Adsorption and humidity sensing

Objective

The objective of this laboratory is for you to explore how a piezoelectric resonator coated by a thin polymer film can be used as a highly sensitive sensor for water vapor.

Preparation

Read pages 6-12; 16-19; 27-28 of the operating manual for the quartz crystal monitor; read the introductory section of the 1993 paper by Zografi posted at the Compass web-site.

Equipment and samples

- Quartz crystal monitor (QCM) and control electronics; flow cell for the QCM; quartz crystals
- Solutions of PVP (poly(vinylpyrrolidone)); spin coater.
- Apparatus for creating flows of dry air mixed with moist air that is saturated with water vapor.

Introduction

Gas sensing is an important technology for environmental and personal safety; control of combustion process, food storage, and energy efficiency. Many of you probably have a CO sensor made from SnO in your apartment or home; essentially every car has an O_2 sensor made from ZrO_2:Y_2O_3 mounted in the exhaust manifold; and most modern clothes dryers incorporate a humidity sensor made from a conducing polymer that detects when the clothes are dry enough to turn off the heat. In this lab, you will use the equilibrium adsorption of water in a polymer film as a humidity sensor.

Session 1: Quartz crystal monitor and spin-coating of thin polymer films

- Observe the resonance frequency of the quartz crystal monitor (QCM) over a time period of 100 seconds. How stable is the frequency? Be quantitative: for example, what is the average and standard deviation of the frequency if you write down the frequency every 10 seconds for 100 seconds?
- In the following step, you are going to measure the mass of a polymer film coated on the crystal by changes in the resonance frequency of the crystal. Therefore, you will want to know how much the resonance frequency changes because of small variations in exactly how the crystal is mounted in the apparatus. Remove and replace the quartz crystal a few times to see how well the resonance frequency can be reproduced. What is the average of the resonance frequency and the standard deviation? For measuring the mass of a polymer

film coated on the crystal, which is more important: the frequency stability or the reproducibility?

- Spin-coat the quartz crystal with a thin layer of PVP. How accurately can you measure the mass per unit area of the polymer film by measuring the change in the resonance frequency of the crystal? You can assume that the density of PVP is 1.2 g cm^{-3} and that the thickness of the polymer is the mass per unit area divided by the density. Remove the crystal from the QCM and remove the polymer layer from the quartz crystal. Repeat the coating process. How well can you reproduce the thickness of the polymer film?

- If you have time, repeat the coating process at a different rotational speed of the spin-coater or different concentrations of solution. How does the areal density, i.e., mass per unit area, of the polymer film change with the rotational speed or concentration of the solution?

Session 2: Humidity sensing by water vapor adsorption in a polymer film

- Measure the mass uptake of water vapor in the polymer film as a function of the partial pressure of water in the gas flow for both increasing and decreasing humidity. In your report, compare you data to the models we discussed in class, Henry, Langmuir, and BET. Over what range of partial pressures, if any, are these models useful?

- Does this sensor for humidity show hysteresis?

- Does this sensor for humidity have good time resolution? In other words, if you change the gas flows suddenly, does the sensor react quickly or slowly? Estimate the time that is required to change-over the gas in the flow cell and compare that time-scale to the response time of the sensor.

Instrument procedures

The Sauerbrey equation is

$$\Delta f = -C_f \Delta m,$$

where Δf is the change is observed frequency in Hz, Δm is the change in mass per unit area in g/cm^2, and C_f is the sensitivity factor for the crystal. For our 5 MHz AT-cut quartz crystal at room temperature, C_f =56.6 Hz μg^{-1} cm^2.

The QCM200 System incorporates a method of a nulling C_0 capacitance to insure that the frequency and resistance values correspond to the true series resonance parameters of the quartz oscillator. The front panel of the controller includes a ten-turn dial to control the bias voltage required by the varactor C_v and a switch to choose between Adjust and Hold modes for the controller. To set the null capacitance, put the controller into Adjust Mode. The unit will modulate the varactor bias with a 75 Hz sine wave and indicate if the C_0 compensation is High, Low, or Nulled. Start with the ten-turn dial set to 8.0 (an LED should indicate that the crystal is oscillating) and adjust according to the High/Low/Null status given by the controller. Lock the dial in when the two Null LEDs glow with equal intensity. Flip the switch on the controller to the Hold mode.

The chamber in which the crystal is held has a maximum flow rate of 5 mL/min. Using the flow charts, make sure that your total flow rate is not greater than this value.