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A novel method for the fabrication of ATPES silanized SPR sensor chips: Exclusion of Cr or Ti intermediate layers and optimization of optical/adherence properties

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ABSTRACT

The present work discloses a protocol for the production of APTES treated gold films on glass substrates without intermediate chromium or titanium layers with high adherence of the coated gold layer to the glass substrate and suitable optical properties for using as a SPR sensor chip. A thorough optimization study of the APTES coating of nano-gold layers on glass procedure has been performed for the first time. Different media (liquid water, liquid toluene, vapor phase iso-propyl alcohol and vapor phase APTES) and thermal treatment methods have been employed. The final products have been analyzed using ATR-FTIR, SPR, AFM and contact angle analysis methods. The adhesive property of the final films has been assessed using two test methods: pull off test and stability test in boiling water. At the end, the coating protocol resulting in the best adhesion property and SPR response is presented as the optimal method.

1. Introduction

One of the main sensing methods of biological molecules is surface plasmon resonance immunoassay. Manufacture of SPR chips constitutes a critical step of the SPR sensing protocol. SPR chips are usually composed of a glass substrate, 2–5 nm titanium or chromium intermediate layer, 40–60 nm gold layer and a cross linker with suitable reactive groups for binding biological species such as antibody or DNA molecules. The use of titanium or chromium intermediate layers is imperative because of the very low adherence of the gold thin layer to the glass substrate. However, titanium and chromium layers absorb light and result in interference during the sensing step [1]. Therefore, exclusion of such intermediate adhesion layers is desired.

On other hand, it is necessary to use a sophisticated chemistry for immobilization of biological elements on the gold surface. Alkanethiols with suitable reactive groups are among the conventional cross linkers used for binding biological components to the gold surface of the SPR chip [2–5]. Another approach is using Langmuir–Blodgett (LB) membranes [6,7]. However, the adherence of these membranes to the surface is weak and the biological components easily detach from surface [2,8]. Another method is based on using plasma polymerization. The latter process requires elaborate vacuum apparatus and control of the film thickness requires delicate plasma power monitoring [9,10]. Finally, a silanization chemistry using 3-aminopropyltrirthoxysilane (3-APTES) has also been used to attach antibodies to the gold surface for sensitive SPR sensing [11,12]. All of the mentioned methods make use of titanium or chromium intermediate layers.

Modification of solid surfaces, especially glass and silicon surfaces, by silanization reactions has been widely studied and implemented in a variety of technological applications [13,14]. Coating the surface with APTES provides a platform witch is suitable for immobilization of biological elements taking advantage of the amine group of the initial APTES molecules. Only few works have appeared in open literature on the silanization of gold surfaces by APTES [11,12]. The latter studies used chromium intermediate layers for increasing the adherence of the gold layer on the glass substrate. Sasaki et al. claimed that excluding the chromium layer, the APTES treated gold layer had a very low adherence to the glass substrate and was unsuitable for the manufacture of SPR sensing chips. In continuation, Sasaki et al. [12] worked merely on the fabrication of APTES treated gold/glass composites with chromium intermediate layers.

The present work discloses a protocol for the production of APTES treated gold films on glass substrates without intermediate chromium layer with high adherence of the gold layer to the glass and suitable optical properties for using as a SPR chip. This

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study presents a thorough optimization study of the APTES coating of nano-gold layers on glass procedure for the first time. Different media (aqueous, organic and vapor phases) and thermal treatment methods have been employed. The adhesive property of the final films is assessed using two test methods: pull off test and stability test in boiling water. On the other hand, the SPR characteristics of the chip before and after imparting the coating procedure are investigated. At the end, the coating protocol resulting in the best adhesion property and SPR response is presented as the optimal method.

2. Experimental

2.1. Materials

Toluene, isopropanol, H_2O_2 (30 wt.%) and H_2SO_4 (94 wt.%) were purchased from MERC. 3-Aminopropyltriethoxysilane (APTES) was purchased from Sigma–Aldrich. Triply distilled water was used throughout the experiment.

2.2. Gold chip preparation

The glass substrates (microscope slides, soda-lime glass) were cut into 10 mm × 10 mm × 1 mm pieces. The substrate surfaces were initially thoroughly treated in piranha solution. Treatment of the surface of glass with piranha solution (3:1 vol. ratio, H_2SO_4:H_2O_2) for 30 min at 80 °C results in cleaning the surface. After cooling, the samples were rinsed with triply distilled water and dried under nitrogen gas flow.

Au layers with a thickness of about 50 nm were sputter-deposited on the glass slides using a BAL-TEC SCD 005DC sputtering system. No intermediate chromium or titanium layer was used. Sputtered metal thickness was examined using a Stylus Profilometer DEKTAK3 (Veeco) instrument.

2.3. Gold chips silanization

Preparation of silane films on the sputtered Au layer was performed according to Wang and Waughn [13] silanization methods with slight modifications.

Concentrated vapor-phase deposition (CVPD): APTES (50 μL) was added to a 200 mL clean glass bottle. Au coated piranha treated glass slides were put inside the bottle. The bottle was sealed and placed in an oven and heat treated at 100 °C for 1 h.

Dilute vapor-phase deposition (DVPD): APTES (0.1 mL APTES in 10 mL isopropanol, 50 μL) was added to a 200 mL clean glass bottle. Au coated piranha treated glass slides were put inside the bottle. The bottle was sealed and placed in an oven and heat treated at 100 °C for 1 h.

Organic-phase deposition (OPD): Au coated slides were immersed into the solution (2% APTES–toluene solution, 10 mL) and reacted at room temperature for 1 h. After washing with toluene and triply distilled water, the slides were placed in the bottle. The bottle was sealed and placed in an oven and heat treated at 100 °C for 1 h.

Aqueous-phase deposition (APD): Au coated slides were immersed into the 2% APTES aqueous solution (10 mL) and reacted at room temperature for 1 h. After washing with triply distilled water, the slides were placed in the bottle. The bottle was sealed and placed in an oven and heat treated at 100 °C for 1 h.

All of the CVPD, DVPD, OPD and APD treatments were simultaneously performed on two or more Au coated glass slides.

Table 1
Effect of silanization method on the average roughness (R_a) of the silanized gold coated glass slides.

Sample	R_a (nm)
Glass slide	5.12
Gold sputtered glass slides	12.52
CVPD	13.32
DVPD	12.72
OPD	24.05
APD	12.35

2.4. Surface analysis

Surface topology of the original and treated gold films was analyzed by a Nanoeducator AFM apparatus using a non-contact mode. An Iranian commercial SPR instrument (Nano SPR) with a resolution of 0.02° was used to investigate the SPR characteristics of the original and treated samples. This Nano SPR system uses a goniometer (θ–2θ geometry) and a He–Ne gas source (2 mW) for producing the laser beam (λ = 632.8 nm). Glycerin has been used as an interface layer between the borosilicate glass prism and the glass slides.

Surface functional groups were assessed by ATR-FTIR analysis using a Nicolet (Nexus B70 FT-IR) instrument. Contact angle of water on the treated films was measured according to ASTM D 724-99 test method at three different spots of each sample.

Layer stability was evaluated by the boiling water stability and pull off tests. Boiling water stability test was performed by placing the sample in a 200 cm^3 beaker containing 50 cm^3 boiling water for 30 min. The pull off test was performed as following: the treated side of the silanized Au coated sample was put on an adhesive tape. The latter was put horizontally on a holder. Afterwards a 100 g standard weight was put on the glass side of the slide for 30 s. Finally the tape was cut out from sample. In each of the two stability tests, partial or full detachment of the gold layer was considered as a failed experiment. Each of the stability tests were repeated twice.

3. Results and discussion

3.1. Morphology

Appearance and color of the sputtered gold surfaces showed no change after silanization with APTES. Herlem et al. [11] worked on the electro-deposition of APTES on the Au coated glass and reported a milky aspect of the final product. It is presumed that invariance of the color is due to the much thinner silanized coating subject of this work.

Annealing has a detrimental effect on the SPR characteristics due to the induced change in the microstructure of the gold thin layer. It is well known that thermal treatment of gold nano-layer/glass composites decreases the SPR response, especially at high annealing temperatures [15]. Therefore, it is desirable to decrease the time and temperature of the silanization procedure. The time period and treatment temperature were selected as 1 h and 100 °C, respectively. Larger times and higher temperatures may result in unwanted change of the microstructure of the Au thin film and deterioration of SPR response characteristics.

Table 1 shows the average roughness (R_a) values for the as-deposited and silanized Au films produced according to the different coating processes. It is observed that the average surface roughness of the silane film produced via OPD method (ca. 24 nm) is distinctively larger than that of the films produced by the other methods (12.52–13.32 nm). Fig. 1a–d shows the AFM surface topology of the as-deposited and silanized Au films produced via APD, OPD and CVPD methods. The scan area of the images is 2000 nm × 2000 nm. It is observed that the surface roughness and surface topology of the silane film produced via CVPD and APD is