Electrical Control for Wet Etching of Quartz Resonators

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Abstract − **We report a method to etch multiple quartz crystal resonators in parallel to accuracy better than +/-50 ppm by measuring the sample resonant frequency with a network analyzer while the sample is wet etched. The etch rate of individual resonators is fine tuned with electrical bias to compensate local etch rate and wafer thickness variations. This allows for the final frequency of the resonators across the wafer to be within the required specifications without trimming. By eliminating the need for the final sample trimming, the manufacturing cost can be lowered and further resonator miniaturization is feasible.**

I. INTRODUCTION

Quartz is the preferred material for resonators (clock crystals and frequency references) because of its piezoelectric nature, high mechanical quality factor, and excellent thermal stability. Unfortunately, the quartz crystal processing technology faces serious challenges in further miniaturizing the packaged resonator size. Silicon micromachining has been investigated as an alternative to quartz [1,2]. The large temperature dependency of silicon, however, needs to be compensated in reference applications where accuracy better than ±100 ppm is required over the temperature span. This significantly complicates the system design, lowers the noise performance, and increases the power consumption.

Traditionally, the quartz crystal resonators have been etched in hydrofluoric acid based solutions with the etch depth controlled by etch time, etchant temperature, and etchant concentration. Local variations in the etch rate or initial sample thickness cannot be controlled in etching but require individual trimming by metal deposition. Currently, the quartz crystals are individually trimmed and packaged. It takes considerable amount of time and it complicates further miniaturization of high frequency resonators.

We have previously reported on electrochemical etching of crystalline quartz [3,4]. This etching method allows controlling the local etch rate with patterned bias electrodes. Using the electrochemical etching, the quartz etch rate can be controlled up to +/-100% [3,4]. This opens up a new degree of freedom in chemical etching of crystalline quartz.

Here the electrochemical etching method is augmented with a closed loop measurement and control of the resonant frequency of individual resonators. This in-situ frequency measurement with a network analyzer allows for closed loop control of the etch rate. Moreover, since the etch rate can be adjusted with electrical bias, the etching can be controlled so that all resonators in the wafer are within the final accuracy specifications. The ability to etch resonators to be within the target accuracy (+/-50 ppm for low-end applications, +/-5 ppm for high-end applications) would eliminate the need for the final trimming.

II. EXPERIMENTAL SETUP

AT-cut quartz wafers were selected for the experiments as the AT-cut shows relatively constant resonance frequency from -40ºC to 80ºC. The wafers were double side polished and the starting wafer thickness was 550 µm. Before etching, the wafers were thoroughly cleansed and gold electrodes (200 nm thick with 5 nm thick chrome adhesion layer) were deposited and patterned on to the wafers. These electrodes were used for measuring the resonant frequency and for adjusting the electrical bias to tune the etch rate.

Figure 1 shows the setup for the electrochemical etch process, in which we monitor and control the etchant temperature, the electrical bias voltage, and measure sample resonant frequencies using a computer interface (GPIB). While the resonators are being etched, the etch rate is adjusted with electrical bias. The temperature is kept at 40±0.3ºC throughout the experiment. Saturated ammonium biflouride solution

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was selected as the etchant due to its constant etch rate and ability to polish the quartz surface [5]. The bias voltage was applied between the patterned electrodes and a platinum reference electrode. The use of bias voltage allows for easy control of the etch rate, which can be decreased or increased with the change of voltage [3,4]. The sample resonant frequencies were measured with a network analyzer (Lab Bode 100) and a computer controlled switch matrix. The resonant frequency is inversely proportional to the sample thickness; the resonance frequency is therefore an indirect way to measure the sample resonance frequency. Moreover, since the resonance frequency is the critical specification for the resonator applications, it is natural to monitor the resonator resonance frequency. By accurately controlling the resonance frequency during etching, the requirement for final trimming is eliminated.

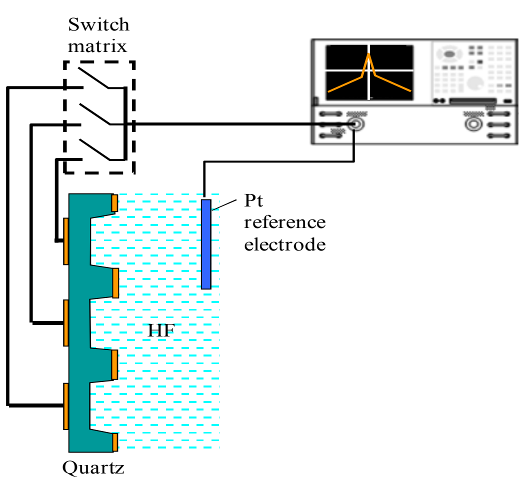

Figure 1 Electrochemical etch setup with capability of monitoring/control etchant temperature and bias voltage. The sample resonant frequency is measured with a network analyzer.

III. RESULTS

With our setup, the frequency of AT resonators can be measured to an accuracy better than +/-50 ppm while multiple samples are being etched. The accuracy is limited by the variations in the measured frequency; further improvement is possible by averaging multiple resonance frequency measurements which makes it feasible to determine the resonance frequency to within +/-10 ppm.

To obtain equal final resonance frequency for multiple samples, the etch rates of individual resonators is adjusted with bias voltage. For example, the etch rate of resonators with lower than average resonance frequency is increased by increasing the electrical bias.

An example measurement as a function of time is shown in Figure 2 where the frequency shift of two samples is shown in parts per million. As the sample thickness is reduced with the etch time, the resonance frequency is increased. The frequency shift can be correlated to the etch rate by [6]

$$\frac{f_1}{f_2} = \frac{h_1}{h_2}, \quad (1)$$

where f_1 is the initial resonant frequency, f_2 is the final resonant frequency, h_1 is the initial height of the sample, and h_2 is the final height after etching. With Equation (1), the 3000 ppm frequency shift shown in Figure 2 corresponds to a 1770 nm change in sample thickness. As the etch rate is strongly dependent on temperature, the etch rate can be greatly increased by increasing the enchant temperature. For example, increasing the etchant temperature to 80ºC would result in 11X increase in the etch rate [5].

Figure 2 also illustrates the control of the etch rate with electrical bias. The etch rate for the biased sample is about 30% larger than for the sample with no bias.

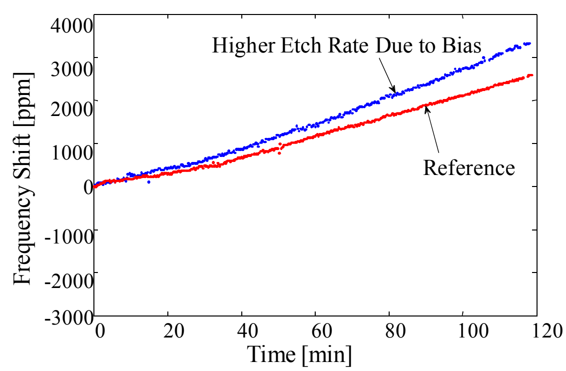

Figure 2 Samples measured for 2hrs showing the increase in etch rate due to the bias voltage.

In order to verify that the change in the resonant frequency equated to a change in the etch rate we used a KLA-Tencor stylus profiler to physically measure the sample depth after etching. Figure 3 shows an example that was measured with the profiler. The sample that was measured was etched for a four hour period. The depth was around 3500 nm at the center of the sample. The calculated etch rates are shown in Table 1 where the profiler data is compared to the electrical measurement. Twelve samples were measured (six with bias and six without bias). The measurement results are consistent and show a clear 27% increase in etch rate with electrical bias.

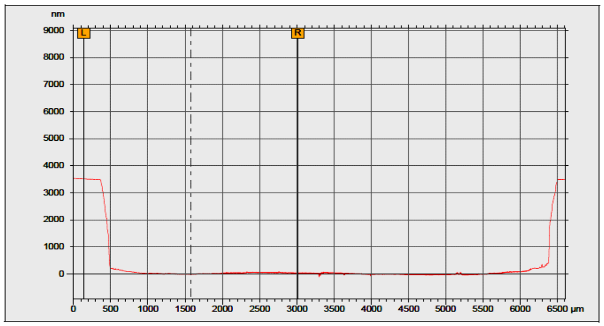

Figure 3. Measurement of the etch depth with the profiler after a four hour etch.

TABLE I. Measured etch rates with and without the bias voltage.

	Reference etch rate [µm/min]	**Biased etch rate [µm/min]**
Electrical resonant frequency measurement	0.011±0.001	0.014±0.001
Profiler measurement	0.011±0.001	0.015±0.001

To verify that the etch rate change is not a transient effect, we also etched samples for a longer time period. Figure 4 shows the frequency shift over four hours with and without applied bias. The etch rate continues to be higher for the bias than the reference sample even after four hours into the experiment. This shows that the etch rate is not a transient effect but the etch rate can be adjusted over the entire etching time.

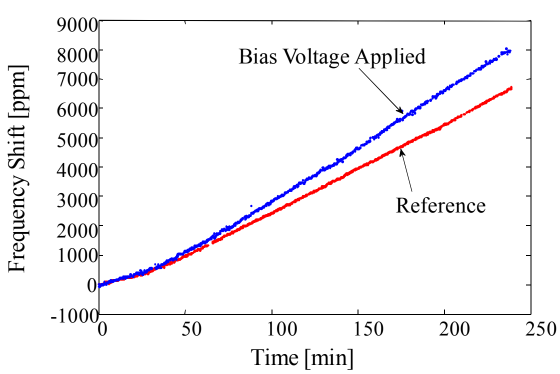

Figure 4. Resonant frequency as a function of time for a 4 hour etch.

To obtain further insights of the electrochemical etch, we measured bias voltage induced current through the sample. Figure 5 shows the typical sample current as a function of time. The initial current is high and shows several peaks. After about 30 minutes, the current is reduced and shows exponential decay. This indicates that the current is ionic in nature and that once mobile ions within quartz are depleted, the current decays. Our measurements indicate that once the sample is depleted of ions, the etch rate is not reduced back to the reference level but stays at a higher level. This further supports the conclusion that the bias causes changes in the crystal by depleting it of mobile ions.

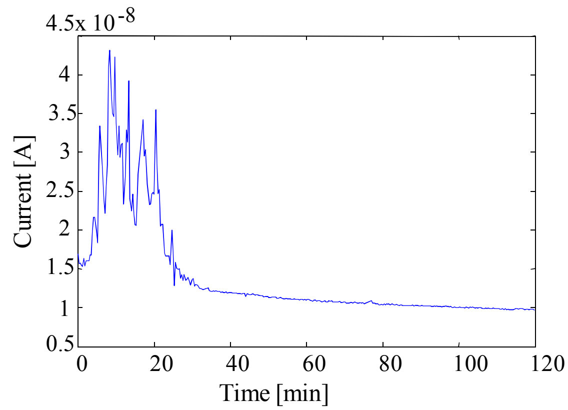

Figure 5. Sample current as a function of time.

IV. Discussion

Our experimental results indicate that we can controllably increase the etch rate by 27% which at 40ºC corresponds to etch rate increase of $\Delta R = 900$ nm/hr. Given that typical wafer thickness variations are less than ±0.1µm across the wafer, the 27% etch rate increase is more than sufficient to compensate for the typical manufacturing variations encountered in the quartz wafers.

With this ability to monitor the resonant frequency of each of the resonators and adjust the etch rate accordingly, we have eliminated the need for individually trimming the resonators. The etch rate can be controlled simply with the bias voltage which is easily controlled using computer controlled interface.

The electrochemical etch method offers an additional degree of freedom in the well established wet etching of quartz. In addition, the traditional methods to change the etch conditions can still be applied: it is possible to change the etchant or vary the temperature to vary the etch rate and surface morphology.

The measured bias induced current was initially sporadic but showed exponential decay after about 30 minutes. The current decay indicates a limited number of charge carriers which is strong evidence that the current is ionic in nature. It is well known that the quartz crystals contain significant amount of ions that could explain the current levels seen in the experiment. The total charge transport in 30 minutes is approximately $6.0 * 10^{-4}$C/cm^2 which corresponds to initial ion density of $7.0 * 10^{16}$/cm^3.

We speculate that the depletion of the mobile ions within the crystal generates unterminated bonds within the crystal. This could explain the increase in the etch rate as these unterminated bonds can act as local initiation points for SiO_x dissolution.

Electrical field and temperature is sometimes used to remove impurities in cultured quartz crystals [7]. This "sweeping" of quartz increases the resonator quality factor which is important in some critical applications, especially at higher temperatures. Although the temperature in this experiment is well below what is used in quartz sweeping, it is possible that the electrochemical etching that removes the ions from the crystal, could increase the resonator quality factor. Experiments to study this are currently ongoing.

Finally, future work will focus on improving the accuracy of the frequency measurement. Due to the liquid loading on one side of the resonator, the resonator quality factor was significantly loaded limiting the accuracy of the frequency measurement to ±50 ppm without averaging. Different electrode patterns and resonator geometries will be studied to increase the frequency measurement accuracy.

V. CONCLUSION

We have demonstrated electrochemical etching of AT-cut quartz crystals combined with the ability to measure the resonance frequency in-situ while the sample is etched. The accuracy of the frequency measurement was ±50 ppm without averaging which is sufficient for low end frequency references. Further improvements in the measurement process may result in the accuracy required by the high end communication systems. The electrochemical etching allows computer control of the etch rate which is used to compensate etch rate and wafer thickness variations across the wafer. The ability to etch all resonators within the wafer to specifications may eliminate the need for final trimming.

Acknowledgement

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