A Novel Polymer Nanofiber Interface for Chemical and Biochemical Sensor Applications

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ABSTRACT

Polymer thin films are used extensively as a chemically sensing medium in variety types of acoustic sensors. It is well known that the sensitivity of a sensing film is proportional to the surface area of the film per unit mass. In our research we have studied the feasibility of using thin polymeric films made of nanofibers (NFs) as novel sensor interface. Thin NF films have surface area approximately one to two orders of the magnitude larger than continuous films. The NF films made of Poly-Lactic Acid-Co-Glycolic Acid (PLAGA) polymers were studied with Thickness-Shear Mode (TSM) resonator operating at 10 MHz. The response of the NF sensor to gaseous and liquid media under various ambient conditions was studied in details.

Keywords: Nanofiber; Piezoelectric Sensors, Quartz Crystal Microbalance; TSM; Chemical Sensor

1 INTRODUCTION

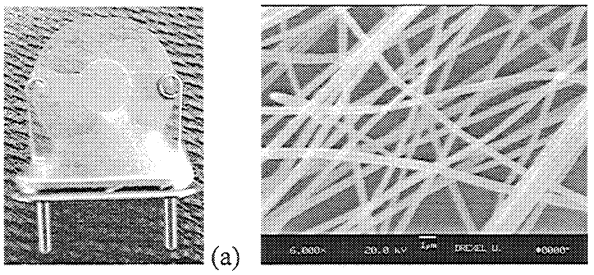
A considerable attention has been given to different interfaces for chemical and biomedical sensors; metal oxides films for gas sensors, polymer films for gas and liquid phase sensors, biologically active films such as antigens, enzymes, DNA, cells, etc., for biomedical sensors [1,2]. Since the properties of the interface influence significantly the sensor performance (sensitivity, selectivity, time response, aging) [3,4], several advanced techniques such as RF & DC sputtering, electron beam, Langmuir-Blodgett, spinning, and sol-gel have been used for fabrication of thin sensing film. All these techniques make continuous films that have relatively low sensing surface area. In this paper we propose to use a NF thin film produced with electrospinning technique as a new sensing interface.

It is well known fact that the sensitivity of the sensing film is proportional to the surface area of the film per unit mass. Thin film made of NFs has surface area approximately one to two orders of the magnitude larger than continuous films [5]. Poly-Lactic Acid-Co-Glycolic Acid (PLAGA) polymer NF with the diameter about 500 *nm* were deposited on the gold surface of AT-cut TSM quartz crystal operating at the resonant frequency of 10 MHz. The response of the NF sensor to gaseous and liquid media under various ambient conditions was studied in details and acoustic and viscoelastic properties of NF thin films were measured.

2 EXPERIMENT

2.1 Preparation of NF Thin Film

Electrospinning technique was used to fabricate thin NF films [6]. In our case, the applied voltage was 15,000 volts DC and the distance between the target TSM sensor and the tip of the micronozzle was maintained all the time at 20 *cm* [7]. NF films were deposited on one surface of AT-cut TSM disk-shaped quartz crystals of the diameter of 13 *mm* having 5 mm circular electrodes (Fig. 1a). The 5% PLAGA in DMF (Dimethyl formamide) solution was applied to fabricated NF films at several different deposition times equal to15, 30, 45, 90, and 120 seconds.



(a) (b)

Figure 1. Photograph of the TSM sensor with deposited NF film (a) and the SEM picture of the NF film at 6000X magnification (b).

2.2 Measurement Systems

Initially NF films were characterized using SEM microscope, which provided data on their size, structure and thickness (Fig. 1b). HP 4395A network / spectrum / impedance analyzer based measurement system was used to measure electrical characteristics of the NF sensors. The amplitude and phase components of the scattering parameter S_{21} were measured as a function of the frequency, and based on it the resonant frequency and amplitude of the sensor were determined. A Precision Mechanical Convection Oven, Model STM 80 was utilized for measuring temperature behavior of the sensor in the

temperature range from 25°C up to 100°C. The influence of the air pressure on the sensor response was studied using a high vacuum Kurt Lesker system, Model SuperSystem I/II. An in-house developed gas delivery system was utilized for to study of the sensitivity of the NF film to benzene gas, and a custom-made liquid delivery system was used for study of the sensor response to different liquid loadings.

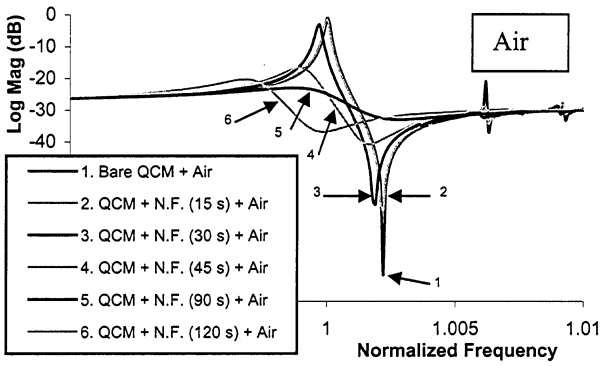


Figure 2. The S_{21} amplitude, α, characteristics, of the NF sensors in air as a function of frequency for five different deposition times.

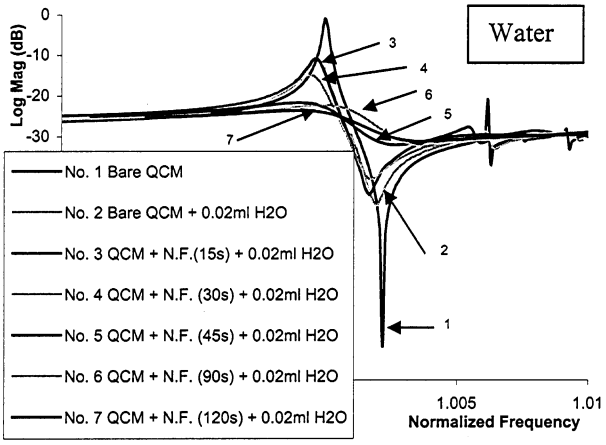


Figure 3. The S_{21} amplitude, α, characteristics of NF sensor with Newtonian liquid loading as a function of the deposition time.

3. RESULT AND DISCUSSION

3.1 Response of NF Sensor in Air and Vacuum

The changes in the resonant frequency, f_r, attenuation, α, frequency shift, Δf, and attenuation shift, $\Delta\alpha$, due to acoustic loading of NF film are presented in Figure 2 and 3. The presented S21 characteristics show the response of the TSM transducer loaded with the NF films of different thickness, which corresponds to different deposition times equal to 15, 30, 45, 60, 90, and 120 seconds. In Figure 2 and 3 the NF film are exposed to air, and water correspondingly. The NF sensors evidence the response, which is typical for viscoelastic loading (Figure 2, 3). The resonant frequency decreases and the attenuation increases. Due to the whole 3-D structures of NFs and the NF mesh, the mechanism of the interaction between the shear wave generated by the TSM resonator and the NF film is different in comparison to a continuous polymer film. The propagation of the shear waves through the NF film depends on the viscoelastic properties of single NF, internal fiber bonding, the NF structure and the effective thickness of the NF film.

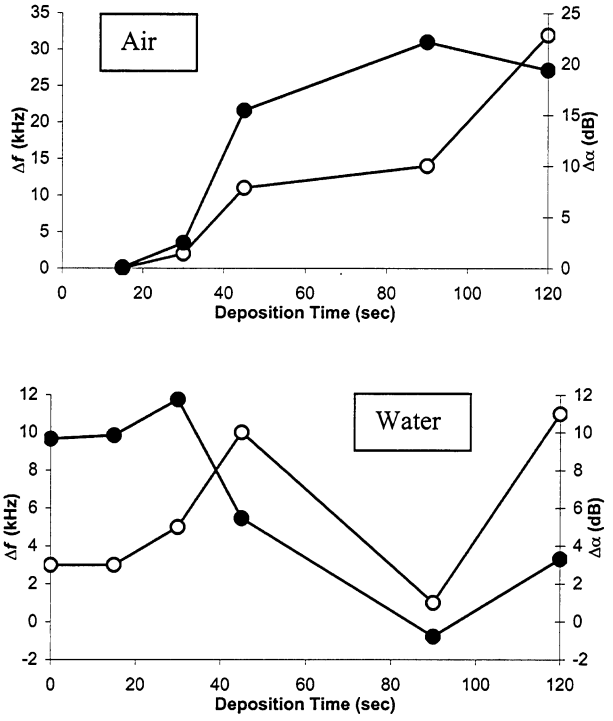


Figure 4. Resonant frequency shift ○ and attenuation ● of NF sensors in air (upper) and with Newtonian liquid loading (lower) for five films fabricated at different deposition times (corresponding to different NF film thickness).

From the Figure 2-4 it can be seen that the NF film corresponding to 90 second deposition time exhibits resonant behavior. This effect could be the case when the acoustic resonant features of the film having the thickness about half of the wavelength. The 90 seconds deposition time NF sensor showed relatively small Δf in air and with Newtonian liquid loading. The attenuation factor at that thickness is smaller with water in comparison to air loading. This phenomenon can be described as the coupled resonant systems between TSM resonator and NF film [8].

Because of the mesh structure of the NF film, the question of the influence of a trapped air on the sensor response was studied. The NF sensor was placed inside a high vacuum chamber to test the effect of the ambient air. The air pressure was slowly decreased from 760 Torr to

10^{-6} Torr and the resonant frequency, attenuation and phase at the resonant frequency were measured.

As one can notice from Figure 5 there is clear changes in both attenuation and phase between the pressure at 760 Torr and less than 10^{-3} Torr. This shows that the ambient air pressure is affecting the response of the NF film.

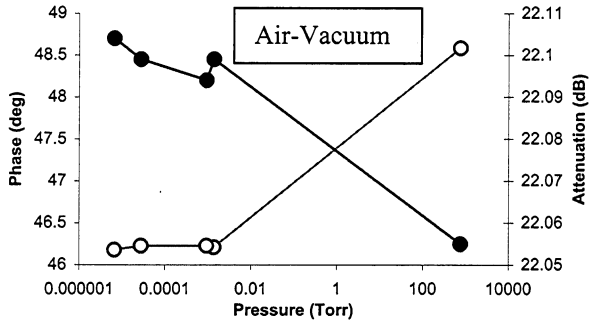


Figure 5. Attenuation (•) and phase (○) changes of NF sensor under different pressure

3.2 Influence of Temperature on NF Sensor Response.

Since the mechanical losses in the NF sensor were relatively large, we studied the influence of the temperature cycling treatment on the NF sensor behavior. Figure 6 shows response of a bare TSM resonator as a function of temperature, and Figure 7 presents the temperature dependence of the sensor with 120 seconds NF film. The results show typical polymer thin film interacting with TSM resonator. NF film shows dramatic shift in mechanical resonant frequency and attenuation at around its glassy transition temperature, T_g, 52°C. However, at about 100°C the resonant frequency returned back to the value closed to that at room temperature, but the attenuation factor was large and clearly growing. After cooling the sensor back to room temperature, both the resonant frequency and the attenuation returned to the initial values, which were held before the experiment. In this experiment we expected that the heat treatment would have an impact on the sensor room temperature operating parameters, however, the results showed that the impact was almost negligible.

3.3 Response of NF Sensor to Benzene

A preliminary study of the sensitivity of NF film for gas sensor applications was performed with benzene gas. Benzene gas does not chemically react with PLAGA film, so only physical sorption was detected by the NF sensor. The NF sensor with 120 seconds film deposition time was tested with benzene gas. Figure 8 shows the attenuation and phase response of the NF sensor. Right after the benzene injection, the responses of both the S_{21} attenuation and phase were detected. From the phase track in Figure 8 one can notice the mass loading mechanism in NF film by decreasing in phase after benzene injection. After 30 minutes from the injection the phase stopped the decreasing and the response was stable over several minutes.

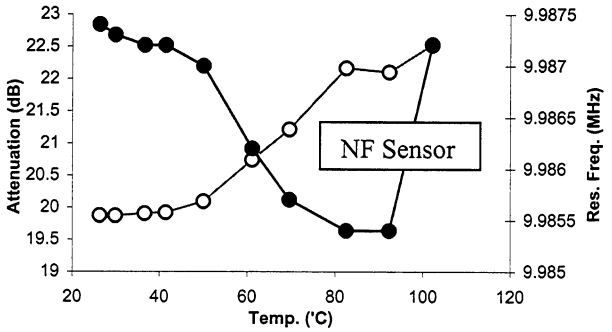


Figure 6. Response of NF sensor to different temperature. (•: resonant frequency and ○: attenuation)

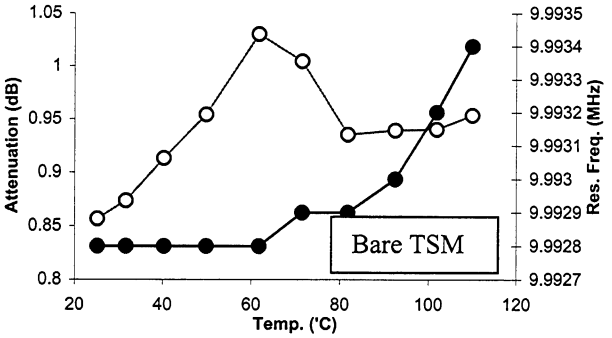


Figure 7. Response of bare TSM resonator to different temperature. (•: resonant frequency and ○: attenuation)

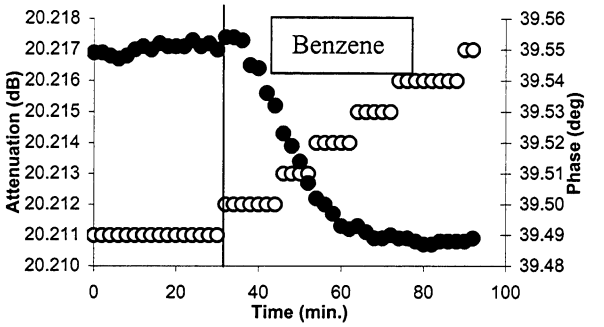


Figure 8. NF sensor response to Benzene injection. (•: phase, ○: attenuation and vertical line: injection time)

3.4 Response of NF Sensors to Hydrophobic and Hydrophilic Liquid Loading

This experiment explains an important issue about different interactions of NF film with hydrophobic and hydrophilic liquids. PLAGA polymer exhibits moderate hydrophobic properties with respect to water and moderate hydrophilic with respect to propanol. The presented S_{21} response of the NF sensor shows clearly that the NF film responded very differently to these two different liquids (Figure 9). We observed during the experiment that water was rather "sitting" on the nanofiber film, but propanol

immediately penetrated the film and directly loaded the surface of the TSM resonator. Also, it is interestingly to notice, that the NF sensitivity to water loading was very small, because the response of the sensor to air and water loading was almost the same.

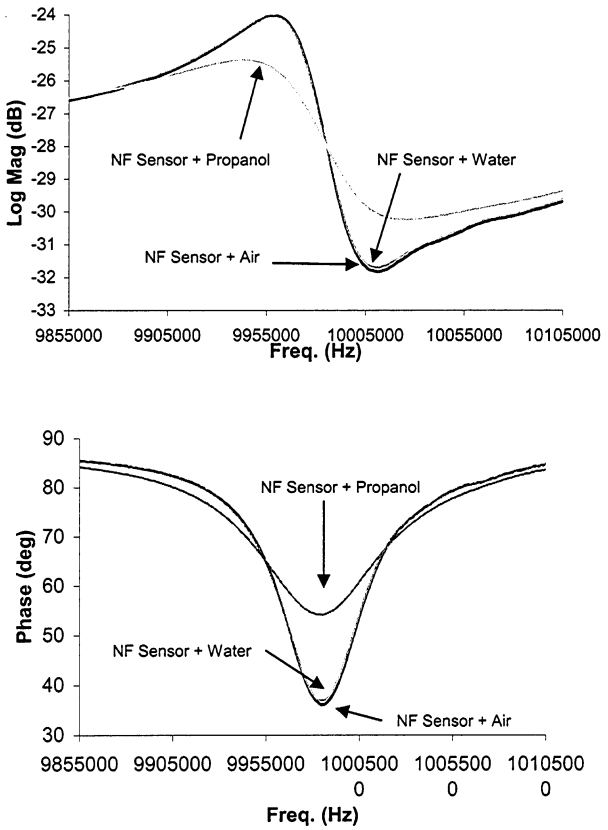


Figure 9. NF Sensor S_{21} response to hydrophobic (water) and hydrophilic (propanol) loads. [Amplitude (upper) and phase (lower) responses].

4 CONCLUSIONS

The results describing the properties of TSM resonator coated with NF thin film operating under different ambient conditions are presented. NF sensors were tested in air and vacuum, with hydrophobic and hydrophilic liquids. Also, the sensor was exposed to benzene gas and the influence of temperature was examined.

The geometrical arrangement of the PLAGA NF film has a 3-D mesh structure that is totally different then continuous polymer film. However, NF sensor exhibited quite high strong viscoelastic characteristics, which on macroscopic scale was similar to viscous loading. The NF film also strongly responded at glassy transition temperature with the changes in both amplitude and frequency. Also, the NF film exhibited some dependence on the pressure of air. When the NF sensors were exposed to benzene gas it showed a strong resonant frequency shift due to additional mass from benzene gas molecules.

Among these responses of NF sensor, the most interesting result was the different response of NF sensor to hydrophilic and hydrophobic liquid loading. Even the areal density of water is larger than one of propanol, NF sensors showed more loading from propanol. This effect is very unique and presents a very advantageous feature of NF films as a chemical or biochemical sensing interface.

Future work will be focus on the intrinsic properties of NF film. As a sensing film, the density and thickness are very critical to evaluate the performance of the NF film. However, in contrary to continuous polymer films, it is very difficult to determine the density and thickness of the NF films. Therefore, new approaches which could measure exactly density and thickness of the NF film will be developed. Also, applications for biological and biochemical sensors will be explored.

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