# METHOD FOR MEASURING PARYLENE THICKNESS USING QUARTZ CRYSTAL MICROBALANCE

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Abstract: At present, the exact final thickness of parylene coating is difficult to specify in the beginning of the coating process since the parylene thickness is a function of many components. The elements that control the thickness are substrate surface area in a vacuum chamber, program parameters, and amount of dimer charge. This paper describes a method for measuring parylene coating thickness using quartz crystal microbalance. The thickness is measured by an oscillation frequency change of quartz crystal as parylene deposites on the quartz crystal plate. These results can be used for specifying the parylene thickness real-time during the coating process.

## 1 INTRODUCTION

Biomedical implants have many strict requirements as they are being implanted for a long time under the skin. Implantable medical devices need to be coated hermetically before implantation. The coating material has many strict requirements. One very important, biological aspect is that the implant must be biocompatible. To reduce inflammation, all of the components of an implant should be nontoxic to cells (Wolgemuth 2002). Since most of the materials used in the device's electronics are not biocompatible, the encapsulation of the device with nontoxic materials is needed to prevent elusion into the body. The human body is a very hostile environment for any foreign materials. Therefore, the implant must be biostable. This electrical characteristic means that the device operation must be protected from the living tissue (Wolgemuth 2002). Otherwise the body tries to destroy or isolate the device. These two fundamental aspects, the protection of the device against the biological environment and the protection of living tissue against device's materials must be ensured before the device is implanted in a human being (Wolgemuth 2002). In addition, the long-term stability of the device and the coating needs to be high and meet the specifications.

Materials, which are used as coating materials for medical applications and qualify above-mentioned requirements, include many metals, metal alloys, ceramics, polymers, and polymer composites (Ratner et al. 1996). Small and rigid implantable devices, like pacemakers and drug pumps, could be coated with a metal case unlike the devices that must be extremely small scale, like in MEMS applications, or devices that must conform to the tissue movements. These latter mentioned devices like neural prosthesis should be made from flexible substrate with flexible coating.

Many types of polymers are widely used for medical purposes. Polymers like epoxies, silicones, polyurethanes, and parylenes, have many desirable properties, such as ease of tailoring and processing, low cost, and an excellent corrosion resistance (Ratner et al. 1996). Parylene conformal coating is ideal for the medical applications because of its many unique properties. Vacuum deposited parylene is applied in a chamber by means of gas phase polymerization (Noordegraaf & Hull 1997). Compared to liquid coating processes, vacuum deposited parylene coatings exhibit uniform coverage of medical implants and electronics components without the presence of pinholes or pooling. During the coating process, all of the exposed substrates in evacuated vacuum chamber are coated and the coating grows as a conformal film simultaneously on all surfaces and parylene penetrates into the pinholes (Noordegraaf & Hull 1997). During the parylene coating process, no impurities are generated and hence parylene coatings



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are, like silicone, one of the highest purity coatings on the market (Licari 2003). Parylene is flexible coating material just like silicone, but compared to silicone, parylene has better moisture and chemical resistance and also extremely thin coatings are tight enough for insulation and implants (Stieglitz et al. 2002). In addition, parylene has excellent adhesion to most surfaces (Licari 2003, p. 157).

# 2 BACKGROUND

## 2.1 Parylene

Parylene (poly-para-xylylenes) is a universal term for members of a unique polymer class (Licari 2003). By using dimer of di-para-xylylene, parylene has the ability to be deposited by vacuum deposition onto exposed surfaces at room temperature (Licari 2003). Varying the process parameters of deposition can control the thickness of parylene and the thickness may vary from 0,025 µm to several tens of micrometers. According to Licari (2003), the final thickness of coating can be controlled to ±10 % of desired thickness. Nevertheless, our laboratory results have proven that the thickness variance can be even greater. The parylene coating is inert and conformal and hence provides dielectric and environmental isolation. Parylene coating is used in many applications like aerospace, automotive and military industry, and also in medical applications. Nowadays, the four most frequently used commercially available parylene variations are parylene N, C, D, and HT. The two first have the longest history of use and are most commonly used in medical coating applications. This paper concentrates on coating with the polymer parylene C. (Specialty Coating System 2007)

Parylene C can provide extremely thin, uniform, and pinhole-free coating. It has low electrical dissipation factor, high dielectric and mechanical strength, and good chemical, electrical, and biological stability. It also has significantly lower moisture, chemical, and caustic gas permeability than parylene N. Above-mentioned reasons make parylene C very compatible for medical implants. In addition, parylene C is not cytotoxic and it is proven to be compatible with body tissue and blood. (Yang 1998)

## 2.2 Parylene Coating Process

The parylene coating process can be divided into three stages. The first stage is vaporization, the second is pyrolysis, and the third stage is deposit. In the beginning of the coating process, the raw material, dimer that is white powder, is vaporized under vacuum (1.0 mbar) and heated to a dimeric gas at approximately 150 ˚C. During the second stage, pyrolysis, the gas is pyrolized to cleave the dimer to its monomeric form under vacuum (0.5 mbar) to approximately 680 ˚C. In deposition stage the monomer reaches the room temperature deposition chamber. The monomer gas simultaneously absorbs and polymerizes on the substrate as a transparent parylene film. The substrate temperature never rises more than couple of degrees above the room temperature. (Specialty Coating System 2007; Pang et al. 2005, p. 4)

The surface area of substrates in deposition chamber can vary a lot. The substrates to be coated are positioned in a stand that spins in a vacuum chamber. When a small amount of dimer is used, it does not matter where the substrates are located in a stand. Also the stand area might vary a lot. The stand might for example have several levels and the grid on each level might be tight. The coating thickness is mainly a function of substrate surface area in chamber and amount of dimer charge. Program parameters have also minor importance. Even 1 µm thick coating is discovered to be tight enough for implants (Stieglitz et al. 2002). Thus it is very important to be able to measure the thickness of the coating accurately. The process is controlled by the deposition process parameters. The process parameters for our measurements are found from known coating process recipes that are used also in Para Tech Coating, Inc. in Sweden (Para Tech Coating, Inc. 2006). Recipes determine the amount of dimer, process temperatures and times, and approximate final parylene thickness. It has been proven that when different recipes are used for same amount of dimer, the final thickness might be different. Therefore, in addition to the amount of the dimer, also the process parameters affect the final thickness of parylene.

After the coating process, the achieved thickness could be measured by releasing a sample parylene film from the top of a preparat glass that has been in vacuum chamber, and then measuring the thickness of film. This does not give very accurate results, since the thin film is charged electrically and it might be creased. Also, after releasign the film from the top of a preparat glass, the film surface might already contain some impurities from the air that affect the result. Moreover, as the parylene thickness can depend on the location in the camber, the thickness of the film on the preparate glass can be

different from the thickness of the sample coating. Since the final thickness is hard to predict before the coating process or to measure accurately after the process, a real-time thickness monitoring system would be useful in many cases.

## 2.3 Quartz Crystal

A crystal oscillator is an electronic circuit that creates an electric signal with a certain frequency by using the mechanical resonance of a vibrating quartz crystal. The crystal is made of piezoelectric material and it is placed between a pair of electrodes. When these two electrodes are connected to an alternating electric field, the quartz crystal starts to oscillate at its resonance frequency due to the piezoelectric effect.

A quartz crystal microbalance (QCM) measurement technique is based on the oscillation at a precise frequency. When any type of mass is added on the surface of the crystal, the resonance frequency of the quartz crystal decreases. According to the Sauerbrey equation,

$$f_o - f = -\Delta f = \frac{2f_o^2}{A\rho_q v_q}\Delta m = \frac{2f_o^2\rho_p}{\rho_q v_q}\Delta x \qquad (1)$$

the change in mass, $\Delta m$, is proportional to the change in frequency, $\Delta f$. Here $f_o$ is the initial resonant frequency of the crystal, $f$ the resonant frequency of the coated crystal, $A$ is the effective area of the crystal (between electrodes), $\rho_q$ is the density of quartz, and $v_q$ is the shear velocity in quartz. The change of mass is written in terms of parylene thickness, $\Delta x$ and density, $\rho_p$. When very accurate measurements of very small mass changes need to be performed, the QCM technology is very appealing and it has already been studied as a system for measuring film thickness during deposition of different materials. (Eggins 2002; Gulati, Auras, & Rubino 2006) In addition to rigid deposits, the QCM has been widely used for its respond to changes in a liquid's viscoelastic properties. Some targets of using QCM have been for example humidity sensor (Ito et al. 2003), bacterial spores detector (Lee et al. 2005), and proteins detector.

# 3 MEASUREMENTS

## 3.1 Preliminary Study

The starting point for the real-time thickness measurements method was the conclusion that if parylene penetrates inside the crystal oscillator and covers the quartz crystal (Fig. 1), the mass of the quartz crystal must increase. Based on the QCM technology, the mass change of the crystal should be directly proportional to its frequency change. Moreover, since the mass change is proportional to crystal area and parylene thickness, the frequency change is proportional to parylene thickness, as given in eq. (1). By increasing the parylene thickness, the frequency of crystal oscillators placed in vacuum chamber should linearly decrease.

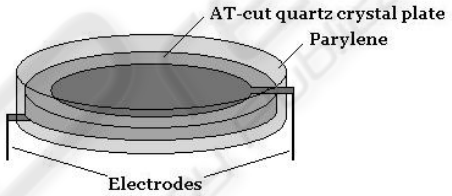


Figure 1: A quartz crystal covered with parylene.

In order to enable parylene penetration to the surface of the quartz crystal, small holes must be drilled to the metal case of the crystal oscillator. As a preliminary study for the measurements, the number of holes on the sides of the oscillator required to achieve the largest frequency change, was determined. It seemed that three 1 mm holes generated larger resonance frequency change than one or two holes, even if all of the crystal oscillators were in the same run of parylene equipment in vacuum chamber. At the same time making four holes on both sides gave the same result as three holes so there was not need to increase the hole number to more than three. Thus it seems that full covering of the quartz resonator was not obtained with only one or two holes in the resonator case. These results bear evidence that parylene can not penetrate through all pinholes easily.

## 3.2 Measurement Set-up

For the measurements, 21 crystal oscillators were used. The resonance frequency of these crystal oscillators was 3.579 MHz. Three 1 mm holes were drilled on both sides of the crystals' metal case. Each crystal was numbered with consecutive numbers. After drilling the holes, the resonance frequency of

each oscillator was measured with a network analyzer.

The measurement arrangement was carried out in the following order. After measuring the initial frequency, all of the crystals in metal case were coated with parylene. Model 3000 Labtop, Parylene Deposition System, Para Tech Coating (Aliso Viejo, USA) equipment was used for coating. The resonators were coated using 1.7 g of dimer and process parameters for 2 µm coating. Therefore the estimated thickness of the parylene film was 1.7–2.0 µm. The same procedure was repeated 11 times for all crystals. Each time there was an estimated 1.7–2.0 µm growth on the preceeding coating. The frequency of each crystal was measured with network analyzer after each coating run, and results were documented. The frequency decreased due to the mass increment on the quartz crystals.

To be able to analyse the results, an accurate film thickness after each parylene coating must be known. These measurements were done visually, by using microscope Olympus BX60M. For reference data, silicon samples were coated in the same processes with the crystal resonators. Eleven silicon chips (approximately 1.0 cm x 1.0 cm), in addition to crystals, were placed into the vacuum chamber in the beginning of the first coating. One silicon chip was taken away from the chamber after every coating and marked with consecutive numbering. Meaning chip having number $i$ should have approximately $i \times 1.7$–$2.0$ µm parylene film on the silicon. To be able to define the accurate thicknesses of parylene coats, each chip was placed in a mould and covered with epoxy. The cross-sectional samples were then mechanically prepared for microscopic thickness examination by grinding and polishing.

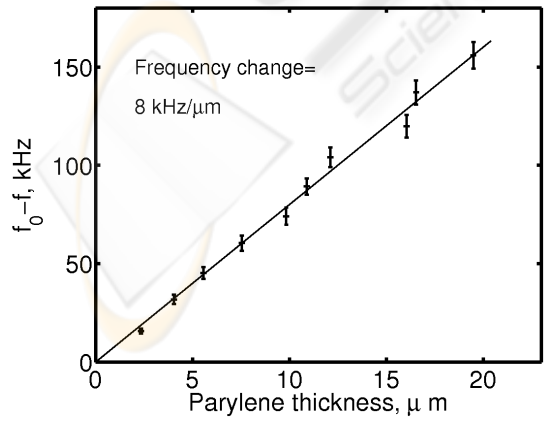


Figure 2: The frequency change of crystals as a function of parylene thickness. The vertical lines indicate the average value ± standard deviation of 21 crystal samples.

# 4 RESULTS

After 11 coating runs, measurement results proved that there is a certain interrelation between the resonance frequency and the thickness of parylene. The measurement results are illustrated in Fig. 2. The frequency change of crystals increases linearly as parylene thickness increases. The slope of this line is 8.0 kHz/µm.

The coefficient appearing in the Sauerbrey equation, (1), is 3.64 kHz/µm. As compared to this value, the frequency change in Fig. 2 is quite a lot larger. There are several possibilities that can explain this discrepancy.

On each coating run, parylene was added on the last coat of parylene. It is possible that these layers or the interfaces had collected some impurity that affected the results; though impurities were not seen in visual microscope examination. Another source of discrepancy might be in the coating process parameters. When different recipes for same amount of dimer are used, the final thicknesses are unequal. Therefore, it seems that the process parameters affect the final density of parylene, and/or the parylene coats different locations in the chamber with different thicknesses. Furthermore, the parylene density after each coating is not measured, and hence it is unreliable to use the literature value for parylene density in Sauerbrey equation. Finally, when the crystal is coated, parylene covers the entire quartz crystal area including the sides of the crystal and the electrodes connected to the quartz crystal. Hence it might prevent the vibration of the quartz crystal and measurement results in frequency change are not equal to frequencies measured with Sauerbrey equation.

In the future, these measurement results are usable basis for developing the parylene thickness measurement set-up, though additional experimental results will be needed for accurate reference data. Idea is to control the deposition thickness of parylene during the deposition process by monitoring the resonance frequency change of crystal oscillator in vacuum chamber. The real-time measurement set-up would be composed of the crystal oscillator placed in vacuum chamber, the network analyser, and the measuring cables for generating the connection between the crystal oscillator's electrodes and the network analyser. The possibility to produce sealed hole, for example to the observation window of vacuum chamber to allow measuring cables to pass through, should be studied. In real-time measurement, the network analyser measures the resonance frequency change and as the

earlier defined frequency change for target parylene thickness is reached, the coating run could be cut off.

## 5 SUMMARY

We have presented a method to measure the thickness of parylene coating, especially for medical electronic devices. The method is based on frequency change of coated quartz crystals. We proved that the frequency change is proportional to the parylene thickness, and determined the factor relating the thickness and frequency change. The applicability of this factor to different parylene coating processes was discussed. The method is applicable also for real-time measurements enabling the measurement of parylene thickness during the growth process. In real-time measurements, the growth process could be stopped after the target thickness has been reached.

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