Using a quartz crystal microbalance for low energy ion beam etching studies

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A quartz crystal microbalance (QCM) has been used for etching yield measurements in a low energy ion beam system. The goal is to obtain etching yields for ion energies below 150 eV for various ion chemistries and target materials. Typical beam currents are about 0.5 μA, and the mass change per unit time on the QCM is much smaller than that for typical QCM applications. A number of problems with the application of a QCM were encountered and a description of how they were overcome is presented in this article. Quantitative etch yield results for the etching of two different photoresists and SiO₂ down to 25 eV ion energy are presented. © 2000 American Vacuum Society.

I. INTRODUCTION

The quartz crystal microbalance (QCM) is a device which utilizes the piezoelectric resonance effect of quartz to measure very small mass changes. The resonance frequency of such a crystal is a function of its mass load and mass changes of less than a monolayer can be measured,¹ which has made QCMs popular for a variety of applications. For instance QCMs are being used in deposition tools² to measure deposition rates and as electrochemical microbalances (EQCMs) where the crystal is used as part of an electrochemical cell to measure the mass arrival at the crystal surface.³,⁴

For most applications of the QCM the measurement appears to be straightforward, e.g., when a QCM is used as a deposition rate monitor. The measurement becomes less straightforward when the mass load on the QCM is not uniform as in the case of the EQCM. In this case the nonuniform mass sensitivity of the QCM has to be taken into account. The problem becomes worse when the change of mass load on the QCM is so small that small changes in the electrical circuitry or the environment cause frequency changes that are of the order of those that correspond to the mass change.

We employed a QCM to measure etch rates of materials under low energy ion bombardment. The energy range of interest is below 150 eV. The ion beam currents that can be achieved with our ion gun at these energies are of the order of 0.5 μA and therefore typical etch rates are about 0.1 monolayers/min assuming uniform etching. Some of the materials are expected to exhibit depth dependent etch rates. The problems encountered with the use of the QCM for this application and their solutions are the topic of this article. In addition, we will present selected quantitative results we have obtained.

II. EXPERIMENTAL SETUP

The QCM crystals used in this work are Leybold Inficon 008-0100-G10 crystals. They are AT-cut crystals with a resonant frequency of 6 MHz. The top electrode covers the crystal area which has a diameter of 13 mm. The bottom electrode has a diameter of 6.6 mm. The mass sensitive area between the electrodes where the resonance takes place is 0.08-0100-G10 crystals. They are AT-cut crystals with a resonant frequency of 6 MHz. The current distribution in a cross section of the QCM can be determined by measuring the current flowing to the QCM’s top electrode. An HP 531B frequency counter is used to measure the QCM resonance frequency. The experimental setup and a schematic electrical circuit for the measurement are shown in Fig. 1.

The ion gun has a focusing unit which allows one to maximize the ion beam current impinging onto the QCM crystal. The current distribution in a cross section of the beam is unknown and cannot easily be determined or controlled. The focusing parameters can be tuned to maximize the beam current, but the ion flux distribution within the beam cross section cannot be controlled. In experiments where a NaCl crystal is bombarded by argon ions the current distribution can be observed visually since the NaCl crystal will emit light when hit by argon ions of sufficiently high energy. From such experiments we know qualitatively that the current distribution can vary significantly. Besides a cir-

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cular shape with different diameters, a donut shape was also observed where the current in the beam center is less than that at an intermediate distance from the center. At low ion energies the current distribution across the ion beam is generally unknown and cannot be assumed to be uniform across the exposed target area. If a uniform current distribution across the exposed target area is required, the \( \frac{x}{y} \) deflection unit shown in Fig. 1 can be used to scan the ion beam across the target. When the scanning area is sufficiently large, there will be a center area within the scanned area that has a uniform current distribution. Experiments can be done with and without the shield in front of the QCM as can be seen in Fig. 1.

III. OBSERVATIONS AND DISCUSSION

In Fig. 2 the measured etching yield as a function of QCM position is shown. The QCM was moved beneath the ion beam which hits the center of the QCM at position 0. The ion energy is 1 keV, for which the beam can be focused within an area of less than 0.1 mm in diameter. The yield distribution reflects the nonuniform mass sensitivity of the QCM.

![Fig. 1. Overview of the experimental setup. On the left is the ion gun with the \( x/y \) deflection unit and the QCM. On the right is a schematic of the QCM.](image1)

The literature\(^5\) shows that the mass sensitivity is a radially symmetric function of the distance from the QCM center and can be described in very good approximation with a Gaussian curve,

\[
Y = Y_0 \exp \left( -a \frac{r^2}{r_0^2} \right),
\]

where \( Y \) is the measured yield, \( Y_0 \) is the maximum measurable yield, \( a \) is a shape constant, \( r_0 \) is the radius of the bottom electrode, and \( r \) is the position where the beam hits the QCM, assuming an ideally narrow beam. In our case the curve constant \( a \) is 1.5. This value has been measured by other researchers to be 1.76 (Ref. 6) and \( 2.5 \) \( r_0 \) is in our case 3.3 mm. When a shield with an aperture in front of the QCM is used, the conversion factor for the conversion from frequency change to mass change must be determined. This factor is known in case of a uniform mass change on the entire mass sensitive area. In that case, discussed by Sauerbrey,\(^7\) the frequency changes \( \Delta f \) (Hz) is linearly dependent on small mass changes in areal mass \( \Delta m_a \) (ng/cm\(^2\)):

\[
\Delta m_a = D_{\Delta} \Delta f;
\]

The proportionality factor \( D_{\Delta} \) in our case was calculated from manufacturer given values to be 12.40 ng/(cm\(^2\) Hz). Equation (2) is valid for small mass changes as long as the mass change is uniform across the entire mass sensitive area. A mass change is considered small if it changes the frequency by no more than 2% which corresponds to 120 kHz for a 6 MHz crystal.\(^8\) In our experiments even after exposure to ion bombardment for several days the frequency change of a sample is in the order of 0.1 kHz, so we are working well in the linear regime.

Since we will use a shield in front of the QCM with an aperture that limits the ions flux to a smaller area, the appropriate conversion factor needs to be derived. For a uniform ion flux the conversion factor for a given aperture is only a
function of the mass sensitivity curve and the radius of the aperture. The conversion factor multiplied by the areal integral over the mass sensitivity for the exposed area is the same for any exposed area assuming a uniform ion flux:

\[ D_R \int_0^R r \exp \left( -a \frac{r^2}{r_0^2} \right) dr = D_\infty \int_0^\infty r \exp \left( -a \frac{r^2}{r_0^2} \right) dr, \]

where \( R \) is the radius of the aperture, \( D_R \) is the correct frequency to areal mass density conversion factor for that aperture, and \( D_\infty \) is the conversion factor when no shield is used. Therefore the factor can be calculated

\[ D_R = D_\infty \frac{f_0^R \exp \left( -a \frac{r^2}{r_0^2} \right) dr}{f_0^\infty \exp \left( -a \frac{r^2}{r_0^2} \right) dr} = D_\infty \left[ 1 - \exp \left( -a \frac{R^2}{r_0^2} \right) \right]^{-1}. \]

For an aperture of 2 mm diameter \( D_R \) calculates to be 7.77 times the conversion factor \( D_\infty \) for exposure without a shield, \( D_R = 96.37 \text{ ng/(cm}^2\text{Hz)} \). Since we are not interested in the change in areal mass density but rather in the etch yield, the amount of mass removed per incident ion, we can determine that value by measuring the frequency change induced by ion bombardment as a function of time as well as of the ion current. If the frequency changes by \( \Delta f \) during the time period \( \Delta t \) at a beam current (BC) using an aperture of radius \( R \), then yield \( Y \) can be calculated as

\[ Y = D_R \pi R^2 \frac{\Delta f e}{BC\Delta t} = D_R \frac{Y'}{BC} \frac{\Delta f}{\Delta t}, \]

Frequency, time, and beam current can be measured directly and the conversion factor \( D_R \) computes to \( 2.92 \times 10^5 \) (amu nA s)/(Hz ion) for the 2 mm aperture using the elementary charge \( e \) to convert the current to number of ions and the Avogadro constant to convert mass to atomic mass units (amu).

When the shield with the 2 mm aperture is used then for experiments with identical real yields, the maximum discrepancy between two measured yields that is due to the nonuniform mass sensitivity is 13% according to Eq. (1). The measurement error due to the nonuniform mass sensitivity is less than 7% even when the current distribution of the incoming ion beam is unknown, and only the total beam current can be measured. Therefore experiments were done using the shield with a 2 mm aperture in front of the QCM. However, large discrepancies, larger than 40%, between measured yields for different beam profiles were observed. Using the \( x/y \) deflection for beam scanning together with the shield we ensured that the beam current was uniformly distributed across the target area of the QCM. The time for one scan was less than 1 s whereas a yield measurement took more than 10 min. It is therefore safe to assume the beam current was uniformly distributed by beam scanning. The measured etching yield with and without beam scanning on a QCM sample with a shield of 2 mm aperture is shown in Fig. 3. The energy of the \( \text{Ar}^+ \) ions was 400 eV. Figure 3 shows three types of data: the measured raw data which is the beam current and the offset in frequency from the initial value with respect to time, and the etching yield which is calculated from the raw data using the above conversion factor. The frequency increases with time because of the loss of mass due to etching. The beam current clearly shows the time period that the beam was scanned. The mass loss per unit time corresponds to the slope of the frequency versus time curve and can be determined by a linear fit. This value divided by the average beam current in the fitting range gives the etching yield after applying the conversion factor. The left-hand side bar which is attached to each yield data point indicates the time period over which the linear fit was taken.

The resulting measured yields are different by a factor of almost 2, and cannot be explained by the nonuniform mass sensitivity of the QCM. This indicates that the difference in yield is real and not an error of the measurement. The QCM in this experiment was previously etched for a long time without beam scanning. We have observed from visually examining the etch craters of other samples exposed for long times that most of the beam current is concentrated in an area roughly 0.1 mm in size. Etching with this kind of beam current distribution results in a highly nonuniform sample surface which might be responsible for the different yields. We therefore investigated the difference in measured yield with and without beam scanning on a sample that had previously been etched only with beam scanning and hence had a uniform topography.

The results of such an experiment are shown in Fig. 4. In addition to the raw data the fitted results are shown. Besides the yield an etch rate is also plotted and it is proportional to

FIG. 4. Yield measurements on a sample with uniform surface topography. The etch rates shown are proportional to the slope of the frequency. The horizontal bars for the yield and etch rate data represent the fitting range. (a) Comparison of yield with beam scanning on and off for two different ion energies. (b) Comparison of yields for different scanning parameters.
the slope of the frequency curve. The etch rate is only shown in order to give the reader an idea about the order of magnitude at which a sample is etched in units that are more familiar. To compute the etch rate a material density of 1 g/cm³ was assumed. Figure 4 shows the change in yield from a change in ion energy as well as the fact that the yield is the same whether the beam was scanned across the target or not. In Fig. 4(b) the yield results for different scanning settings are shown. The scanning settings are the size of the scanned area and the time it takes for one scan. It is demonstrated that the etching yield is independent of those settings.

We believe that a nonuniform surface profile created by etching with a nonuniform beam is responsible for the discrepancy in etching yields shown in Fig. 3. The specific reason that explains why the surface profile has an impact on the etching yield has not been investigated. We can speculate that one reason may be a depth dependent etch yield which would result in a wide distribution of etching yields on a sample that has been etched to different depths at different positions. Another reason may be angle dependent etching yields. Whatever the reasons are, we have shown that by ensuring uniform etching with beam scanning the etching yields become reproducible.

Another category of problems that were encountered had to do with the stability of the measurement electronics. Since the etch rates and the mass change per time in low energy ion beam etching are much lower than in typical QCM applications the frequency change that has to be measured is very small. Typically it takes a few minutes of etching to increase the QCM frequency by 1 Hz at low ion energies. In Fig. 3 it can be seen that after 20 min of etching in scanning mode the frequency changes by 50 Hz when exposed to 400 eV Ar⁺ bombardment at a beam current which is close to the maximum we can achieve. Since it is our goal to measure etch yields at much lower ion energies, below 100 eV, we must be able to keep the resonance frequency of the quartz crystal stable in the 1 Hz range.

The frequency counter used for our experiments has a time base with a thermal stability value of $5 \times 10^{-6}$. Since the base frequency of the QCM is 6 MHz, the value measured with the frequency counter may vary by a few hertz, depending on the room temperature. We have observed that a change in the room temperature during a QCM experiment will likely invalidate the result. A temperature change of the QCM itself has been shown to have a significant impact on the resonance frequency. A change of 1 °C in the QCM temperature results in a frequency change of 3 Hz, even though its temperature sensitivity is low near room temperature. The low energy ion beam is unable to cause this temperature change at the beam currents that can be achieved. A 100 eV beam of 1 μA only delivers $10^{-4}$ J/s. A change in room temperature would affect the QCM temperature in a time range that is too large to interfere with the yield measurements. Therefore we attribute the disturbing effect of a room temperature change to the frequency measurement device. To resolve the problem either a frequency counter with a high stability time base has to be employed or the environment temperature has to be controlled.

Another example of disturbance of the measurement is the impact of a range change of the ammeter on the measured
frequency. This disturbance causes the frequency to change by \(1\) Hz which would be insignificant for most applications, but has a major impact on the results of our measurements at low ion energies. The time until the disturbance has decayed can be of the order of 1 h.

When a new sample is transferred into vacuum, the resonance frequency increases for several hours. The etch rates corresponding to that initial frequency change of a new QCM sample are of the order of real etch rates caused by the ion beam. Only after approximately 10 h can the ‘‘background frequency change’’ be neglected as compared to actual etch yields. The initial increase in frequency is likely due to outgassing of the material that has been deposited onto the QCM.

IV. RESULTS

The QCM was used to determine argon sputter yields for two photoresist materials and SiO\(_2\). The photoresist materials are novolac and UV6. The sputter yields were obtained for ion energies down to 25 eV. During the measurements a hysteresis effect for the etch yield was observed. Depending on the previous etching condition the yield result would change. This is shown in Fig. 5. The frequency change and the etching yield, which is determined by a linear fit of the frequency data in the time interval indicated, are shown. The data are plotted versus time. The etching of the photoresist material at 300 eV reduces the initial yield of subsequent 170 eV etching to almost half of its final value. Only after long-time erosion does the yield approach a steady state. This effect is due to surface modification induced by the ion bombardment.

Figure 6 shows the yield results for the two resists in the energy range below 300 eV. For ion energies lower than 25 eV no etching could be observed. Figure 7 shows the sputtering yields for SiO\(_2\) and compares them to results obtained by transport of ions in matter (TRIM) simulation that was developed by Ziegler et al.\(^{12}\) The experimental results agree very well with TRIM as well as with previous work.\(^{13}\)

V. SUMMARY

The application of a quartz crystal microbalance to yield measurements for low energy ion beam studies has been demonstrated. Several problems related to very low mass removal rates, nonuniformity of the mass sensitivity of the QCM, and the stability of the setup have been encountered and overcome. A shield with an aperture of 2 mm in front of the QCM was used to overcome the nonuniform mass sensitivity problem. Beam scanning was used to resolve nonuniform etching effects. Other problems related to stability have been documented. Control of these factors is essential for accurate yield measurements with the QCM. Initial quantitative yield measurements were performed for photoresist and SiO\(_2\) and agreement with TRIM simulations has been demonstrated.

11. H. K. Pulker and J. P. Decosterd, in Ref. 1, p. 70.