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# Spraying spin coating silanization at room temperature of a $SiO_2$ surface for silicon-based integrated light emitters

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ABSTRACT

A new silanization method for $SiO_2$ surfaces has been developed for Si-based light emitters which are intended to serve as light sources in smart biosensors relying on fluorescence analysis. This method uses a special silanization chamber and is based on spraying and spin coating (SSC) in nitrogen atmosphere at room temperature for 10 min. It avoids processes like sonication and the use of certain chemicals being harmful to integrated light emitters. The surface of a $SiO_2$ layer serving as a passivation layer for the light emitters was hydrolyzed to silanols using an in situ-hybridization chamber and catalyzed with MES (2-(*N*-morpholino)ethanesulfone acid hydrate) buffer solution. Subsequently, the substrates were silanized with the SSC method using two coupling agents as (3-Aminopropyl)trimethoxysilane (APMS), and *N*′-(3-(trimethoxysilyl)-propyl)-diethylenetriamine (triamino-APMS).

The structure of the $SiO_2$ surface, the APMS and the triamino-APMS layers was controlled and characterized by Infrared spectroscopy, Raman spectroscopy and X-ray photoelectron spectroscopy. The results show a covalent binding of the silane coupling agents on the surface. Atomic force microscopy was used to investigate the roughness of the surface. The silanized samples exhibit smooth and densely covered surfaces. Finally, the suitability of the SSC method was verified on real light emitters.

## 1. Introduction

There is an increasing demand for fast detection methods for organic substances like estrogen in water, but current detection methods base on laboratory facilities with a turn-around time of one to three days between sample acquisition and the final result. Sensor applications which utilize the lab-on-chip technology will benefit from the advantages of current silicon technology, especially from the savings of costs, energy consumption and natural resources which come along with miniaturization and large-scale production. The first approach for more portable systems was realized with the development of the RIANA [1] and the AWACSS system [2]. Both of them are based on the total internal reflection fluorescence method, and the light of an external laser diode is coupled into a waveguide, where the evanescent field of the guided light excites an analyte-labelled antigen which is immobilized on the surface of the waveguide. Further miniaturization can be achieved by using light sources integrated on the chip. In this concept, known as direct fluorescence analysis and outlined in [3,4], a metal-oxide-semiconductor based light emitting device (MOSLED) is placed directly beneath the bioactive layer consisting of a silane linker, a receptor and a dye-labelled analyte. However, MOSLEDs are sensitive to most of the silanization methods described in the literature.

Silane coupling is a widely used method to attach other functional groups onto a surface by the formation of covalent bonds between the surface and a silane group [5]. The pre-treatment to get hydroxyl groups on the surface described in the literature bases mostly on the use of an oxidizing acid washing step in “piranha” solution, a mixture of $H_2O_2$ and $H_2SO_4$, for several times [6,7]. The surface modification methods described in the literature such as liquid-phase silanization often include a thermal pre-treatment at elevated temperatures, preferably in the range of 100 °C and 150 °C [8]. There are a few reports applying room temperature silanization, e.g. by Hong et al. [6], whereby in this case the substrate was placed in an APMS solution in dry $CHCl_3$ and refluxed for 3–4 h. However, such APMS immersion times can dramatically damage the structure of the MOSLED. The trichlorethylene used by the washing process may also damage the MOSLED by etching the front and back contact. The gas phase silanization [6,9] which gives better controlled self-assembled monolayer is not suitable for our system because of the high plasma operating temperature and the high fabrication cost.

In this work we present a room temperature spraying spin coating (SSC) silanization method which considers the sensitivity of the MOSLED to certain chemical treatments and is able to derivatize the surface with (3-Aminopropyl)trimethoxysilane (APMS), and *N*′-(3-(trimethoxysilyl)-propyl)-diethylenetriamine (triamino-APMS). In

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the following, the SSC silanization is developed and characterized on plain $SiO_2$ substrates, and finally its suitability for MOSLEDS is verified on real devices.

## 2. Materials and methods

### 2.1. Materials

$SiO_2$ substrates used to develop the specific silanization process were 200 nm thick $SiO_2$ layer deposited by PECVD on top of a 4-in. {100} oriented n-type silicon wafer. (3-Aminopropyl)trimethoxysilane (APMS) (purity >97%), *N*′-(3-(trimmethoxysilyl)-propyl)-diethylenetriamine (triamino-APMS) (technical grade), and a 0.27% (w/v) buffer solution of MES-2-(*N*-morpholino)ethanesulfone acid hydrate ($C_6H_{13}NO_3S{\cdot}xH_2O$) in ultrapure water (18 MΩ) were purchased from Sigma–Aldrich, Germany and used without further purification.

### 2.2. Methods

#### 2.2.1. Integrated light emitter fabrication

The integrated light emitters are based on a metal-oxide-semiconductor (MOS) structure which consists of a 200 nm thick gate oxide thermally grown by a LOCOS (LOCal Oxidation of Silicon) technology on 4-in. {100} oriented n-type silicon wafers. This oxide layer is implanted with Ge or rare earth ions followed by annealing and SiON deposition. Depending on the implanted element there is a broad palette of MOSLEDs emitting light from the UV up to the red spectral region [10]. For the use in fluid media the surface is finally passivated by a thick oxide layer to prevent shortcuts caused by the wet ambient. The MOSLEDs used to verify the SSC silanization have a diameter of 300 $\mu$m. Further details of the MOSLED fabrication and their electrical and optical properties are published elsewhere [10–12].

#### 2.2.2. In situ-hybridization process

Prior to silanization the surface of the $SiO_2$ substrates was cleaned by immersion in an isopropanol solution for 10 min followed by sonication and immersion in methanol and acetone for 10 min each. As chips with integrated MOSLEDs are sensitive to sonication, another and gentler surface cleaning procedure has to be applied. The chips were immersed sequentially for 5 min in a boiling 30% (v:v) solution of 1,1,1-trichloroethane ($Cl_3CCH_3$), followed by immersion in acetone and methanol for 5 min by drying in a nitrogen gas stream between each step.

We use a hybridization chamber, which was mounted in a Eppendorf Thermomixer comfort device with an exchangeable thermoblock “slides”. The catalysis solution MES (2-(*N*-morpholino)ethanesulfone acid hydrate) will be dropped on the substrate or chip surface and planished to a thin film with the help of special $1 \times 1\ cm^2$ plastic foil. Subsequently, the sample is exposed to this solution at about 50 °C for 16 h, with an agitation of 500 rpm of the thermoblock. To sustain a proper humidity, reservoir pads of the thermoblock slides were dampened with deionised water and placed in the cavities of the thermoblock. After taking out from the in situ-hybridization chamber the samples were dried in a nitrogen gas stream.

#### 2.2.3. In situ silanization process

In order to modify the chip surface the SSC silanization method has been developed and optimized. A special silanization chamber made of glass was constructed and built which has an opening for a compression sprayer. The idea behind the use of the spray mode is to give a kinetic energy to the coupling agent molecules to reach the substrate and to react directly with deprotonated hydroxyls on the surface. In this case an early polymerization of the silane molecules leading to disordered films on the sample can be avoided [13]. The second opening on the top of the chamber serves as an inlet for a nitrogen gas stream. The chamber is coupled with the Eppendorf-thermoblock and allows spherical shaking of the chamber in order to achieve a better film homogeneity. The silanization itself was performed by using a APMS- or triamino-APMS-solution which was diluted 1:1 in an acetonnitrile solution and sprayed at the sample surface from a distance of about 1 cm. The spray step is followed by the shaking process for an optimized operation time of 10 min, followed by drying with compressed air.

For comparison the $SiO_2$ surface has been silanized with the same method reported by Hong et al. [6], which is called the 4 h-APMS silanization in the following. As known from the literature [14], APMS films are highly hydrophobic, which is inert to protein adsorption [15].

#### 2.2.4. FTIR spectroscopy

A MagnaFTIR Fourier transform infrared spectrometer (Nicolet) with an angle of incident of 9° was used to check the film composition after hybridization and silanization. Spectral analysis was performed between 4000 and 400 $cm^{-1}$, and the line identification was performed using the data given in [8,16].

#### 2.2.5. Raman spectroscopy

The silane layer deposited on $SiO_2$ with SSC was characterized using Raman spectroscopy. Raman spectra were collected with a LABRAM HR 800 microspectrometer at an excitation wavelength of 532 nm. The spectral resolution achieved with the system is 1 $cm^{-1}$, and the spectral slit width is 4 $cm^{-1}$.

#### 2.2.6. X-ray photoelectron spectroscopy

The chemical composition of the chip surface was analyzed by X-ray photoelectron spectroscopy (XPS) with the help of a Microlab 310 F device (Fisions instruments). The XPS measurements were carried out at a base pressure of about $5 \times 10^{-10}$ mbar using an Mg K$\alpha$ X-ray (1253.6 eV) source. The electron analyser pass energy in the XPS high-resolution scans was constantly 10 eV. Whereas the incidence angle of the X ray beam amounts to 60°, the line of detection is parallel to the sample's normal.

#### 2.2.7. AFM

The topography of the samples was investigated by atomic force microscopy (AFM) at room temperature in air using a Veeco Digital Instruments Multimode SPM operating in non-contact tapping mode.

## 3. Results and discussion

### 3.1. FTIR spectroscopy

The infrared spectra in Fig. 1a taken after the hybridization procedure of the silicon oxide surface showed an anhydrous surface due to the water complex from the MES buffer. Whereas the peak for free water at 3280 $cm^{-1}$ could not be observed, a broad peak between 3500 and 3100 $cm^{-1}$ due to the bonded silanol $\equiv$Si–OH is recognized [8]. We also observed sharp peaks at 3748 $cm^{-1}$ and 3687 $cm^{-1}$ which are related to the bridged Si–OH stretching mode and the free hydroxyl group, respectively. We assume that the basic reaction of the methoxy part of APMS- and triamino-APMS-molecules with deprotonated hydroxyls depends critically on the quality of the in situ hybridization results.

As shown in Fig. 1b the silanization procedure with APMS and triamino-APMS was also characterized by FTIR spectroscopy. The main peak at 1060 $cm^{-1}$ related to the asymmetric stretching mode ($\equiv$Si–O–Si$\equiv$) from the silicon oxide substrate is shifted to 1040 $cm^{-1}$ for the APMS formed film. The $\equiv$Si–O–$CH_3$ part of the