
http://dx.doi.org/10.1016/j.proche.2009.07.056
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Postprint available at: Linköping University Electronic Press
http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-58423
Proceedings of the Eurosensors XXIII conference

Optically addressable field effect nano-environments for chemical imaging

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Abstract

An optically addressable field effect device incorporating functionalized nano-environments is demonstrated for the generation of multiple response signatures of a same analyte-sensing material combination. The device can operate unsupervised and different response mechanism can be simultaneously tested and incorporated in a multidimensional response. This proof of concept explores the well-known Pd-H₂ case, while the concept is a breadboard for chemical imaging experiments.

field effect chemical sensing; chemical images; scanning light pulse technique; suspended gate devices; optical chemical sensors

1. Introduction

Light addressable interrogation of field effect chemical sensing devices, such as in the scanning light pulse technique (SLPT[1]) offer a versatile platform for the study of sensing mechanisms and the generation of high resolution chemical images, which are an alternative to collections of discrete devices, composing sensing arrays in electronic noses[2]. In this technique a focused and micro-positioned laser beam generates a local transient photocurrent in a field-effect device, for instance a metal-oxide-semiconductor (MOS) capacitor. The charge content of the local photocurrent (\( u \)) is related to gas sensitivity through flat-band voltage shifts in the \( u \) versus bias voltage characteristics (\( u(V) \)) or changes in the gate conductance \([3,4,5]\), which upon subsequent scanning of the laser beam allows to construct a photocurrent map suitable with chemical recognition.

Chemical sensing with field-effect devices, as hydrogen sensors based on Pd gate metal oxide semiconductor (MOS) capacitors[6] is a consolidated sensing approach with thirty years of existence. Catalytic metals are typically used as gate electrodes in this kind of structures, providing selective adsorption/dissociation of target molecules (or their reaction product species) that become detected by modulating the semiconductor surface potential. This sensing procedure demands the concurrent biasing and physical access of the chemical stimulus to a same place[3]. Unfortunately, these are conflicting requirements and, e.g., thick gates that provide good biasing prevent the access to the metal-insulator interface, whereas the ultrathin electrodes that favor the access are unstable for biasing. As a result a trade off between stimuli access and electrode stability is found in practical devices [1,2].

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In SLPT, a two-dimensional scanned laser beam excites local photocurrents (typically illuminating through a semitransparent metal gate), which carry specific chemical information depending on the gate composition at the laser coordinate. The use of thickness, composition and temperature gradients are the natural evolution from discrete devices, where the effect of morphology and temperature on the sensing properties of the gate is well known [1,3,6]. However, devices specially designed for SLPT [3-5] permit to disentangle the electrical from the chemical functions of the sensing gates. In particular, grid-gate devices provide a stable inert biasing electrode besides SiO2 surfaces where sensing materials can be deposited. In such configuration, the sensing materials are not restricted to continuous metal films, but metal cluster and arbitrary functional materials can be used [5].

One further refinement for this structure would be to incorporate functionalized nano-environments into the sensing breadboard. In this paper, we present first results of a device combining functionalized optically addressable nano-environments with a grid-gate structure. Thus, we investigate the extension of the grid gate concept by combining such a device with an optically transparent microstructure that defines micro-regions delimiting nano-cavities on the grid gate structure. Deposition of functional sensing materials on the grid and on microstructures suspended on the grid confers varied detection mechanisms to these nano-environments.

2. Experimental

Grid gate devices were fabricated from (100) p-type silicon wafer, 10-20 Ω.cm and 525 µm thick, thermally oxidized to 200 nm. On the SiO2 a 300 nm Al grid was produced by wet Al etching and standard photolithographic procedures. Fig. 1a illustrate details of the grid gate. The devices were completed with a 200 nm thermally evaporated Al backside contact.

The micro-regions where defined by an optically transparent microstructure mounted on top of the grid-gate. 30 µm high SU-8 pillars on glass slides were produced by photolithographic methods using a Cr-etched mask directly transferred on the glass surface[7]. In this fabrication procedure SU-8 is deposited on the Cr mash and exposed to UV through the glass substrate. The procedure contributes to surface adhesion and provides good control of pillar tapering, and in this case also create a self aligned chromium mask that enables illumination of the grid-gate device only through the pillars. The geometry of the pillar forest is shown in Fig. 1b, and comprises circular and triangular pillars.

Fig. 1a) Scheme of the proposed device with functional materials deposited in a combinatorial arrangement. b) SU-8 pillar structure supporting suspended materials in regions 2 and 4. Cross-section of the device (not in scale) for the condition 2. c) Standard SLPT measuring setup using a 635 nm laser as a light source focused on a ~200 µm spot on the sensor surface. The operating temperature was 85°C.
Thermally evaporated Pd films (5 nm thick, gravimetrically controlled with an Inficon XTC) are used as sensing material, and deposited on rectangular areas defined by a mechanical shadow mask. The Pd films are simultaneously deposited on the grid gate and pillar forest and transversally mounted in the final device in order to provide 4 different regions: Pd on Grid, Pd on pillars, Pd on grid and pillars and no Pd.

The nano-environments are created by the spacing between the SiO2 surface and the tips of a SU-8 pillar forest defined by the Al grid thickness (300 nm). The SEM image (Fig. 1b) on the right shows the geometry of the forest used in this work. The pillars are supported on a glass slide, and light can only be transmitted through the pillars due to a self-aligned Cr mask on the glass surface. The cross section (not in scale) highlights the formation of the nano-environments as the separation between the pillar tips and the SiO2 surface. According to the proposed arrangement a same functional material can be tested in multiple ways (numbers 1 to 4 in the figure), and at the same time a suspended functional material can be in contact with the biasing grid or not (cross section).

The device is mounted in a tight gas cell with a glass window 20 x 25 x 2 mm3, which has a thermally controlled base (golden coated brass) that also serves as back-side contact. The base is heated by a halogen lamp to 85 °C by illuminating the underside of the platform. During SLPT measurements, the laser is scanned over the device using an X-Y positioning table, with a spatial accuracy of 1.3 µm, on which the heater, sample, and gas chamber are mounted (Fig. 1c). The laser beam (Melles Griot laser diode 5 mW, = 635 nm modulated at 2 kHz) was modulated by a reference sinusoidal wave from the lock-in amplifier (Princeton Applied Research, PAR 186A) and subsequently collimated by an aperture plate and focused with an objective lens. The resulting illuminating spot locally excites the MOS structure within an area of 200 µm in diameter. The current transients produced by the pulsed light beam are amplified (Stanford Research current amplifier, SR 570) and integrated with the lock-in amplifier (PAR 186A) providing a signal proportional to the charge content of the current transient. This signal (u) generated under the laser spot is that used for composing the photocurrent maps (e.g. Fig. 2a).

The sensor was exposed to synthetic dry air as reference atmosphere and 2500 ppm of H2 in air as testing gas, using an automatic gas bench supplying a total constant mass flow of 100 ml/min. The difference between these photocurrent maps obtained for a reference atmosphere and the target environment can thus render conventional chemical images.

3. Results and Discussion

Fig. 2a shows the photocurrent map of the device for a biasing condition in the inversion region, where grid gates typically sense changes in surface conductivity [3,4]. Eight different locations on the areas 1 to 4 are marked in the
figure, also indicating the approximate size of the illuminating beam. Contrast in Fig. 2a is determined by differences of amplitude in the $u(V)$ characteristic, which correspond to optical modulations of the photocurrent generation when the beam is masked thought the Al grid and the Pd films. A larger amplitude is observed in regions 3 and 4, because the grid is covered with a very thin layer of Pd that helps to bias the space between Al electrodes, while introducing minimum attenuation of the laser beam. The photocurrent amplitude of region 4 is smaller than region 3 because of the extra optical absorption introduced by Pd on pillars in this region.

Fig. 2a is produced by scanning the beam in 150 x 150 steps, which for the indicated beam spot size produce a photocurrent image that is the convolution between the beam and the pillar - grid structure. Photocurrent maps such as that in Fig. 2a are useful to identify the different parts of the structure, however, the selection of a particular bias voltage conditions to analyze chemical responses dismiss other regions of the $u(V)$ characteristic, which could carry valuable information. For instance, grid-gates responses dominated by flat-band voltage shift must be monitored for bias voltages around the inflexion point of the $u(V)$ characteristic, whereas responses caused by changes in surface conductivity, which affect the photocurrent in the inversion region, are not seen in this condition.

In order to compose a robust signature of the sensing regions that retain all the information that the $u(V)$ characteristic can carry, the complete $u(V)$ curves before and after exposure are collected and subtracted in the selected coordinates indicated in Fig. 2a. Pure flat band voltage shifts, of sigmoid functions such as $u(V)$ curves produce Gaussian responses (Fig. 2b, f-d), while pure changes in amplitude in the inversion region generate constant value signatures in that region (Fig. 2b, g). The collected signatures in Fig. 2b, show all these possibilities, intermediate cases and some unexpected ones such as a negative shift in inversion (Fig. 2b, h).

Responses f an b are pure Pd-H$_2$ responses as seen in grid-gate devices [3] (no Pd on pillars), the difference between them is the specific location of the laser beam, which in f takes a larger contribution from the Al grid (small peak in the figure). H and d (Pd on grid and on pillars) still contain a dominant grid gate response, but also additional features, such as a negative inversion value in h that cannot be explained by surface conductivity changes of the grid gate device. Condition g (Pd only on pillars) show a response with a dominant positive feature in the inversion region, although the details of the mechanism must be further investigated, since the pillar tips are in principle not biased. Finally, in areas without Pd (e and a) or with poor biasing (c) there is not significant response.

These signatures offer a diverse picture of a same sensing material tested in different conditions that highlight work function contributions (A) and resistivity changes (B) depending on the coordinates and functionalization of the nano-environments. At the same time, the method is robust to arbitrary selection of biasing conditions by acquiring the complete multidimensional image of the sensing regions, which can eventually be used for unsupervised materials screening.

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