

# Nanostructured Stearic Acid for Gas Sensing Applications

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## ABSTRACT

In this paper we report the fabrication of nanostructured thin films of long chain polymer molecule Stearic Acid by direct vapor phase deposition method. Thin films of stearic acid were characterized by Fourier Transform Infra-red spectroscopy to identify the functional groups and were compared to as-obtained powders. The micro-nanostructures of stearic acid were studied by scanning electron microscope technique. We demonstrate the fabrication of gas sensors based on the stearic acid thin films.

**Keywords:** Stearic acid, x-ray diffraction, gas sensing

## 1 INTRODUCTION

Stearic Acid, (SA), ( $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$ ), is a long-chain saturated acid, since there are no double bonds between neighboring carbon atoms, the hydrocarbon chain is flexible and can roll up to form a ring or stretch out to form long zig-zag structures<sup>1, 2</sup>. SA is being used for assessing the self-cleaning activity of photo catalyst film in which titania induced annihilation of SA is monitored as a function of time<sup>3</sup>. Due to SA's ability to form a thin film nanolayer and compatibility with standard evaporation techniques, SA and other long chain polymeric compound thin films<sup>4</sup> have been used as lubricating layers to reduce the friction coefficient of inorganic substrates for MEMS applications<sup>5</sup>. Vapor deposition methods are demonstrated to provide epitaxial growth of alkyl-aromatic polyamide<sup>6</sup> and other higher order long chain molecules on specific substrates<sup>7</sup>.

In this paper, the deposition of long chain fatty acid molecule, SA is reported using Direct Vapor Phase (DVP) technique. Since, the literature report SA films being sensitive to selective gases like nitric oxide (discussed later), we focused our efforts on ethanol gas and reproducibility of the gas sensor. The sensing of ethanol vapor molecules was studied by current change measurements on nanostructured thin films of SA deposited on pre-patterned Si substrate with inter-digitated chrome electrodes. SA nanostructured thin film behaving like a chemi-resistor type gas sensor, with sensitivity to ethanol gas is discussed.

## 2 EXPERIMENTAL

The SA nanostructured thin films were deposited by direct vapor phase (DVP) method. SA powder obtained

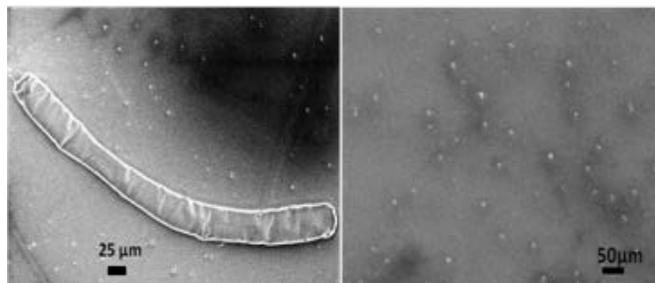
from Sigma Aldrich (99.999% purity) was used as a starting material. In DVP method, the source material was kept in the center of fused quartz tube furnace and substrates were placed at the downstream of gas flow. The ultrasonic degreased and oxide etched fused silica (FS) and Si with pre-patterned inter-digitated comb patterned electrodes were used as substrates. The furnace was ramped up to 70°C (melting point of SA =69.6 °C) at 10°C/min while maintaining measured flow of argon gas. The furnace was ramped down at the same rate. Deposition of SA thin film was carried out for 60 minutes.

## 3 RESULTS AND DISCUSSION

Vapor deposition techniques have been modified for depositing thin films of organic and polymeric thin films so as to get better adhesion and thermal stability of these materials. In the DVP method, the evaporated molecule is transported by inert gas flow to the substrate. The nucleation reaction takes place at the polymer chain ends and is governed by polymer chain relaxation, bond strength and the substrate surface temperature.

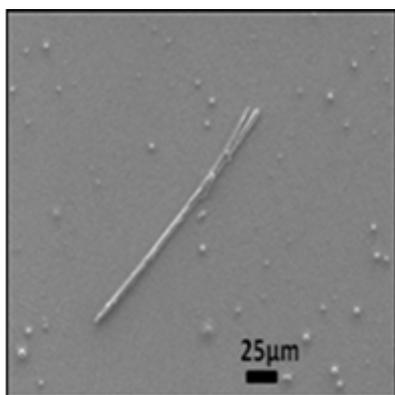
### 3.1 Morphological Studies of SA thin films

Thin film growth normally depends on the nature of substrates. The physical properties of organic crystalline thin films mostly depend on growth morphology, polymeric crystallization, transformation and molecular orientation. When the deposited thin film material come upon the substrate surface, the interaction between the incoming burst of atoms and the substrate surface cause severe changes at the interface. All the interface properties are very important in deciding the electronic structure of the thin films. In this work, we selected Si with pre-patterned inter-digitated comb patterned electrodes and fused silica as substrates. **Figures 1.** show SEM of SA deposited on Si substrate.



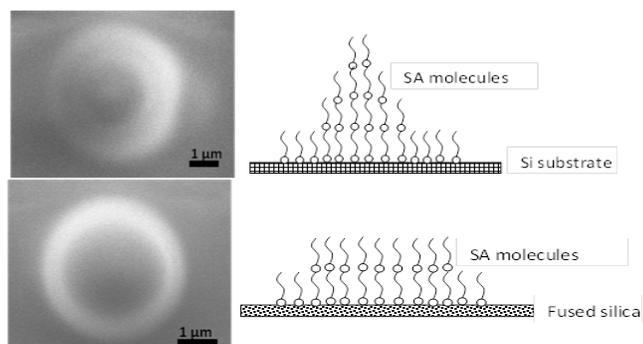
**Figure 1.** SEM of SA on Si with pre-patterned inter-digitated comb patterned electrode substrate.

**Figure 2** is a micrograph of SA nanostructured thin film deposited on fused silica substrate. Along with nanoparticle nucleus centers, we observe micro-nanowire formation that is branched out and further branching sites are seen on the wires.



**Figure 2.** SEM of SA on fused silica by DVP method.

Therefore, to understand the origin of micro-nanowires, we focused on one nucleation center. Formation of nucleus on both fused silica and silicon substrates are seen in **Figure 3**.



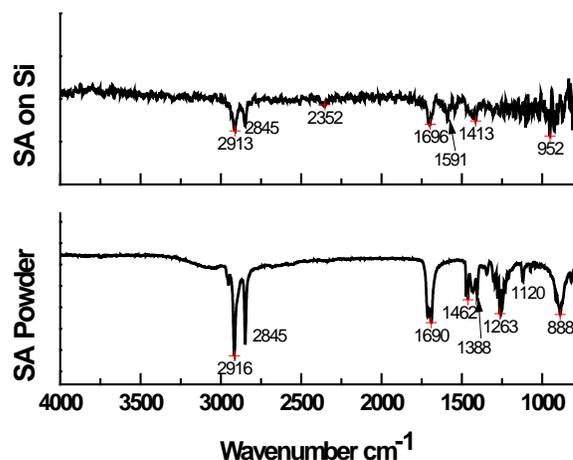
**Figure 3.** FE-SEM of nucleus and the schematic of mechanism of SA nucleus formation on Si and fused silica.

SEM micrograph reveals that the nucleation pattern differs. thus the corresponding schematic of molecular orientation of SA molecules on fused silica and Si substrates are shown. There might be a possibility of molecules lying parallel to the substrates in a spiral orientation forming a nucleus or oriented at an angle giving conical shape to the nucleus. A constant over layer growth in case of nucleus on fused silica substrate is seen. Whereas, on Si substrate we observed a few layers of SA get deposited followed by the formation of conical pyramidal nanostructures. The fundamental processes in organic thin film formation are mainly nucleation and crystal growth. The nucleation phenomenon observed here is discussed based on the classical nucleation theory (Kubono et. al.)<sup>6</sup>. According to critical nuclei concept

(Kubono 1992), when the size of a nucleus becomes larger than a certain critical size, where the free energy reaches maximum, the nucleus will grow impulsively. Probably, the nucleus on nanowire reaches its critical size and starts branching out. Thus, formation of micro nano wires of SA is seen with nucleation sites onto the wires, giving rise to new branches of wires. Therefore, if the deposition is carried out for longer time it might give rise to fractal nature of organic molecular micro-nanowires. Literature also reports that the nucleation may occur spontaneously as lateral growth hillocks are formed at lower substrate temperatures whereas the normal growth occurs at higher substrate temperatures.

### 3.2 Spectroscopic Studies of SA thin films

FTIR studies were carried out to understand the presence of functional group within the molecules in the films. **Figure 4** shows FTIR spectra of stearic acid powder for reference and SA thin film deposited on Si using DVP method.



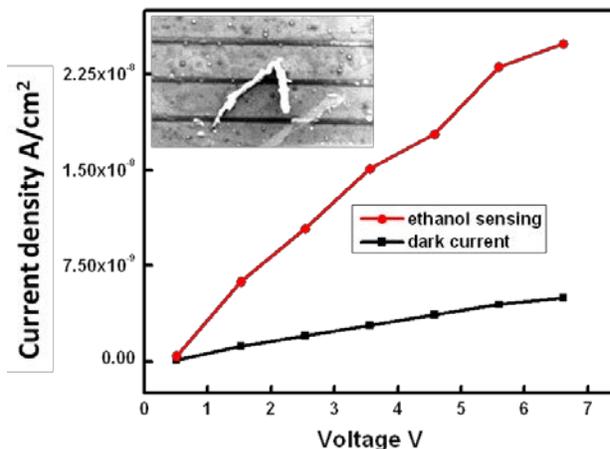
**Figure 4.** FTIR of SA powder, SA on silicon substrate, SA on Al<sub>2</sub>O<sub>3</sub> substrate and a freestanding film, indicate the presence of SA molecules being deposited.

SA strongly absorbs in the IR region of 2700-3000 cm<sup>-1</sup> with peaks at 2953 cm<sup>-1</sup>, 2916 cm<sup>-1</sup> and 2848 cm<sup>-1</sup> due to the asymmetric in-plane C-H stretching in CH<sub>3</sub> in the methyl group and asymmetric and symmetric stretching in CH<sub>2</sub> groups, respectively. For SA deposited on silica, the IR absorption peaks are seen at 2860 cm<sup>-1</sup> and 2920 cm<sup>-1</sup> that correspond to hydrocarbon, -CH<sub>2</sub>- methylene group having C-H stretching mode. Carbonyl compound C=O in the range 1720-1701 cm<sup>-1</sup>. Thus, long chains of -CH<sub>2</sub> from SA powder C<sub>17</sub>H<sub>35</sub>COOH exists on the surface of substrates at RT.

### 3.3 Gas sensing measurements of SA thin films

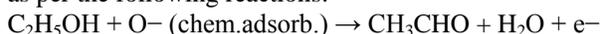
When SA is evaporated, the individual long chain molecules are directed towards the substrate, in enough concentration as governed by the flow rate. When the molecules land on the surface substrate, there is a molecular ordering which is governed by the type of substrate, orientation and temperature that have a combined effect on the surface migration of the arriving molecules. Based on the enthalpy and free energy of molecules, either of two processes, physisorption or chemisorption takes place at the initial stages. The SA micro-nanowires thus grown are used to fabricate gas sensors. Inset of **Figure 5** shows the SEM image of SA on the inter-digitated comb patterned electrode - device configuration being used for current-voltage gas sensing applications. The SA based sensor consists of chemiresistor type pre-patterned electrodes on Si substrate with inter-digitated spacing of 50  $\mu\text{m}$  and has approximately 6 spacings and a total length of the individual device is 1 mm. The specific contact resistance of Cr/Cu bilayer was independently measured to be  $3.8 \times 10^{-5} \Omega \cdot \text{cm}^2$ . The electrical measurements were carried out on SA micro-nanostructures grown between the interdigitated comb pre-patterned electrodes.

**Figure 5** shows current density versus voltage characteristics (calculated using the formula  $J = I / (S_0 \times N)$ , where,  $S_0$  is the thin film deposited area between the electrodes), after exposing the thin film to organic gas molecules. The electrical characterization study of stearic acid deposited on pre-patterned Si was carried out for ethanol gas sensing at dry atmosphere (RH 12%). Sensor exhibited a current of  $2.00 \times 10^{-8} \text{ A/cm}^2$  upon exposure to ethanol and a dark current density of  $3.00 \times 10^{-9} \text{ A/cm}^2$  at 5V. There is significant increase in the current with respect to the dark current. There have been reports showing the increase in the current by two orders of magnitude when stearic acid based sensors exposed to gases like nitric oxide. When exposed to oxide gases like nitric oxide, the electron affinity between the analyte gas and the surface activity of the nanowires lead to enhanced detection of gases. The analyte gas thus diffused into the stearic acid nanowires leads to quicker intra-chain electron transfer and reduces the resistance of the film thus increasing the sensor current. In our studies although the films are formed using vapour deposition method and the film formation is by nucleation method, we do see change in conductivity upon exposure to organic gas ethanol. The conductivity of SA films might be due to diffusion of organic gas in the pores observed in the nanostructured films and onto the nanostructured films. According to electrical characterizations carried out by Kim et. al (1998, Ref.1), of LB films, the current for 3-39 layers is in pico-amps, whereas, for the SA films deposited, in this work, by vapour deposition method (as seen in Figure 5) the current is higher by almost 10 orders of magnitude nano amps. The plot of ethanol vapour induced current



**Figure 5.** Current-voltage characteristics for ethanol gas sensing of stearic acid thin films. Inset shows the SEM image of SA on the inter-digitated comb patterned electrode device configuration.

against time upon exposure to ethanol gas indicates that initially the current is low and gradually increases. A constant 2 volts bias was applied to the sensor through the measurement. A typical pattern is observed where current increases upon exposure to ethanol gas and then decreases with a hump. The rise in sensor current is related to the oxidation of ethanol on the SA sensor active area through dehydrogenation to acetaldehyde in the presence of chemisorbed oxygen species such as  $\text{O}^-$  and  $\text{O}^{2-}$ , thus releasing additional electron(s) back to the conduction band as per the following reactions:



## 4 CONCLUSION

The process described in this paper to deposit a long chain SA molecule is compatible to standard microelectronic fabrication techniques and will pave the way for utilizing long chain bio-compatible organic compounds in sensor applications. The feasibility of vapor deposition is demonstrated for fabricating long chain organic molecular thin films for organic electronic applications. The successful application of SA based coatings for active sensors or as a passivating layer will be helpful to address the technology hurdles in chemi-resistor type sensors.

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