X-RAY ASSISTED ETCHING OF INSULATORS

Correspondence Address:
JONES, WALKER, WAECHTER, POITEVENT, CARRERE & DENEGRE, L.L.P.
5TH FLOOR, FOUR UNITED PLAZA, 8555 UNITED PLAZA BOULEVARD
BATON ROUGE, LA 70809 (US)

Appl. No.: 12/479,482
Filed: Jun. 5, 2009

Classification of materials based on band gap.

Conductor band

\[ E_g \]

Valence band

\[ E_g \]

Insulator

Semiconductor

Metal

\[ E_g \approx 0 \]
Figure 1. Classification of materials based on band gap.
### Wavelength [nm]:

<table>
<thead>
<tr>
<th>.00001</th>
<th>.001</th>
<th>.1</th>
<th>10</th>
<th>200</th>
<th>400</th>
<th>700</th>
<th>5,000</th>
<th>100,000</th>
</tr>
</thead>
<tbody>
<tr>
<td>COSMIC RAYS</td>
<td>GAMMA RAYS</td>
<td>X-RAYS</td>
<td>ULTRA-VIOLET</td>
<td>VISIBLE LIGHT</td>
<td>INFRA RED</td>
<td>RADIO WAVES</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure 3.**
Figure 5.
Figure 6.
Figure 7.

Figure 8.
Figure 9B
Figure 10.
Figure 11.
Figure 13.
Figure 18.
Tungsten and Acceleration Plates

Figure 21.
Figure 25.
Figure 26.
Figure 27.
X-RAY ASSISTED ETCHING OF INSULATORS

PRIORITY CLAIM

[0001] This invention claims the priority benefit of U.S. provisional applications 60/947,129 filed Jun. 29, 2007, and U.S. Provisional application No. 60/871,393 filed Dec. 21, 2006, the contents of each are incorporated by reference.

BACKGROUND OF THE INVENTION

[0002] 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 temperate 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.

[0003] 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 hundreds 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.


[0005] The strong chemical bonds between the atoms in an insulator such as quartz result in slow etch times with little control over the process. Hence, very limited shapes are possible with wet etching. A notable exception is Z-cut wafers where high aspect ratios are possible. However, the Z-cut present a sizable frequency-temperature coefficient and its use is limited to sensors and low performance tuning clock oscillators.

[0006] 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. See U.S. Pat. No. 6,511,915. In a typical arrangement, shown in FIG. 6 some parts of the Si sample are exposed to the electrolyte, typically an acid. Electrical contact is made with the sample (considered an electrode). A counter electrode, typically platinum, is immersed within the liquid. By applying electrical bias in the form of an applied voltage between the sample and counter electrode, current flows through the sample-liquid interfaces. The current affects the availability of electrons to take part in the silicon dissolution process. Typically, it is observed that small currents increase the etching rates while higher currents decrease the etching rate, or may even stop the etching. A typical etch rate versus bias voltage for electrochemical etching is shown in FIG. 7. Depending on bias voltage, the etch rate can vary by almost two orders of magnitude. This can be used for etch stops and to make microstructures such as membranes. Additionally, visible light has been used to generate excess carriers in semiconductors to enhance electrochemical etching. See U.S. Pat. No. 6,511,915.

[0007] Because electrochemical etching relies on a current across the sample-electrolyte interface, the suitability of a material to this process will depend on the availability of electrons (or holes) to create a current flow. Electrical properties of materials are characterized by electronic band structure: valence bands and conduction bands. Metals have partially filled conductance bands which allows electrons to move freely, making them good conductors. Semiconductors have a filled valance band structure and at 0K, they are perfect insulators, as electrons in completely filled band cannot contribute to current. However, at normal temperatures, thermal energy is sufficient to lift electrons from a filled valence band to an empty conductance band above the filled valence band. As the valence band and conductance band are no longer completely filled, the electrons in those bands can now contribute to current. Thus, semiconductors conduct electricity and the conductance typically depend on temperature. See Charles Kittel (1996) /Introduction to Solid State Physics, Seventh Edition, New York: Wiley, hereby incorporated by reference. Insulators are characterized by their high band gap energy $E_g$, separating the valence band from the conductive band. In these materials, thermal energy in normal temperatures (~50 C to 150 C) is not sufficient to lift a large number of electrons to the conductance band to sustain significant electrical current. These energy gap relationships are depicted in FIG. 1. Typical materials and their band gaps are shown in Table 1.

[0008] Quartz is a typical example of an insulating piezoelectric crystal. FIG. 2 shows measured current and resistance through a quartz sample with bias ranging from 10V to 500V. As can be seen from this Figure, the current through the sample is small and consequently the resistance is high. The resistance also remains approximately constant over the measured bias range. This is to be expected for electric fields less than 25 kV/mm. At very high voltages, dielectric breakdown will occur and high currents can flow through the sample. However, these high voltages are not a practical way to force large currents through the sample as the breakdown is largely uncontrollable and it is difficult to prevent arcing. Thus, insulators, such as quartz, will not sustain a significant electrical current with just a voltage bias, and consequently are not susceptible to the classical electrochemical etching process.
The large energy band gap in insulators (>3 eV) also makes the technique of assisting the electrochemical etching process by using visible light to generate carriers in the materials unsuitable. Visible light is characterized by photon energy less than 3 eV which is not sufficient to overcome the band gap $E_g$ in insulators. Hence, other techniques are needed if electrochemical etching of an insulator is to be undertaken.

<table>
<thead>
<tr>
<th>Material</th>
<th>Band gap [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Germanium</td>
<td>Ge</td>
</tr>
<tr>
<td>Silicon</td>
<td>Si</td>
</tr>
<tr>
<td>Indium Phosphide</td>
<td>InP</td>
</tr>
<tr>
<td>Gallium Arsenide</td>
<td>GaAs</td>
</tr>
<tr>
<td>Cadmium Telluride</td>
<td>CdTe</td>
</tr>
<tr>
<td>Aluminum Gallium Arsenide</td>
<td>AlGaAs</td>
</tr>
<tr>
<td>Gallium Phosphide</td>
<td>GaP</td>
</tr>
<tr>
<td>Silicon Carbide</td>
<td>SiC</td>
</tr>
<tr>
<td>Gallium Nitride</td>
<td>GaN</td>
</tr>
<tr>
<td>Lithium Nitride</td>
<td>LiN</td>
</tr>
<tr>
<td>Tantalum Pentoxide</td>
<td>Ta2O5</td>
</tr>
<tr>
<td>Lithium Tantalate</td>
<td>LiTaO3</td>
</tr>
<tr>
<td>Aluminum Oxide</td>
<td>AlO3</td>
</tr>
<tr>
<td>Diamond</td>
<td>C</td>
</tr>
<tr>
<td>Titanium Oxide</td>
<td>TiO2</td>
</tr>
<tr>
<td>Silicon Nitride</td>
<td>SiN3</td>
</tr>
<tr>
<td>Lithium Tetra borate</td>
<td>Li$_2$B$_4$O$_7$</td>
</tr>
<tr>
<td>Lanthane</td>
<td>La$_2$Ga$<em>3$SiO$</em>{14}$</td>
</tr>
<tr>
<td>Quartz</td>
<td>SiO2</td>
</tr>
</tbody>
</table>

**SUMMARY OF THE INVENTION**

The invention is a method of inducing a sufficient current in an insulator to allow electrochemical etching to take place. The current can be induced by illuminating the insulator with sufficiently high energy electromagnetic radiation in order to lift electrons from the valence band to the conduction band and applying a voltage bias to the insulator to direct the current as desired. The insulator can also be made conductive by illuminating the insulator with charged particles, such as electrons. The absorbed charged particles can be used to create a current in the insulator for electrochemical etching. The method can be used with etch masks and x-ray or electron masks.

**BRIEF DESCRIPTION OF THE DRAWINGS**

**0010** FIG. 1 depicts the classification of materials based on the electronic band structures.

**0012** FIG. 2 graphs the experimental current through a quartz plate and sample resistance.

**0013** FIG. 3 shows the energy spectrum for electromagnetic radiation.

**0014** FIG. 4A depicts a quartz sample irradiated X-rays.

**0015** FIG. 4B shows the variation of current in the quartz sample with x-ray tube cathode voltage variation.

**0016** FIG. 5A is a graph of the variation of the current in the sample of FIG. 4 with variation of the biasing voltage, while the x-ray radiation energy is held constant.

**0017** FIG. 5B is a graph of the variation of quartz resistance with the biasing voltage, while the sample is under a constant x-ray flux with average energy of 2.5 keV and intensity of approximately 1 W/cm$^2$.

**0018** FIG. 6 shows a typical electrochemical etching setup (PRIOR ART).

**0019** FIG. 7 shows a typical etch rate vs. bias voltage curve for electrochemical etching (PRIOR ART).

**0020** FIG. 8 depicts a set-up to electrochemically etch normally insulating materials such as quartz using photons such as x-rays.

**0021** FIG. 9 depicts a set-up to electrochemically etch normally insulating materials such as quartz using electrons (9e) and X-rays, (9b).

**0022** FIG. 10 shows a graph depicting etch rate and current for a sample irradiated with an electron beam. The sample was crystalline quartz plate and the electron energy was 10-15 kV. The etchant used was saturated ammonium bifluoride solution at 30° C. Negative current density indicates current from etch surface to back of the sample (electrons move from back surface to etch surface).

**0023** FIG. 11 shows a typical arrangement for the electrochemical etching of an insulator (hereafter referred to as a quartz sample), using photons such as x-rays.

**0024** FIG. 12 depicts electrochemical etching (EE) using a mask on each side of crystal material and no bias is uses, simply a grounded platinum electrode

**0025** FIG. 13A depicts the arrangement of FIG. 12, but employs a biasing voltage.

**0026** FIG. 13 B depicts an EE application of a back bias voltage to steer electrons to reduce the etch rate at particular locations.

**0027** FIG. 13 C depicts EE using a back bias to steer the electrons towards to middle to obtain angled etch.

**0028** FIG. 14 depicts the method using an x-ray mask is positioned between the sample and the x-ray source. The etchant can be alternatively on the side of or opposite to the x-ray source. The reference electrode is not needed but can be used to monitor the x-ray generated current through the sample.

**0029** FIG. 15 depicts the method using a variety of biasing configurations shown in figures (b) and (c) to selectively vary the etch rate.

**0030** FIG. 16 depicts the method using a conductive electrode is positioned over a first side of the crystal material and etch masks placed on the side of the crystal exposed to a etching solution. An x-ray mask is positioned between the sample and the x-ray source. A variety of bias electrode configurations can be used on both sides of the crystal as shown in figures (b), (c), (d), and (e) to selectively vary the etch rate. In (b), the back bias is used to steer the current flow to obtain sloped etch. In (d), selective biasing is used to obtain different etch rates in different locations. In (c), the back bias is used to steer electrons to obtain reduced side wall etch rate.

**0031** FIG. 17 depicts the method using a conductive mask is positioned over both sides of the crystal material. A variety of bias electrode configurations can be used on both sides of the crystal as shown in figures (b), (c), (d), and (e) to selectively vary the etch rate.

**0032** FIG. 18 depicts the method using multiple electrodes positioned on the sample.

**0033** FIG. 19 depicts the method using masking layers on each side of the crystal material. Both sides of the crystal are exposed to a hydrofluoric acid etching solution. A bias current is induced across the crystal by connecting a voltage source between lead electrodes placed in the etching solutions.

**0034** FIG. 20 depicts the penetration of X-rays into a quartz sample, showing (a) Soft X-rays, below 1 keV, (b) Slightly harder x-rays, 1 keV-20 keV, and (c) Hard x-rays, >100 keV.
FIG. 21 depicts a functional diagram of electron gun.

FIG. 22 is a graph showing the measured etch rate of a quartz sample as control, using not electrochemical etching.

FIG. 23 is a graph showing the measured etch profiles using an electrochemical etch.

FIG. 24 depicts the selective etching through controlled charge carrier injection (or radiation illumination) using the electrochemical etching method, as opposed to chemical etching of an insulator. Etching in the direction of the current is 3× faster than other directions allowing for sharper defined wall structures.

FIG. 25 depicts one process for creating flat resonators.

FIG. 26 depicts one process for creating inverted mesa resonators.

FIG. 27 depicts one process for creating mesa resonators.

DETAILED DESCRIPTION OF THE INVENTION

The invention is electrochemical etching of an electrically insulating material by assisting the production of current in the insulator. To increase the current through an insulator, the number of current conducting carriers should be increased. Two possible ways to generate free carriers (electrons or holes) in insulators are:

1. Expose the material to photons or electromagnetic radiation having energy greater than the electron band gap; or

2. Impacting the material with electrons (or to create excess electrons in the conductance band. Both techniques are considered a means to generate free carriers in the substrate.

By making the insulator temporarily conductive, larger current flows can be induced and electrochemical etching becomes possible.

A. Illumination with Electromagnetic Radiation

Valence band electrons must be provided with sufficient energy to lift them to the conduction band. For insulating materials, this implies that electromagnetic radiation having frequencies higher than visible light is needed. The natural division between low band gap and high band gap materials is 3 eV. As used, an "insulator" is a material having a band gap greater or equal to 3 eV. This energy level corresponds to the edge of the visible light spectrum. Suitable electromagnetic radiation will be ultraviolet light or higher frequency radiation, such as x-rays.

The relationship between the photon wavelength and energy is:

\[ E = \frac{1240}{\lambda} \text{ eV-mm} \]

For photons to lift electrons from the conduction band to the valence band, the energy of the photons needs to be larger than the band gap energy. For semiconducting materials such as silicon, optical photons (visible light) have sufficient energy to excite electrons from valence bands to conduction bands. For high band gap materials, photons with higher energy are required. For example, lithium niobate crystals (LiNbO\(_3\)) which are used for high frequency filters have a bandgap of 4 eV. This translates to photon wavelengths of about 300 nm and thus photon wavelength should be 300 nm or smaller to excite electrons in this material. Another example is quartz crystal which has a band gap of 9 eV. This translates to photon wavelength of about 135 nm and thus photon wavelength should be 135 nm or smaller to excite electrons in this material.

Several different sources could be used to generate photons with sufficiently high energy to excite electrons in the high band gap materials. These sources include:

- Xenon flash lamp
- Plasma source
- X-ray tube
- Synchrotron x-ray source
- Penetration of UV light into any material is usually very low and UV is therefore not preferred as the illumination radiation. X-rays can be readily produced with available sources, such as the x-ray tubes or synchrotrons, and x-ray sources are a ready source of the high energy photons needed. The high energy photons or x-rays provide the benefit of penetrating deeper inside the material before being absorbed. This penetrating property of x-rays is useful for samples that employ a metal sheet or metal conductor used as the electrode for the electrochemical etching process. Lower energy photons would be easily absorbed by a sufficiently thick metal sheet, thus blocking the photons from entering the sample. The higher energy x-rays can more readily penetrate through the electrode into the sample, thus making the sample more conductive.

FIG. 4A shows the experimental set-up used to verify photon induced conductivity in an insulating quartz crystal. The sample used was a quartz crystal plate with thickness of 380 μm and is biased electrically between two gold conductors with thickness of 100 nm. The sample was exposed to x-rays with energies ranging from 100 eV to 40 keV using x-ray tube. FIG. 4B shows resulting current vs. x-ray tube cathode voltage variation. Due to photon generated carriers, the currents are significantly larger than that shown in FIG. 2 for a quartz sample that was not exposed to x-rays. As expected, as the cathode voltage increases (increasing the energy of the generated X-rays), the current through a normally insulating quartz crystal increases. (see FIG. 4B)

FIG. 5A shows the variation of the current in the sample of FIG. 4 with variation of the biasing voltage, keeping the x-ray radiation energy constant with average energy of 2.5 keV and intensity of approximately 1 W/cm\(^2\) using a synchrotron x-ray source. Due to photon generated carriers, the currents are significantly larger than that shown in FIG. 2 for a quartz sample that was not exposed to x-rays. Note that the current-voltage dependency is non-linear, and the effective resistance decreases with increasing bias (FIG. 5B). This non-linearity can lead to positive feed-back (breakdown) where a modest change in bias can lead to a drastic increase in quartz current.

Electrochemical Etching of Insulating Materials:

The electrochemical etching process can hence be used with insulating material if coupled with illumination of the sample with sufficiently energetic electromagnetic radiation. For a particular insulating material, the known chemical etching process parameters (etchant chemical, pH, and process temperature) can be employed, with the biasing voltage and energy level and intensity of the illumination radiation...
chosen to produce the desired current levels in the material. As noted above, increasing current levels will generally increase the etch rates. FIG. 10 shows the experimental data showing the variation of etch rate with the current density. Although the data shown in this figure arises from the electron illumination method described later, it is equally applicable to illumination with photons such as x-rays. For example, an x-ray tube biased at 35 keV and operating at 1 mA electron beam current gives sufficient x-ray flux so that quartz crystal sample that is 380 µm thick will have current of ~10 nA/cm² to ~10 nA/cm² when biased between 1000 V and 2000 V. This current variation through the sample results in similar etch rate variations as obtained with the e-beam set-up.

[0058] From the graph it can be seen that by controlling the current 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. The optimum current density to be generated through the crystal material will depend on numerous factors, including the etching solution, the solution temperature, the solution pH, the material being etched, and the structure to be created by the process. As one nonlimiting example, quartz being etched with hydrofluoric acid at 32°C exhibits large etch rate variations at a current density between 0-5 nA/cm².

[0059] In certain applications, a rapid etch rate may be desired to create fine grained shape features in the etched material. In other applications, the rates may be varied over time to produce three dimensional structures in the insulating material. The inventive process thus allows for a degree of control of the etching process not possible with chemical etching alone.

[0060] The technique can be employed in a variety of equipment configurations. Etching apparatus typically includes a container for containing a supply of electrochemical electrolyte or etchant (etchant and electrolyte will be used interchangeably). The container generally has an open side or bottom which is scalable against the insulator to be etched, allowing the electrochemical etchant to contact the substrate. An electromagnetic radiation source for generating electromagnetic radiation in excess of 3 eV is positioned adjacent to container. Typically, the radiation source will be x-rays as x-ray sources are readily available, and x-rays have the necessary energy. Radiation energy of greater than 100 eV is preferred, and greater that 1 keV more preferred. Intensity of the radiation should exceed 1 uW/cm², with a preferred intensity of about 1 mW/cm². The radiation source directs the radiation through a window onto the sample for generating electron-hole pairs (henceforth simply referred to as “electrons”) (see FIG. 9C).

[0061] An electrical bias is applied to the substrate by connecting a bias source (a voltage source) by wire to a contact (typically a metallic film) on the back side of the substrate, and by wire to a reference electrode immersed within the etchant. Typically, the bias generated is from a DC source, although in limited circumstances, an AC generated bias can be used. A reverse bias (or back bias) source can be applied to the substrate by connecting an electrical bias source (it may be the same source) to a contact on the front side of the substrate (typically a metallic film) to counter or reduce the bias applied to the substrate from the back side of the substrate. Note for a reverse bias, the bias is created between the contact and the electrolyte, but the electric field created also extends into the substrate and has effects in the substrate. The combination of radiation and electrical bias generate a current, and the current density needed will depend on the activity of the electrolyte and the desired speed of the etch reaction. Current densities greater than 10 pA/cm² are useful for etching quartz in hydrofluoric acid (HF).

[0062] The illumination radiation can be sourced to illuminate the sample from any angle, through the etchant, or using direct exposure of a portion of the sample or substrate isolated from the etchant. A typical setup is shown in FIG. 9C. If the radiation source must pass through a substantial volume of the etchant to reach the sample, the radiation flux or radiation energy levels may have to increase to account for energy absorption by the etchant (variation in the etchant temperature may also be effected in this instance). The process can be used with etch masks and radiation masks, as further described, and other configurations commonly used in electrochemical etching.

[0063] In the following examples, the radiation is shown illuminating a portion of the sample that is isolated from the etchant. This is shown for convenience only, and in application, it is possible that there will be at least a thin layer of etchant material through which the radiation must pass. Also, the radiation is shown incident on the sample at right angles. Again, this is shown only for convenience, and using angled incidence radiation may be preferable to create specific structures. Additionally, multiple radiation sources could be employed simultaneously to create specific structures. Further, in the following examples, the polarity of the applied electrical bias is shown as negative on the substrate and positive on the reference electrode. This is shown for convenience only and the desired polarity of the bias will depend on the composition of the substrate, the reference electrode, and the electrolytic materials, and the effect to be achieved. For instance, when etching quartz using HF, if very fine structure details are desired that would necessitate reducing the etch rate, the polarity of the applied bias could flip (+ on the substrate) and (-) on the reference electrode.

[0064] FIG. 8 shows a typical arrangement for the electrochemical etching of an insulator (hereafter referred to as a quartz sample), using photons such as x-rays. One side of the quartz is in contact with the etching solution. Electrical contact is made to a region on the other side of the sample to enable current flow through the sample. By biasing the sample electrically, limited current will flow through the sample. This current is normally too small to significantly affect the etch rate. However, when the sample is exposed to ionizing radiation, mobile electrons are generated within the sample and significant current flow can be established through the sample. Thus, the availability of electrons at the etch front can be adjusted by controlling the current, resulting in the ability to control the etch rate.

[0065] The preferred etching solution depends on the material of interest. For materials containing oxides, for example quartz or lithium niobate, fluoride based acids are commonly used as fluoride is more electronnegative than oxygen and can break to oxygen bonds. Examples of acids are hydrofluoric acid (HF), ammonium fluoride (NH₄F), and ammonium bifluoride (NH₄HF₂). The pH of the fluoride solution is known to strongly affect the etch rate and this effect can be used in optimizing the electrochemical etching.

[0066] The electrochemical etching can be used to adjust the etch rate variations across the insulating wafer sample to obtain better control of the final product, such as individual resonators. For instance, FIG. 11 shows an example where individual electrodes are positioned at two regions of the
substrate and used to control the etch rates in two different locations on the exposed surface. By individually adjusting the bias of each electrode, the current can be used to speed up or slow down the etch rate in different locations on the substrate’s surface. This degree of control was unavailable in prior techniques, and can be used to produce a variety of differing structures, or mass produce a number of uniform structures.

For instance, the prior typical quartz resonator manufacturing process first uses chemical etching to thin down a quartz wafer. This process is not accurate as the initial wafer thickness and the etch rate across the wafer may not be uniform. After the rough etching, the quartz wafer is typically divided into individual resonators for individual etching. This is a costly process. Using the current technique, it should be possible to mass produce a quantity of resonators from one quartz wafer using a single etch process. It is possible to individually compensate each resonator structure on the wafer if the electrode at the location of each resonator is biased individually. To further increase the control over each resonator (e.g. thickness) it is possible to continuously measure the sample thickness and adjust the etch rate by modifying the bias voltage. One possible way to measure the sample thickness is to use optical methods such as time of flight measurement, or ultrasonic transducer for thickness measurement by time of sound propagation through each resonator structure. For piezoelectric materials, it may be preferable to measure the resonant frequency of the sample by electronically exciting the sample while it is being etched, and using the detected frequency as an indicator of thickness. Another method would be to directly (or indirectly) measure the current through each individual structure by monitoring voltage drop, resistance or current through each sample in the region(s) of interest.

To change the rate of etching, the biasing voltages can be modified (including modification by initializing or increasing an applied back biasing voltage). Alternatively, when a particular structure on the substrate reaches the desired configuration, the biasing voltage directed through that structure (such as a cavity or well) could be discontinued, thereby greatly reducing the etch rate occurring near that structure. Alternatively, when the desired thickness is reached, a back biasing voltage or rear bias voltage can be used to reduce the current flow through the structure, such as shown in FIG. 13B.

Alternatively, a series of electrodes could be positioned across the wafer substrate and used not to create multiple structures, but a single structure of uniform thickness. As can be seen, the degree of control that is possible with the present technique is orders of magnitude greater than that previously available. Other variations in the technique are shown in FIGS. 12-19. In these figures, x-rays are considered the illumination source, but any high energy radiation can be employed. Also shown are electrodes, x-ray masks and etch masks. The electrode is simply a conductor, and if the electrode is immersed in the etchant, the electrode should be inert to the etchant. Gold is a typical electrode for use in quartz etching using HF as the etchant. An etch mask is a substance placed on the insulator that is inert to the etchant, and hence, reduces the etching process wherever the etch mask is located. Again, if the etchant is HF acid, an etch mask can be made of gold. An x-ray mask is a material designed to block x-Rays. A patterned mask, opaque to the radiation employed, is applied either to the substrate, or supported adjacent to the substrate. For finer control, the “opacity” of the mask could be varied, providing regions where the mask is semi transparent, allowing a certain reduced flux of radiation through (hereafter, we will refer to x-ray mask). X-Ray masks and mask composition are well known in the art, and have considerable use in lithography. Gold can also be used as an x-ray mask if thick enough, as well as lead and other metal compositions. The required thickness of the x-ray mask will be dependent on incident energy of the illuminating radiation, and the material of the mask. As shown in FIG. 20A, low energy photons (soft x-rays, <1 keV) are effectively blocked by the metal electrode on the sample (depending on thickness) and will not assist in current generation. For example, the attenuation length for 100 eV photons in gold is just 20 nm and for 1 keV photons the attenuation length is 100 nm. As shown in FIG. 20B, higher energy photons can be stopped by a thicker mask but can penetrate through the a thin electrode on the sample. For example, 5 keV photons have attenuation length of 1 μm in gold and 20 μm in quartz. Thus, these x-rays can pass through on electrode that is a few hundred nanometers thick and generate carriers within a sample. Even higher energy X-rays can be used as shown in FIG. 20C, these X-rays penetrate deeply into the sample but are harder to mask. The X-ray mask can be positioned directly on the sample, or positioned off the sample as there will be only minor diffraction effects using X-rays. The preferred range of X-rays will depend upon the applied bias and material thickness, but 1 keV-1000 keV are believed to be suitable for many applications.

FIG. 12 shows a variation using an X-ray mask (shown as a gold mask) and an etch mask. No biasing voltage is provided. Instead, the Reference voltage is grounded, providing a sink for the X-ray generated electrons. This is usually not preferred as the current generated will be low for a comparable apparatus using a biasing voltage, such as shown in FIG. 13.

FIG. 13 A is arrangement of FIG. 12, but using a biasing voltage applied to the X-ray masks (typically, the X-ray mask will be several micrometers thick). A biasing voltage (preferred range is about 100-3000 volts) is used to induce a current across the crystal material by connecting a voltage source across the sample by applying a voltage to the electrodes (one of which is preferably is in contact with the insulator sample). In FIG. 13, gold is used as the bias electrode (typically, about 100 nanometers thick). FIG. 13B is similar, but a second biased voltage is applied to the etchant mask, to attempt to provide a degree of control over the current flow that is not available in the configuration shown in FIG. 13A. In FIG. 13B, a back bias or reverse is used to steer electrons to reduce the etch rate at the sidewalls. In FIG. 13C, a reverse bias is applied to the front middle or center structure and is used to steer the electrons towards to middle etchant mask to obtain an angled etch pattern. As shown, a reverse bias has the same polarity as that of the bias applied (that is, the bias conductors applied to the substrate have the same polarity (as shown, a negative polarity), but the bias is “back” or “reverse” as it is applied on the opposite side of the substrate, thereby countering the bias applied on the irradiated side of the substrate. It is possible to use a bias using reversed polarity, such as shown in FIG. 16B.

FIG. 14 shows photons used to make certain portions of the sample conductive, but no biasing voltage is applied, similarly to FIG. 12. FIG. 14A shows a ground on the reference electrode, and also shows a ground on the back of
the insulator. In this instance, high energy X-ray would be required to generate electrons deep in the sample at or near the etchant surface. Such a configuration is not preferred except possibly for fine detail, as the current generated is small. FIG. 14B shows a similar arrangement, except the X-rays must traverse a volume of etchant prior to incidence on the insulator.

FIG. 15 shows variations of the arrangement using a biasing voltage, but without employing an etch mask. In FIG. 15A, the negative electrode covers one side of the crystal, while in FIG. 15A, the negative electrode is selectively placed in multiple locations on the crystal (generally opposite the well or cavity to be formed). FIG. 15B shows an arrangement where the biasing electrode is surrounded by another electrode biased at different potential. The second electrode will change the electric field lines and steer the current flow. For example, if the second electrode has the same negative polarity as the first electrode but is biased at higher potential, the electric field will focus the electrodes in the region of the first electrode. FIG. 15C shows another arrangement employing two different biasing voltages on the crystal at different locations, resulting in differing currents and variations in the etch rate across the crystal surface.

FIG. 16 depicts comparable configurations to FIG. 15, but further shows how the electrochemical etching combined with the traditional physical etch masking. FIG. 16A shows a conductive electrode positioned over a first side of the crystal material, with a mask placed on the side of the crystal exposed to a hydrofluoric acid etching solution. An X-ray mask is positioned between the sample and the X-ray source. X-rays are directed past the gold mask to the crystal material. A current is induced across the crystal material by connecting a voltage source between the conductive mask and a lead electrode placed in the etching solution. FIG. 16B shows the arrangement of FIG. 16A but employs a back voltage applied to the etch masks. FIG. 16 depicts a variety of bias electrode configurations that can be used on both sides of the crystal, as shown in FIGS. 16A, C, D, and E to selectively vary the etch rate. In B, the back bias is used to steer the current flow to obtain a sloped etch. In D, selective biasing is used to obtain different etch rates in different locations. In E, the back bias is used to steer electrons to obtain reduced side wall etch rate. Note that the back bias voltage used in FIG. 16B could be used with the reverse polarity.

FIG. 17 shows variations in the equipment using etch masks, but without X-ray masks. Arrows within the crystal approximate the current paths (field gradients). Note that FIG. 17A shows a common electrode across the back of the crystal, while FIG. 17B shows select locations of the negative electrode on the back of the crystal. By selective placement of the electrodes (and select use of back bias such as shown in FIGS. 17A and 17D) it is possible to customize the electric field within the crystal to best steer the current to the desired etch area. Note that the arrangements using a back bias (FIGS. 17A and B) are more directed to the desired etch area. In FIG. 17, electrons will be produced across the entire back of the crystal structure as no X-ray masks are used. Focusing of these currents is accomplished by use if a back bias (FIGS. 17A and D). Lacking a back bias, control of the current can still be accomplished by selection of the bias to be applied and selection of the locations of application of the bias (FIGS. 17B and D). It is believed that sidewalls of the well or cavity being etched will be sharper when using a back bias (and also sharper when using electrochemical methods then using only chemical etching (see FIG. 14B)). Additional control can be achieved by using etch masks. FIG. 17 shows how the local etch rates can be varied without masking the X-rays. The current can only flow from the electrodes placed on the sample and thus the etch rate around the electrode can be increased or decreased.

FIG. 18 also depicts current paths in the crystal, but the arrangement in FIG. 18 lacks etch masks. Note the current times using a back bias (FIG. 18B). FIG. 18 shows how this local etch rate control can be obtained without electrodes at the etchant side of the sample. FIG. 19 shows an arrangement where both biasing electrodes are positioned remotely from the crystal (as shown, both electrodes are located within the etchant), allowing etching to be undertaken at each side of the crystal, although the rate of etching should be faster at the side of the crystal closest to the positive electrode, as the electrons will be steered to that side due to the applied bias.

As can be seen, by employing X-ray masks (radiation masks in general), etch masks, use of back bias, selective application of the forward bias using a predetermined pattern for the electrodes, an energy of the incident radiation, the ability to steer the radiation induced electrons to the area desired to be etched is possible. Such control is not feasible using standard chemical etching of insulators. The techniques allow fine control of steering the generated current, and by varying the radiation energy, the amount of current induced can be controlled. Variation in the current density allows control of the etch rate, and steering of the current (and/or the use of masks) allows for control of areas to be etched. The system thus allows for simple electrical control of the etching.

Complex geometries can be formed in a substrate by substitution or replacing of masks (either radiations masks or etching masks) with a second mask, and performing the radiation assisted electrochemical etching a second time. Micro devices that may be manufactured with this technique include those devices currently created out of primary for non-insulating materials, and include perforated membranes, cantilevered beams, mass balances, microbridges, a tethered proof mass, a micro plate, micro mirrors, and other structures.

Examples of use of the techniques to create multiple quartz resonator structures on a single wafer substrate are shown in FIGS. 25-27. As used, a resonator is a physical device that oscillates at specific frequencies because its dimensions are an integral multiple of the half wavelength at those frequencies that exhibits resonance or resonant behavior, that is, it naturally oscillates at some frequencies with greater amplitude than at others. Quartz resonators are commonly used in cell phones and other RF devices, as quartz is piezoelectric, a crystal, and has excellent frequency stability across a wide range of temperature. Current quartz generators are millimeters in lateral dimensions. Smaller dimensions are needed for integration in RF micro-devices or integrated chips.

The process is shown for creating three resonators (in cross section), but thousands could be produced at a time. In use, a matrix of individual devices will be created, such as shown in the top views of the figure (all show square resonators, but other geometries are used, such as circular or rectangular). FIG. 25 shows the process for flat resonators, FIG. 26 for "inverter mesa" resonators, and FIG. 27 for "mesa" resonators. The resonator structures shown are typical resonator geometries, and many other geometries are employed in the art. In addition, similar shapes can be used for non-resonating applications. For example, pressure sensors require a
thin membrane and structures illustrated in FIGS. 25-27 could be used as pressure sensors. Especially pressure sensors made of silicon carbide using the current technique are useful for measuring pressure in harsh environments.

The first step is electrochemical etching of the substrate; after completion of the electrochemical etching process, a quartz wafer is formed having a series of resonator precursor structures. The remaining steps of the process depicted are standard techniques to produce a final resonator, generally creating the electrical contacts to activate the resonator structure, and isolating individual completed resonators. In each process, no radiation masks are shown, but could be employed.

As shown in FIG. 25a, and bias electrode is connected to the substrate, one for each resonator to be formed on the wafer. Typically starting wafer thickness are on the order of 200-400 μm, machined to specification by mechanical polishing and possibly also by chemical etching. Spacing between resonators on the wafer can be on the order of the starting substrate thickness to the final resonator thickness. The spacing allows the bias produced at one resonator to have minimal effects on adjacent resonator structures. The wafer thickness at the location of the resonators is monitored such as using optical time domain reflectometry techniques (or laser interferometric techniques) or monitoring of current levels near the etch surface (monitoring in the electrolyte) or near the etch surface (monitoring on an adjacent conductive etch mask), or monitoring the resistance or the voltage drop across or near the area of concern. For piezoelectric crystals, it may be easiest to use the sample resonant frequency to determine the wafer thickness and the location of the electrode. The individual bias is adjusted to speed up or slow down the etch rate at each resonator structure to achieve a uniform thickness (or a desired thickness if it varies across the structure) of the finished product. Each of these techniques is considered “monitoring the etch rate” by monitoring a parameter related to the etch rate and correlating the detected parameter (or evolution of the recorded parameter) with a thickness of the substrate or directly correlating to the etch rate (allowing a calculation of the thickness by integrating the etch rate over the time of etching). The thickness is then compared with the desired thickness, and may be compared with the thickness of the surrounding structures, in order to modify the process parameters at the particular structure (generally the bias DC voltage). This will generally be under computer control, where the computer can access a database having stored an experimentally determined etch rate versus process parameter look up table.

In FIG. 25b, after etching, metal electrodes about 100 nm thick are deposited to the wafer on the opposite sides, such as vapor deposition or sputtering. Prior to deposition of the metal electrodes, typically any bias electrodes and etch mask are removed. A final trim may be achieved by adjusting metal thickness. As shown in FIG. 25c, the wafer is cut to pieces to form individual resonators. The typical dimensions for the common “AT-strip” resonators are thickness of 10-100 μm and lateral dimensions of 1-3 mm. Using the current techniques, lateral dimensions can be greatly reduced allowing for much smaller quartz resonators, such as on the order of 10-100 μm, lateral dimensions, allowing quartz resonators to be more readily used in micro RF devices and integrated circuits, although larger resonators can be made as well.

FIG. 26 shows the process to make multiple “inverter mesa” resonators on a single wafer. Shown in FIG. 26A is the electrochemical etching of the wafer. The wafer is masked to form wells that will be used as the resonators. Again, there is an electrode for each resonator on the wafer. The wafer thickness at the location of the resonators is monitored and the bias is adjusted to speed up or slow down the etch rate. In FIG. 26B, after etching, metal electrodes about 100 nm thick are deposited to the wafer on the opposite sides. A final trim may be achieved by adjusting metal thickness. The wafer is cut to pieces to form individual resonators FIG. 26C. The typical dimensions for the common “inverted mesa” resonators are thickness of 1-100 μm and lateral dimensions of 100 μm-3 mm. The advantage of the inverted mesa structure is that as the resonator is supported by a thicker frame, a thinner resonator structure is possible. It is also possible to make high frequency filters by connecting several resonators together.

FIG. 27 shows the process to make multiple “mesa” resonators on a single wafer. In FIG. 27A, the wafer is masked to etch pits or cavities that will form individual resonators. There is an electrode for each resonator on the wafer. The electrode has a smaller footprint than the cavity’s floor so that it can be used to slow down the etch rate at the center of the pit. Alternatively, additional smaller electrodes could be positioned adjacent to the center electrode, and aligned with the desired “side” wells. After formation of the central pit, these electrodes can be activated (or remain activated) while the center electrode is deactivated. Alternatively, the central cavity could be created as in FIG. 26, and the wafer removed. A new etch mask would be deposited, covering a portion of the central cavity, and the wafer re-inserted into the electrochemical etching apparatus to etch the side cavities (with or without a reverse bias applied to the new etch mask, not shown). Alternatively, variations in the cavity depth can also be achieved by using X-ray masks that vary in opacity—more transmissive at the “edge” of the cavity, less transmissive at the center of the cavity, to vary in the current in the substrate accordingly (not shown). These techniques is will form a mesa structure where the resonating portion of the wafer surrounded by a thinner portion to trap the vibrations. The wafer thickness at the location of the resonators is monitored (preferably near the center of the cavity) and the bias is adjusted to speed up or slow down the etch rate to control the etch rates at the location of the resonators. After etching, metal electrodes about 100 nm thick are deposited to the wafer on the opposite sides (FIG. 27B). A final trim may be achieved by adjusting metal thickness. The wafer is cut to pieces to form individual resonators. The typical dimensions for the “mesa” resonators are thickness of 5-100 μm and lateral dimensions of 100 μm-3 mm (FIG. 27C).

Another explanation for controlling the etch rate using bias directed currents is to view the combination of electrical bias and illumination with photons as providing localized heating of the sample. The etch rate dependency on temperature is given by

\[ \text{Rate} \propto \text{exp}(\frac{-E_a}{kT}) \]

where \( E_a \) is the activation energy and \( T \) is the temperature. Due to the exponential temperature dependency, even a small change in temperature can have a significant effect in the etch rate. Here the heating is accomplished by passing current through the sample. The power dissipated in the sample is given by

\[ P = \text{VI} \]
where \( V \) is the voltage over the sample and \( I \) is the current through the sample. As an example, a voltage of 500 V and current density of 200 \( \mu \text{A/cm}^2 \) will result in heat power density of 100 mW/cm\(^2\) which can cause local sample heating. As the current can be localized by masking either the photon (or e-beam) flux or by having patterned electrodes to localize the current, selected areas can be heated to increase the etch rate in those areas.

[0087] B. Illumination with Electron Beam

[0088] Instead of using radiation to bump electrons to the conductive level, current can be created by illuminating the insulator (or parts of the insulator) with an e-beam beam, injecting energetic electrons into the insulator’s conduction band making the crystals temporarily conductive.

[0089] To demonstrate the method, Al-cut quartz samples were anisotropically etched using a fluoride based solution. Samples were first pre-etched using a saturated ammonium bifluoride 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 (see FIG. 9B). The sample was aligned to an electron gun, (such as shown in FIG. 21) 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. 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. FIG. 22 shows the measured profiles of an unaffected control etch, while FIG. 23 shows the measured profiles of an electrochemically etched sample. The average depth of etches was recorded as well as the average e-beam and quartz diffusion currents (see FIG. 10).

[0090] From this figure, 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, 

\[ \pm 300\% \]

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. The observed electrochemical effect is primarily a function of the current density through the sample. 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.

[0091] The methods described for use with illuminating the crystal with radiation will also function with illumination with an E-beam: electron masks, etch masks and use of forward and reverse biasing voltages can be used to steer the injected electrons to the desired surface to be etched. Additionally, traditional electron beam steering techniques can be used (musk as in a television set) to steer the electrons for a incidence pattern that may vary over time.

[0092] While the etch rate is not sensitive to the energy of the injected electrons, the thickness of any electron mask will be highly dependent on the energy of the injected electrons. Heavy metals, such as gold or lead, can be used as an e-mask, and grounding of the E-masks is preferred.

[0093] It is understood that this invention should have practical application to any material with band gap larger than 3.0 eV, but the invention necessarily exclude materials with a band gap of less than 3.0. However, with low energy band gaps, the conventional etching processes may be more efficient.

1. A method of forming a device comprising: providing a substrate having a electronic band structure with an electronic band gap greater than about 3 eV, exposing a section of the substrate’s surface to an electrolyte, applying an electrical bias between a region of the substrate and the electrolyte; and exposing a portion of the substrate to radiation produced from a radiation source having energy sufficient to generate mobile charge carriers within the substrate, thereby generating a current within the substrate to etch portions of said section of the substrate’s surface exposed to said etchant.

2. The method of claim 1 in which the radiation source is an X-ray radiation source.

3. The method of claim 2 wherein said X-ray radiation has an energy level in excess of 100 eV.

4. The method of claim 2 further comprising positioning a patterned radiation-opaque mask between the substrate and the radiation source.

5. The method of claim 1 further comprising forming a patterned etch mask on the substrate’s surface exposed to said electrolyte.

6. The method of claim 5 further comprising applying a reverse bias between a second region of the substrate and the electrolyte.

7. The method of claim 6 wherein said substrate has at least two opposing sides, and said region and second region are on opposing sides of the insulator.

8. The method of claim 1 wherein the electrical bias is applied between the region of substrate and the electrolyte by connecting a voltage source between a reference electrode in said electrolyte and a bias contact positioned on the surface of the substrate.

9. A method of forming a device comprising: providing substrate, exposing a portion of the substrate’s surface to an electrolyte, applying a first electrical bias between a first region of the substrate and the electrolyte and applying a second electrical bias between a second region of the substrate and the electrolyte, and exposing a portion of the substrate to radiation produced from a radiation source having energy levels exceeding 100 eV, and sufficient to generate mobile charge carriers within the substrate, thereby generating a current in portions of the substrate to etch portions of said substrate surface.

10. The method of claim 1 wherein said substrate consists essentially of quartz, or Lithium Niobate or Lithium Tantalate or Silicon Carbide or Lithium Tetraborate, or combinations thereof.
11. The method of claim 10 wherein said electrolyte comprises hydrofluoric acid (HF) or ammonium fluoride (NH4F) or ammonium bifluoride (NH4HF2) or other solution containing fluoride (F) ions.

12. The method of claim 1 wherein said device is a resonator.

13. A method of electrochemical etching of substrate, comprising the step of supplying electrons to said substrate from an external electron source, exposing a portion of the substrate’s surface to an electrolyte, applying a first electrical bias between a first region of the substrate and the electrolyte, thereby generating a current in portions of the substrate to etch portions of said substrate surface.

14. The method of claim 9 wherein said substrate has a band gap greater than 3 eV.

15. The method of claim 9 wherein said created current has a current density greater than 10 pA/cm² at a region on a surface of said substrate exposed to said electrolyte.

16. The method of claim 12 wherein said X-ray radiation has an intensity of greater than 1 μW/cm².

17. A method of electrochemical etching of substrate having an electronic band structure with an electronic band gap greater than about 3 eV, comprising the step of generating free carriers in the substrate, exposing a portion of the substrate’s surface to an electrolyte, applying a first electrical bias between a first region of the substrate and the electrolyte, thereby generating a current in portions of the substrate to etch portions of said substrate surface, said current having a current density greater than 10 pA/cm² at a region on a surface of said substrate exposed to said electrolyte.

18. A method of forming a device comprising a series of resonator precursors, comprising the steps of providing a substrate having an electronic band structure with an electronic band gap greater than about 3 eV, exposing a section of the substrate’s surface to an electrolyte, applying a series of electrical biases, each applied between an associated region of the substrate and the electrolyte, and exposing a portion of the substrate to radiation produced from a radiation source having energy sufficient to generate mobile charge carriers within the substrate, thereby generating a series of currents within the substrate to etch a series of portions of said section of the substrate’s surface exposed to said etchant.

19. The method of claim 18 further comprising the step of monitoring the etch rate or sample thickness at a plurality of said series of portions of said section of the substrate’s surface exposed to said etchant, and modifying a plurality of said series of electrical biases in response to said monitoring step.

20. A method of creating a series of resonators comprising creating a series of resonator precursors according to the method of claim 18, each resonator precursor having at two sides, forming conductive leads on each side of said series of resonator precursors, and physically separating said series on said substrate into a series of resonators.

21. The method of claim 2 wherein said X-ray radiation source comprises a Xenon flash lamp, a plasma source, an X-ray tube, or a synchrotron X-ray source.

22. The method of claim 18 wherein said series of electrical biases each applied between an associated region of the substrate and the electrolyte are applied through a series of electrodes positioned on said substrate and a reference electrode positioned in said electrolyte.

23. The method of claim 21 wherein said series of biases comprises at least two different bias values.

24. The method of claim 17 wherein said substrates consists essentially of Silicon Carbide, Gallium Nitride, Lithium Niobate, Tantalum Pentoxide, Aluminum Oxide, Diamond, Titanium Oxide, Silicon nitride, Lithium Tantalate, quartz, or combinations thereof.

* * * * *