Electrochemical Etching of Quartz

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Abstract − We present the first results on the electrochemical etching of crystalline quartz. Used for bulk micromachining of silicon, electrochemical etching has not been previously explored as a method for processing quartz because of its insulating nature. By injecting energetic charge carriers into the quartz it can be made temporarily conductive, allowing current to be passed through in magnitudes which will affect the chemical etch rate. This was experimentally verified by etching samples of AT-cut quartz while bombarding the sample with electrons. Etch depths were measured and plotted as a function of current density, showing a variation of +/-3X the control etch rate. The ability to increase and decrease the etch rate can be used to define novel quartz microstructures.

Introduction

We have achieved the first results on the electrochemical etching of crystalline quartz. By passing electric current between the quartz – etchant interface the chemical etch rate can be affected. Depending on the current density, the etch rate can be either accelerated or decelerated. This allows for simple electrical control of the etching.

Quartz crystal resonators are a multibillion dollar a year industry. Crystalline quartz resonators are widely used in high tech electronics, such as communications devices and sensors. These resonators are used as frequency references and clock generators. Quartz is the preferred material for resonators because of its piezoelectric nature, high quality factor, and excellent thermal stability. Where other materials, such as silicon, require external temperature compensation, properly cut quartz resonators are insensitive to variations in environment temperature. As the devices which employ these resonators continue to shrink in size, miniaturization of the resonators is important for reduced size, weight, and power consumption.

In spite of its popularity as a resonator material, quartz processing for high frequency resonators is still a process of repeated mechanical and/or chemical polishing of the crystals to achieve the desired shapes. This processing takes significant time and is a barrier to further miniaturization because of increasing production costs. This process is also difficult to scale to larger production levels, since resonator fabrication must be individually monitored. MEMS fabrication techniques allow for wafer level processing which can produce dozens of devices on a single wafer making large scale production more efficient. Unfortunately most traditional MEMS fabrication techniques are not well suited for use on crystalline quartz because of its anisotropy and resistance to chemical etching.

Quartz is an anisotropic material and chemical etching in most crystal orientations tends to be slow with low aspect ratios. This results in very limited shapes that are possible with wet etching of crystalline quartz. A notable exception is Z-cut wafers where high aspect ratios are possible [1]. However, the Z-cut present a sizable frequency-temperature coefficient and its use is limited to sensors and low performance tuning clock oscillators.

Plasma etching is perhaps the most promising of current technologies for producing quartz microdevices. Plasma etching is not limited by the crystal orientation and is capable of producing good aspect ratios, however etch rates tend to be slow and etch selectivity is very limited. A thick masking layer is required for pattern definition and the photoresist mask layer is eaten away during etching process [2].

Electrochemical etching is a form of wet etching which exploits current passing through the material in order to control the etch rate. Fundamentally chemical etching is facilitated by charge transfer between the material surface and the etchant disassociating the surface atoms. By passing current through the material, the number of electrons available at the etch front is changed. This effect has been exploited in silicon micromachining to vary the etch rate, affect the aspect ratio, and create etch stops [3, 4, 5]. Electrochemical etching has the potential to chemically etch quartz in any crystal orientation while providing good selectivity and reasonable etch rates; however, electrochemical etching has not previously been used with crystalline quartz because its insulating nature makes it difficult for current to flow through the sample. We have overcome this by injecting energetic electrons into the quartz conduction band making the crystals temporarily conductive. Charge carriers can then be moved through the crystalline material at current densities sufficient to effect the etch rate.

Experimental Setup

To experimentally verify the electrochemical etching effects, AT-cut quartz samples were anisotropically etched using a fluoride based solution. Samples were first pre-etched using a saturated ammonium biflouride solution to remove any defects in the surface layer, and then thoroughly cleaned with isopropyl alcohol to remove any organic material from the etch surface. The quartz sample was sealed between a UHV chamber and Teflon etch vessel using viton gaskets. The sample was aligned to an electron gun, Figure 1, which was used to bombard the backside of the quartz with high energy electrons during the etching process. The front surface of the quartz was placed in contact with the etchant, which was grounded using a platinum electrode. Current passed from the backside to the grounded material-etchant interface, and was measured using a Keithley 487 Picoammeter connected in series with the Pt reference electrode. Figure 2 shows the electrochemical etching setup.

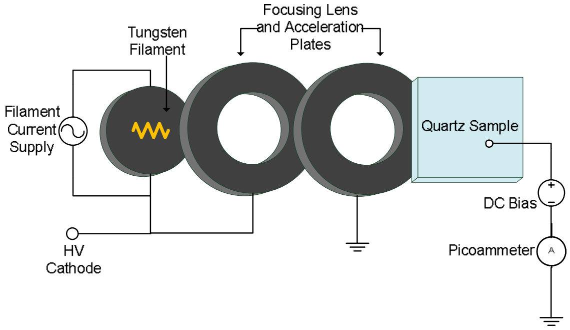

Figure 1: Functional diagram of electron gun.

Samples were etched for a set time period. Temperature was maintained using an infrared heat source. Measurements of the electron beam current and quartz diffusion currents were recorded at regular intervals throughout the etching process. After the specified time the sample was removed and thoroughly rinsed in order to remove any residual etchant. After cleaning, the samples were labeled and the etch depth was measured using a KLA-Tencor stylus profiler. Etches with obvious defects were discarded. Figure 3 shows the measured profiles of an unaffected control etch (left) and an electrochemically etched sample (right). The average depth of etches was recorded as well as the average e-beam and quartz diffusion currents.

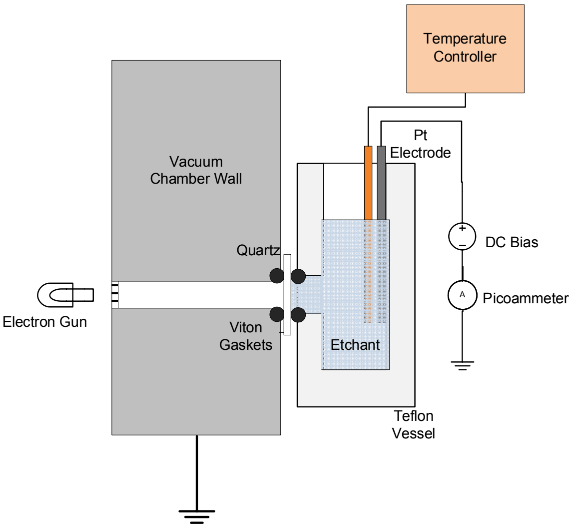

Figure 2: Electrochemical etching setup. The quartz sample is bombarded with electrons from the left side, which then drift through to the biased etch front. Current is measured using a picoammeter connected to ground via a Pt reference electrode.

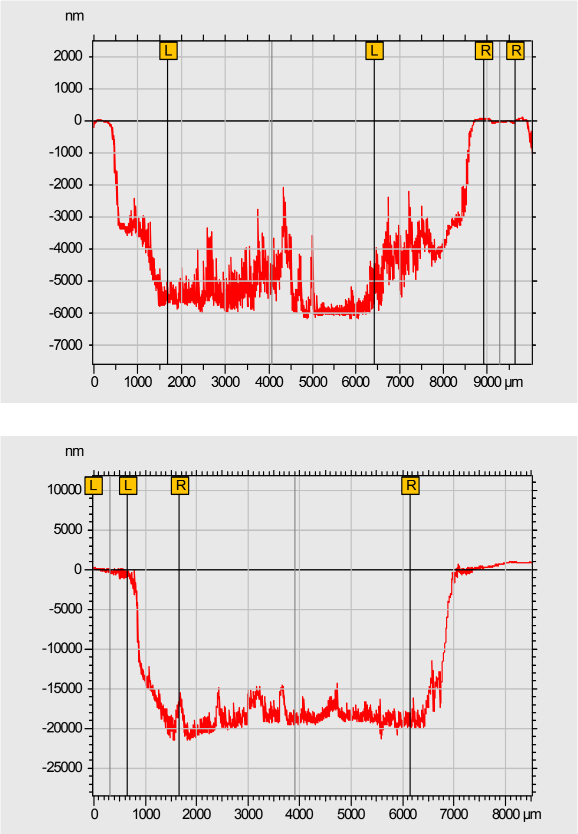

Figure 3: Measured etch profiles of a control (top) and electrochemical etch (bottom).

Results

Etch rate and diffusion current density were calculated and plotted (shown in Figure 4) showing the variation in etch rate with increasing current density. From the graph it can be seen that by controlling the current passing between the etchant and quartz, the etch rate can be either accelerated or decelerated. A maximum variation of approximately 600% is seen, +/-300% from baseline. No correlation was observed between the electron energy and variation of the etch rate, and changes in the e-beam filament current were only observed to vary the electron current. Therefore the observed electrochemical effect is primarily a function of the current density through the sample.

The positive and negative variations in etch rate indicate that the change is due to an electrochemical effect and not localized heating from the electron beam. If the variation were due to local heating due to power dissipation, it would be expect to increase monotonically with increasing current; however at high currents a decrease in etch rate below the control rate is seen.

The electrochemical effect was also shown to be repeatable with multiple experimental etches performed at current densities showing approximately the same etch rate. Roughness of the etched surface was approximately the same for control and experimental samples and compared well to the initial surface roughness of the quartz. Also no visible damage to the crystal was noted as a result of the electron bombardment. Electrochemical manipulation of the etch rate thus allows good etch rate control with minimal side effects to the quartz.

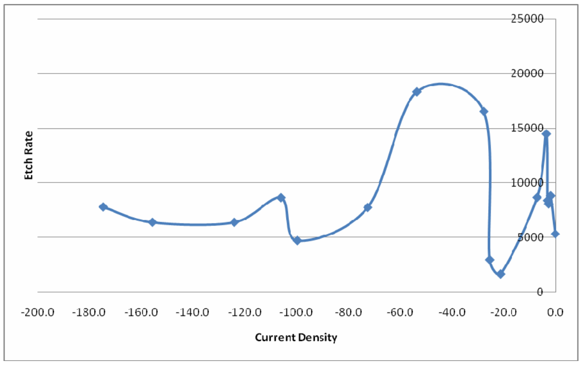

Figure 4: Etch rate versus current density.

Discussion

The observed effect is electrochemical in nature, since variation of the etch rate above and below the control rate were observed. Localized heating due to e-beam power dissipation would have resulted in a monotonic increase in etch rate with increasing current densities. Since a decrease is noted at high current densities, localized heating cannot explain the observed effect.

It has been demonstrated that intense electric fields (~2kV) can affect the etching of thin SiO_2 films by repelling the fluoride ions, decreasing the etch rate by < 5% [7]. However, all applied fields used were well below this threshold, and the observed variations in etch rate were significantly larger (300%). Indicating that the effect is electrochemical and not due to an electric field. The observed electrochemical effect also showed no relation to the energy of the incident electrons. Etch rates at a specified current density were comparable regardless of the energy of the bombarding electrons.

Future electrochemical quartz etching research will focus on exploration of etchant chemistry in order to maximize the observed electrochemical effect, and also the development of methods to selectively etch portions of the quartz surface. It is known that the etchant pH affects the electrochemical etching of silicon [4]. It has also been observed that SiO_2 etch rates decrease in fluoride solutions with increasing pH [6]. Thus, by varying the etchant pH it is possible that a larger electrochemical effect can be obtained.

Selective etching may be possible by adjusting the current flowing through defined regions of the quartz sample in order to manipulate the etch rate at defined portions of the quartz-etchant interface. Proposed methods include patterned electrodes combined with DC biasing, or the use of an electron absorbing mask on the backside of the sample (Figure 5). These methods would allow the definition of paths for the current flow through the quartz either by attracting the injected electrons to specific regions of the etch front, by defining specific areas of the sample for injection of the electrons, or a combination of both.

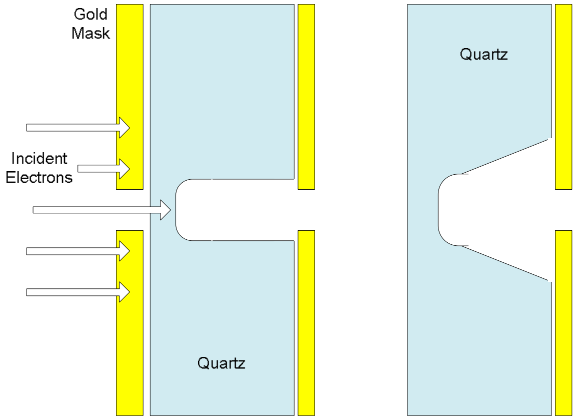

Figure 5: Potential selective etching through controlled charge carrier injection. The sample is bombarded with electrons from the backside. Incident electrons are absorbed by a thick gold mask and only allowed to penetrate the quartz in specific locations. Etching in the direction of the current is 3X faster than other directions.

Conclusions

We have shown that insulating materials such as quartz can be made temporarily conductive by the injection of energetic charge carriers. This allows levels of current sufficient to effect etch rate to be passed through quartz samples. We have also proven the concept of electrochemically etching crystalline quartz, achieving etch rates of +/- 3X the control baseline. While this is not a drastic increase, it is significant since plasma etching directionalities are only marginally better (~10X) [2]. These initial results are extremely promising as the first results of electrochemical etching crystal quartz, and provide a solid start point for future quartz processing development. With further characterization, the electrochemical etching can provide an economical way to process crystalline quartz into a variety of microdevices.

Acknowledgements

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