2010 International Conference on Nanotechnology and Biosensors
IPCBEE vol.2 (2011) © (2011) IACSIT Press, Singapore

Synthesis of Silver Nanoparticles Array and Application of Their Localized Surface Plasmon Resonance in Biosensor Design

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Abstract— **We introduce a method for synthesis of Two-dimensional array of silver nanoparticles. Application of these nanoparticles array as biosensor based on Localized Surface Plasmon Resonance (LSPR) without probe immobilization is introduced too. Silver nanoparticles (NPs) on the carbon thin film are prepared by co-deposition of RF-sputtering and RF-PECVD using acetylene gas and silver target. X-ray diffraction analysis indicates that silver NPs with fcc crystal structure are formed in our samples. Using AFM image and data, average particles size is estimated to be about 7 nm and indicated that array with sharp distribution of silver particle sizes were grown. Real time of LSPR absorption peak of silver NPs in presence of DNA primer decamer (ten-deoxycytosine) at fM concentrations was investigated. The LSPR peak has a blue shift and becomes damped by adding of DNA primer and under DNA exposure up to 3h. Our sample has a good response to low concentration of DNA without employing probe. Furthermore, its time response of the sensor to the introduced DNA primer was short. Both of these are pre-requisite for applying this sample in biosensor design.**

Keywords- Silver nanoparticles (Silver NPs); RF-PECVD; LSPR; DNAprimer; biosensor

I. INTRODUCTION

Refractive index sensitivity of the Localized Surface Plasmon Resonance (LSPR) nanosensor in comparison to the SPR sensor is four orders of magnitude smaller. The short characteristic electromagnetic field decay length provides the LSPR nanosensor with its enhanced sensitivity which it is size dependent [1]. Recently two–dimensional array of silver nanoparticles (silver NPs) with diameter of more than 80 nm has been synthesized by wet chemical method and the effect of particle size and interparticle distance has been investigated [2]. In this work, we introduce a non wet method for growth of 2D array of silver NPs with about 7 nm diameter using co-deposition of RF-sputtering and RF-PECVD for the first time. The growth parameters such as RF power and initial gas pressure were optimized. We had reported this method for growth of Cu nanoparticles [3] and we had studied SPR of Cu nanoparticles [4]. The LSPR is behind of biomedical applications of noble metal nanoparticles as elementary optical biosensors that are able to detect interaction between probe and target biomolecules near the particle surface [5]. We report the detection of DNA primers in fM concentration with no complementary probe immobilized on the surface, using LSPR of this array of silver NPs. Here, we are to discuss the effect of decamers of Deoxycytosine nucleotides on the LSPR.

II. EXPERIMENTAL DETAILS

Silver NPs on the carbon thin films were prepared by a capacitance coupled RF-PECVD system with 13.56MHz power supply. The reactor consists of two electrodes with different areas. The smaller electrode was silver as a powered electrode. The other electrode was grounded via the body of the stainless steel chamber. The deposition was performed at room temperature on the glass substrate on this electrode. The chamber was evacuated to a base pressure of about 10^{-5} mbar (10^{-3} Pa) prior to deposition and was then its pressure was increased to the desired ambient pressure with acetylene gas. The deposition was done in a fix constant RF power of 160 W and initial pressure of 0.04 mbar (4 Pa). The LSPR peak of silver nanoparticles was measured by a single beam UV–visible spectrometer. Atomic Force Microscopy (AFM) in noncontact mode was used to obtain the surface topography thin film and the average particle size. X-ray diffraction (XRD) data of the sample in glancing-angle geometry were recorded in a powder diffractometer. The X-ray source was a Co Kα radiation and the glancing angle was 1°. We used LSPR technique for determining fM concentration of single stranded DNA primers a decamer (ten-deoxycytosine) in T.E. buffer. We investigated LSPR peak of 2D array of silver NPs on the glass substrate in the presence of fM concentration of DNA primers in T.E. buffer up to 3h and recorded LSPR absorption peak with 30 min steps.

III. RESULTS AND DISCUSSION

The AFM image of sample is shown in Fig. 1a. This image is used to estimate the mean size of silver NPs and distribution of the particle size. Fig. 1b shows the topography diagram of this sample that was obtained from AFM data. This figure may be used to interpret the distribution function of the particle size. The maximum of abundance gives average particle size and its width gives the variance of the particle diameter. It can be observed that the average size of nanoparticles is about 7 nm for this sample and the distribution of the particle size is almost sharp too.

Fig. 2 shows Glancing-angle X-ray diffraction profile of silver NPs nanoparticles in the carbon thin film. As it is shown in this figure, silver nanocrystal with (111), (200) and (220) orientation are formed in this sample. A trace of silver oxide can be observed for our sample too. It can due to oxidation of silver nanoparticles after exposure to air.

The UV–visible absorption spectra of silver NPS array in the range of 380 nm- 850 nm in the absence and presence of DNA primer are shown in Fig. 3. There is an absorption peak at about 450 nm that is related to LSPR absorption of silver NPs. The LSPR peak has a blue shift and becomes damped by adding of DNA primer and under DNA exposure up to 3h. This blue shift is quantified in Fig. 4.

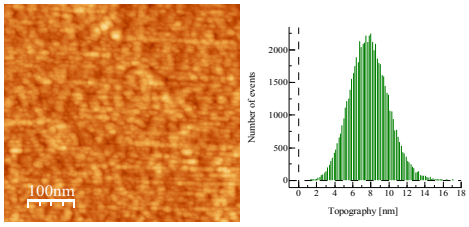

Figure 1. AFM images of sample and abundance of topography.

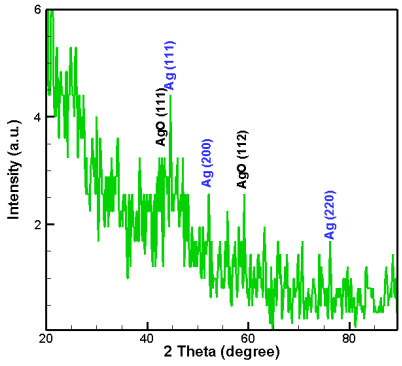

Figure 2. Glancing-angle x-ray diffraction profile of silver nanoparticles array

Real time LSPR wavelength shift of the silver NPs array in presence of DNA primer without probe immobilization at fM concentrations is shown in figure 4. The LSPR λ_{max} did not change significantly after an immobilization time more than 2h. The continued line is the fitting result of experimental data by below equation.

$$\Delta\lambda = S_\lambda(1-\exp(-t/\tau)) \qquad (1)$$

where S_λ is wavelength shift sensitivity and τ is immobilization time. From this fitting we conclude that wavelength shift sensitivity of LSPR was about 25 nm and sample immobilization time at fM concentration of DNA primer was 2h for our sample.

On the other hands, the investigation of aging for the sample showed that the LSPR peak was damped gradually and this could be due to appearance of silver oxide shell over silver core and an increase in the silver oxide shell sizes due to aging occurring under air exposure. This is in agreement with XRD results. Interparticle coupling effect can be neglected since silver NPs diameter are less than 10 nm [6]. The size of silver core and the silver oxide shell, and the environment dielectric constant can be estimated from LSPR peaks in visible spectra using Mie theory.

When a small spherical metallic nanoparticle is irradiated by light, the oscillating electric field causes the conduction electrons to oscillate coherently. In the case of a metal nanosphere with radius much smaller than the incident wavelength, the plasmon response is essentially dipolar and the quasistatic approximation was used. In this case, the absorption cross section is given by dipole absorption:

$$\sigma_{abs} = (8\pi a_c(\varepsilon_s)1/2/\lambda)\mathrm{Im}(\alpha) \qquad (2)$$

Where a_c and ε_s are the radius of the core particle and the dielectric constant of the shell, respectively, and α is the polarizability of copper particles with copper oxide coating and embedded in a matrix that is written as

$$\alpha = [(\varepsilon_s-\varepsilon_h)(\varepsilon_c-2\varepsilon_s)+\Gamma(\varepsilon_c-\varepsilon_s)(\varepsilon_h+2\varepsilon_s)/(\varepsilon_c+2\varepsilon_s)(2\varepsilon_h+\varepsilon_s)+ 2\Gamma(\varepsilon_s-\varepsilon_h)(\varepsilon_c-\varepsilon_s)]a_s^3 \qquad (3)$$

Where ε_c, ε_s and ε_h are core, shell and host dielectric constants, respectively. $\Gamma = (a_c/a_s)^3$ where a_c and a_s are the radii of core and shell (particle), respectively. The size dependent dielectric function of core metallic versus light frequency is written as:

$$\varepsilon_c(\omega,a_c) = \varepsilon_{bulk}(\omega)+[\omega_p{}^2/\omega^2+i\omega\gamma_0]-[\omega_p{}^2/\omega^2+i\omega(\gamma_0+AV_F/a_c)] \qquad (4)$$

Where $\gamma_0 = V_F/L$, V_F is the Fermi velocity and L is the mean free path of the electrons in the bulk material, and ω_p is the plasma frequency. A parameter is a theory dependent parameter that includes details of the scattering processes and is expected to be in the order of unity [4].

Using above equation, we can fit LSPR peak of the silver NPs array in absence and presence of DNA to estimate of DNA dielectric constant. This work is in progress.

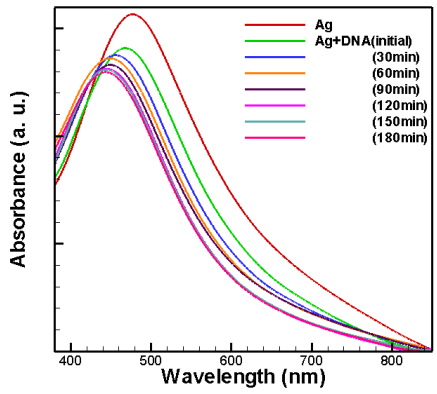

Figure 3. Real time of LSPR absorption peak of silver nanoparticles array in presence of the DNA primer

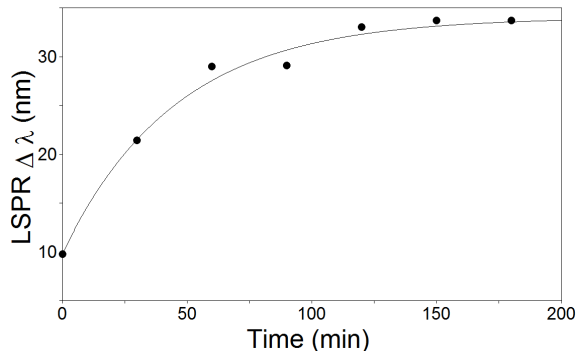

Figure 4. Real time LSPR wavelength shift of the silver NPs array in presence of DNA primer up to 3h

IV. CONCLUSIONS

Two- dimensional array of silver NPs is prepared by co-deposition of RF-sputtering and RF-PECVD. X-ray diffraction analyses shows silver NPs with fcc crystal structure are formed in our samples. AFM image indicates that there are silver NPs array with diameter about 7 nm. Localized surface plasmon resonance biosensor application of this nanoparticles array as biosensor with no probe immobilization is introduced too. The real time Localized surface plasmon resonance in presence of DNA primer sample at fM concentrations was investigated. This founding is very important since they have shown that our sample has a good response to low concentration of DNA without employing probe. Furthermore, the time response of the sensor to the introduced primer was very short, so that the main difference appeared in less than 30 min. In other words, although the absorbance was changed over time for the period of study (180 min, with 30 min intervals) the total changes occurred in 150 min equaled to that of occurred in the initial 30 min period (Fig 3). This is why we are focusing on this stage to detect the earliest changes occurring due to the introduction of DNA primer. We have also distinguished a significant decrease in the wavelength over time (Fig 3). This variation seems that to be biphasic, starting with a rapid phase, again occurring in the initial 30 min period that is followed by a slow linear descending phase. In conclusion we believe that the system is capable to detect much lower concentration of primer (<< fM) and might be used to identify certain number of primers that form the initial fast saturation stage at molecular level. This provides the base for constructing miniature detecting system.

ACKNOWLEDGMENT

The authors would like to thank Mrs S Vaseghinia for AFM images.

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