

## Stability Modification of SPR Silver Nano-Chips by Alkaline Condensation of Aminopropyltriethoxysilane

M. Ghorbanpour\*

Chemical Engineering Department, University of Mohaghegh Ardabili, 56199-11367, Ardabil, Iran.

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### Corresponding author:

E-mail address:

ghorbanpouruma..ac.ir

Phone: 98 9356556010

Fax: +98 451 88006076

### Abstract

The Silver SPR chip was modified by alkaline-silane condensation with aminopropyltriethoxysilane (APTES) in NaOH aqueous solution at different times. Silver sputtered slides coated with APTES were immersed in NaOH solution, enabling us to produce silver surfaces homogeneously covered with APTES. The surface properties of grafted APTES on sputtered silver surface as a function of time were studied using SPR analysis, AFM and contact angle measurement. The mechanical and chemical stability of samples was assayed by tape test and NaCl test. The answers show that hydrolysis and condensation of APTES are activated in alkaline solution and lead to formation of a protective APTES layer on the surface of silver. The morphology of APTES on silver surface is a function of coverage density that is altered by changing time. At short times (< 30 min), APTES molecules physically adsorb to the surface leads to weak protection. At higher condensation times, APTES molecules chemically bond to the surface and each other leads to better protection.

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## 1. Introduction

Surface plasmon resonance (SPR) sensors are valuable instruments for investigating surface interactions. This tool is a very sensitive technique for probing the refractive index changes vicinity of a thin metal film. SPR biosensors have become an established technology for observation of biomolecular interactions. SPR is an optical technique that can detect adsorbates at extremely low quantities and can measure infinitesimal

conformation/orientation changes of the adsorbed molecules. SPR is attractive owing to several inherent advantages (e.g., label-free analysis, simplicity, cost effectiveness, and high sensitivity). The SPR resonance angle variation is dependent on various physicochemical processes occurring at the SPR substrate (a thin metal film) and on the substrate/solution interface [1].

The selection of the metal layer is critical for SPR sensing, as the refractive index  $n$  of the metal film

influences considerably the shape of the plasmon curve. Suitable metals include silver, gold, copper, and aluminum [2]. Gold is most usually applied as it possesses highly stable optical and chemical attributes. Silver offers the sharpest SPR signal with an increased penetration length. However, the chemical instability of silver in the air and particularly in aqueous solutions makes it difficult to record reliable optical signals. An optimal SPR signal in terms of sharpness and minimum intensity was obtained for Ag films with a thickness of approximately 50 nm. The SPR signal could be slightly further improved when silver was deposited right away on the glass interface without an additional tie adhesion layer [3]. All the same, these interfaces were found to be mechanically unstable and not suited for the provision of reliable SPR chips. The optical signal is changing significantly over time due to the chemical oxidation of the interface, visible to the naked eyes as white spots on the surface. This instability is demonstrated by following the change of the SPR signal over 2 h when the interface was immersed in water. The chemical oxidation of the silver thin film on ambient conditions can be prevented by coating the silver interface with a thin protecting layer. For example, the deposition of Indium Tin oxide of silver thin films [4] or functional alkanethiols have been used to form self-assembled monolayers on a silver surface to protecting the interface and allowing further surface modifications [5-8] and using bimetallic silver/gold layers [9,10].

Self-assembled monolayers (SAMs) are monomolecular layers which are spontaneously formed upon immersing a solid substrate into a solution containing functional molecules. Commonly employed examples are alkylsiloxane. SAM formation provides surface functionalisation by organic molecules containing suitable functional groups like -SH, -CN, -COOH, -NH<sub>2</sub> and silanes [11].

Silanes are used for modifying the surface of the inorganic materials, giving an organic character on them. One of the most studied silanes used as surface modifier is the APTES. On siliceous surface attachment is typically mediated by first copying the surface followed by immobilization of biomolecules of interest [12].

When APTES acts as surface modifier, it is not necessary to hydrolyze with water because the aminopropyl group acts as a catalyst by reacting with water molecules adsorbed on the surface. On the contrary, when APTES acts as network former in organic-inorganic materials, water is usually needed for the hydrolysis of the alkoxy groups of APTES. After hydrolysis, condensation reactions take place where hydrolyzed APTES molecules react with other APTES molecules through a self-condensation process, or with different molecules containing hydroxyl groups through a condensation reaction. Condensation reaction usually take place by annealing [8] or seldom by using an alkaline solution [13]. Annealing of silver chips causes weakening of SPR characteristic of silver chip [14]. Therefore, first time we used alkaline condensation of silver SPR chip.

The purpose of this research was modification the stability and SPR response of the silver SPR chip by alkaline-silane condensation with APTES in NaOH aqueous solution at different times.

## 2. Experimental procedure

**Silver chip preparation:** The glass slides (soda-lime glass, 10 × 10 × 2 mm) were cleaned by treatment in piranha solution (3:1 vol. ratio, H<sub>2</sub>SO<sub>4</sub>:H<sub>2</sub>O<sub>2</sub>) at 80°C for 30 min. The treated samples were washed with de-ionized water and dried under nitrogen gas flow. Then, Ag nano-layers with thicknesses of 50 nm were deposited on glass substrates by a BAL-TEC SCD 005 DC sputtering system .

The samples were later put in a solution containing 200 ml APTES in 10 ml water for 60 minute. After thoroughly rinsing the silanized chips with methanol and water, the hydrolysis and condensation of the APTES monolayer were accomplished by immersing the wafers into an aqueous 1 M NaOH solution for 5, 15, 30 and 60 minute.

**Surface analysis of silver chip:** Surface topography of the composite layers was performed using a Nanoeducator AFM instrument using a non-contact manner.

Surface plasmon resonance analysis was performed utilizing a commercial NanoSPR apparatus (Iran).

The contact angle of water along the treated films was evaluated according to ASTM D 724-99 test method at three different spots of each sample.

The pull off test was performed as follows: an adhesive tape was set horizontally on a holder, and then the composite layer was put on it so that the metal came into contact with the tape. Subsequently, a 100 g standard weight was set along the glass side of the slide for 30 s. Afterwards, the weight was raised and the slide was detached manually from the tape. Each pull off test was replicated twice.

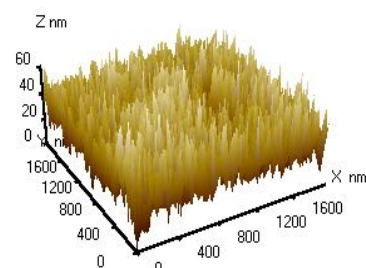
The layer chemical stability test was judged by putting the sample in a 200 cm<sup>3</sup> beaker containing 50 cm<sup>3</sup> 2 M NaCl solution for 60 minute. Partial or full detachment of the silver layer was considered as a failed experiment. If the sample remained constant, the experimentation was considered successful. Each stability test was replicated twice

### 3. Results and discussion

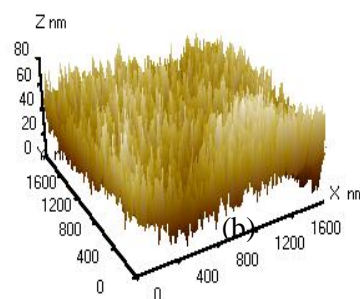
In the presence of water, the hydrolysis of organo silanes and their following condensation occur, leading to formation of silica network. Water helps to hydrolyze amino silanes into silanol (SiOH group) rapidly, whereas the rate of the condensation reaction

of the silanol into Siloxane (Si—O—Si) obviously depends on the pH value. At acidic pH range, the hydrolysis process of silane is essentially activated, whereas in the basic pH range both hydrolysis and condensation is activated [12,13].

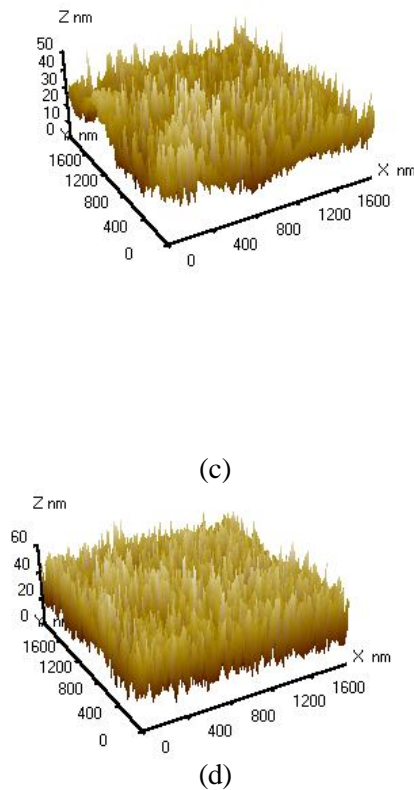
The topography of the silver SPR chips before and after condensation was investigated by AFM. Figure 1 displays the AFM image of a silver surface immediately after exposure to ambient conditions. As this figure show, condensation time induces changes in the surface morphology. The surface of sample condensed for 5 min is composed of grains. As these images shows, the roughness of the samples condensed shorter than 30 min is higher than the supposed thickness of samples condensed more. Interestingly, AFM observations did not demonstrate any significant structural difference between the parent sample and sample condensed for 30 and 60 minute.



(a)



(b)

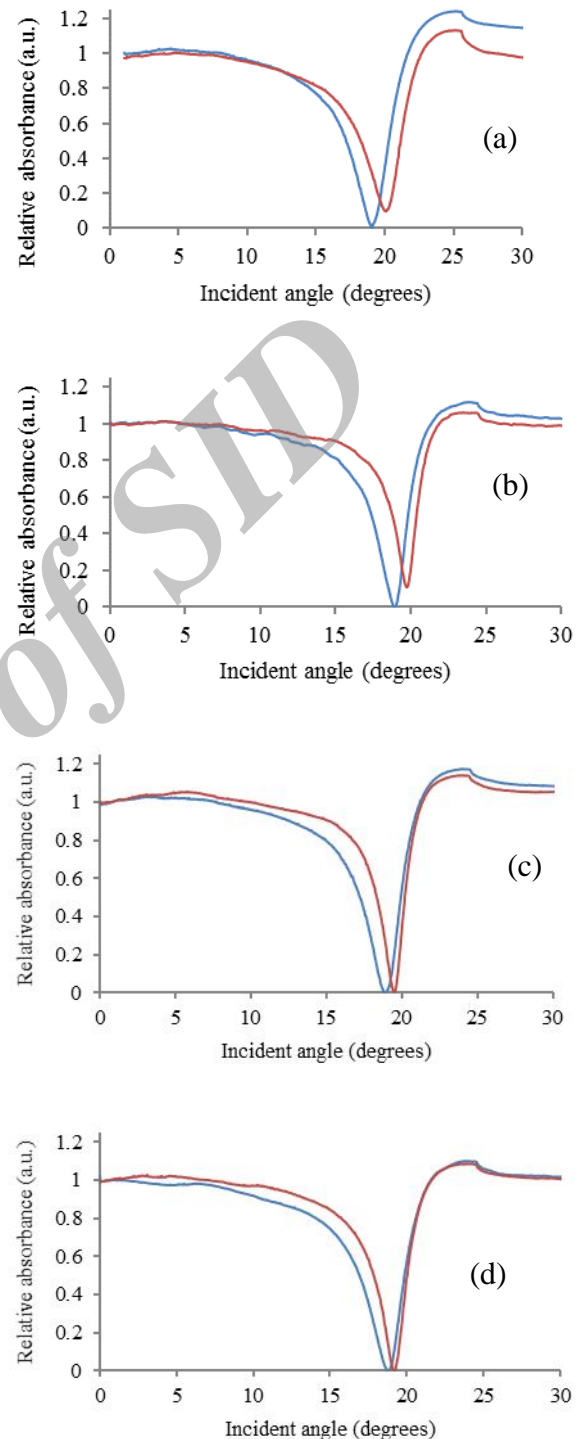


**Fig. 1.** AFM images of the sputtered thin silver films (50 nm) (a) silanized with APTES and condensate in NaOH solution for 5 (b), 30 (c) and 60 min (d).

It can be observed that SPR characteristic peak change after silanization process either in its position or in its shape. Moderate variation in the absorbance can be attributed to the different configuration and dimension of the examined samples. Figure 2 displays the change of the SPR signal with increasing condensation time. The resonance angle is shifted to higher angles and the curves are broadened, seen in an enlarged full width at half-maximum. Condensation shorter than 30 min has broadened SPR curve, while longer condensation time didn't have considerable negative effects on the SPR signal.

It is set up that the SiO<sub>x</sub> film thickness can affect the SPR response of Au/Ti/glass composite layers [8]. This implies that an increase in SPR angle and SPR

width (corresponding to the reduction of peak depth) related to increase of



**Fig. 2.** SPR response of the sputtered thin silver films (50 nm) silanized with APTES and condensate in NaOH solution for 5 (a), 15 (b), 30 (c) and 60 min (d).

silicate film thickness. Because of constant refractive index of the APTES in the different samples, our SPR studies show that the condensation for 60 min results in the minimal and the condensation for 5 min results in the maximal layer thickness. Remember that the condensation for shorter than 30 min resulted in the maximal surface changes. Table 1 shows the contact angle of the original sample and silanized and condensed for different times. It is observed the contact angles of the original and coated samples condensed for less than 30 min differ obviously. Sputtering of the 50 nm thickness silver layer on the hydrophilic glass increases significantly the contact angle to 81.85°, rendering it highly hydrophobic. The terminal values of the contact angle for the condensed samples lie in the range of 60–70°. The condensation for 60 min shows the minimal contact angle, i.e. 60.27°. After the condensation, the contact angle reduces due to the coverage of the surface with a polysiloxane film of hydrophilic character. In addition, exposed -NH<sub>2</sub> groups enhance the latter phenomenon. The observed final contact angle values are in agreement with the reported values of amino-terminated layers in the literature (42 to 68°) [14,15]. It appears that the reduction of contact angle by condensation time may be attributed to the substantially lower content of the hydrophobic ethoxy groups and relative high amount of silanol groups [8].

**Table 1.** Contact angle for various silanization methods on the treated glass slides




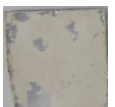

Time of alkalization (min)	Sputtered sample
Parent sample	81.85 ± 0.85
5	69.59 ± 1.80
15	68.93 ± 2.59
30	61.855 ± 2.88

A simple qualitative test was employed to test the adhesion of silver films. A piece of adhesive tape was firmly placed over the Ag film and the surrounding

glass substrate and was then withdrawn. The fraction of the movie that was transplanted to the tape was then a comparative measure of the film adhesion. No transfer to the tape was observed in all of the samples. This is in accord with our previous solution.

By NaCl test, we found that the stability of the silanized silver cup was improved, over that at bare silver to the extent that the non silanized Ag films were completely removed by exposure to saline solution very fast (Table 2). By using NaOH condensation method, the stability was varied with time. If the chip after silanization were not subjected to the condensation, the silver films was lost only after 10 min. Condensation increase the chemical stability of chips, as after 1 h condensation, the chip remains intact even after 1 h immersion in NaCl solution.

**Table 2.** Stability test of the original state and silanized samples

Time of condensation	Time of detaching (min)	
Parent sample	< 2	
0	10	
15	18	
30	30	
60	> 60	

The parent APTES molecules may reach the glass surface by diffusing through the silver particles and interact with the surface silanol groups present. Some

of these molecules may react with the silver surface layer via their amine head. After condensation less than 30 min, due to the relatively high amount of residual ethoxy groups on the reacted/electrostatically bond original APTES molecules, a weak three dimensional connected network between them may form. Nevertheless, after condensation more than 30 min the latter layer has a strong attachment to the glass surface and lie of a compact and mechanically strong layer due to the founding of a 3-D silica based network.

#### 4. Conclusion

Modifying the stability and SPR response of the silver SPR chip silanized with APTES and condensed in NaOH aqueous solution at different times. The results show that hydrolysis and condensation of APTES are activated in alkaline solution and lead to formation of a protective APTES layer on the surface of silver. The morphology of APTES on silver surface is a function of coverage density that is altered by changing time. At short times (< 30 min), APTES molecules physically adsorb to the surface leads to weak protection. At higher condensation times, APTES molecules chemically bond to the surface and each other leads to better protection.

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