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GENERATION OF MICRO-DOMAINS IN AT-CUT QUARTZ BY THERMAL PROCESSING AND
THE EFFECT ON RESONATOR MODES

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Abstract

The fabrication of acoustic sensors with sol-gel selective coatings requires the deposition of thin films on quartz resonators using solution chemistry techniques. Oxide films are spin-cast, then heat treated. A variety of film compositions are deposited, requiring a variety of firing schedules. Network analysis of the untreated AT-cut quartz devices revealed a resonant frequency of 5.0 MHz, corresponding to a pure thickness-shear mode resonance. For devices that were rapidly fired to 400°C and rapidly air cooled, network analysis showed the shear-mode response at 5.0 MHz disappeared, while a predominantly compressional mode response at 7.3 MHz emerged. Structural analysis explored the crystal structure changes induced by processing which resulted in this new mode.

Introduction

The effects of thermal processing on the resonant frequency and mode displacement of a quartz crystal micro balance (QCM) are investigated in this paper. The QCM is utilized in the fabrication of chemical sensors designed to detect metal ions in an aqueous solution. A sol-gel coating is deposited on the surface of a QCM, then fired in a furnace to form and consolidate an oxide film. The firing temperature affects the composition, structure and porosity of the sol-gel film and the optimum firing temperature varies with composition. For titanium dioxide films, a heat treatment to an elevated temperature (400°C) is required. In this paper, the effects and limits of thermal processing extremes on the resonator characteristics were explored.

Sol-gel coatings are spun onto the surfaces of QCMs to fabricate the sensors. After the films are spin-cast, the sensors are fired for 20 minutes in a pre-heated furnace at temperatures of 150 or 400°C, depending upon the coating composition. After firing, the sample is removed and air cooled on an unheated block. In this processing scheme, the sensor structure was rapidly heated and then rapidly cooled, or quenched. This processing cycle is

standard for the sol-gel coatings, which were originally designed for other applications. The quartz resonators used were designed to oscillate at 5.0 MHz. After the rapid processing to 400°C, the dominant resonant frequency of the quartz resonator had shifted from 5.0 MHz to 7.3 MHz. Sensors rapidly processed to 150°C still resonated at 5.0 MHz.

Experimental

The structure of the unfired and fired crystals was probed using X-ray diffraction rocking curve analysis performed with a Blake Industries Double Crystal X-Ray Diffraction System employing a four bounce Si monochromator with a resolution of eight arc seconds. A single Bragg reflection, corresponding to the 101 plane of the quartz crystal, was analyzed. Scanning Electron Microscopy (SEM) of the resonator surfaces was performed on a JEOL 6300V microscope. The surfaces were examined both with the electrode still on the surface, and also with the electrode removed. The resonators with the electrode removed were lightly coated with a thin layer of a gold palladium alloy to compensate for sample charging under the electron beam. The surface of the resonators were also examined using cross polarized light in an optical microscope.

Transmission electron microscopy was performed on plane-view and cross-sectional samples of the quenched crystal. The plane view sample was prepared by mechanically thinning the sample on one side to a thickness of approximately 10 μm , then the sample was thinned to perforation in an ion mill. The cross-sectional sample was prepared by making a sandwich by gluing the quartz crystal together with pieces of a Si wafer to obtain adequate thickness; then the cross-section was thinned and perforated as the plane view sample. The samples were lightly coated with a layer of amorphous carbon to avoid specimen charging under the electron beam. The analysis was performed with a JEM 2000FX microscope.

Results

The chemical sensors are designed to detect metal ions in solution. The resonance of the crystal is

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modified by the contacting liquid. Figure 1a and b show schematic drawings of an uncoated resonator and the shear displacement profile of the quartz and a contacting liquid. As illustrated in Figure 1b, the shear oscillation of the AT quartz causes entrainment of the contacting liquid. Changes in the liquid characteristics affect the resonant frequency and crystal damping[1].

Figure 1. Schematic of the resonator (a) and plot of the liquid entrainment induced by surface oscillation (b). Schematic view of the test case (c).

Figure 1c is a schematic drawing of the sensor configuration used to measure the sensor response. The coated resonator is placed into the test case and sealed; an uncoated reference quartz crystal is also sealed in a test case. An ion-containing solution is passed over the oscillating sensor and reference crystal, and the frequency shifts of both are recorded. The resonant frequency of both crystals will be lowered due to liquid

entrainment. A selective thin film deposited onto the resonator surface will preferentially react with certain ions in solution, altering the resonant frequency of the coated crystal by an additional, measurable amount. Figure 2a shows a plot of the typical response measured for a sol-gel coated device, oscillating at 5.0 MHz for various metal ions. The effect of the interaction of the ion solution with the thin film is to shift the resonant frequency by approximately 40 kHz.

To investigate the emergence of the 7.3 MHz mode, uncoated quartz resonators were fired for various firing times in a furnace preheated to 400°C. The magnitude of the electrical admittance ($|Y|$) vs. frequency for the series of samples is shown in Figure 3. The scale of the expanded ordinate is arbitrary to permit the curves to be included in the same plot. The only peak present in the spectrum of the unfired resonator is at 5.0 MHz. After 5 minutes in the pre-heated furnace, a small peak is present at 7.3 MHz, and the magnitude of the 5.0 MHz peak is decreased. The size of the 7.3 MHz peak increases with longer firing times, while the intensity of the 5.0 MHz peak decreases until, after a 20 minute bake, it is completely absent.

Figure 2. Plot of the sensor response to metal ion solutions

The reproducible and progressive nature of the emergence of the 7.3 MHz suggests the cause is a structural change in the crystal. The longer the firing time, the greater the extent of the damage. The motional resistance or dissipation in the QCM also increased with firing time, by two orders of magnitude. This result is obscured in the figure due to the arbitrarily expanded scale. The increased motional resistance is also an indication of crystal damage.

At the fundamental resonance, the velocity (v) of the acoustic wave propagating across the crystal thickness is related to the frequency, f , and crystal thickness, h , by the expression $v = 2hf$. When $f = 5.0$ MHz, the wave velocity is 3.3×10^5 cm/s, consistent with the shear wave velocity in quartz. When the resonant frequency is 7.3 MHz, the velocity is 4.8×10^5 cm/s, close to the compressional wave velocity. The

change in resonant frequency from 5.0 to 7.3 MHz indicates a conversion from pure shear displacement to dominantly compressional displacement.

The displacements associated with the untreated 5.0 MHz resonance and the treatment-induced 7.3 MHz resonance were investigated by measuring device response resulting from liquid contact. A series of alcohols, with varying viscosities and densities were placed in contact with the quartz crystal. Viscous entrainment of a contacting liquid (see Figure 1b) by shear displacement causes motional resistance changes proportional to $(\rho\eta)^{1/2}$, where ρ and η are liquid density and viscosity. The motional resistance arising from surface-normal displacement, if present, is proportional to ρ and independent of η .

Figure 3. The effect of firing time at 400°C on the resonant frequency of a quartz resonator.

As shown in Figure 4, the motional resistance of the unfired (5.0 MHz) device is proportional to $(\rho\eta)^{1/2}$, indicating a pure shear surface displacement. The fired device (7.3 MHz) resistance also has a component proportional to $(\rho\eta)^{1/2}$, indicating some shear displacement; however, there is a large offset, indicating surface-normal displacement as well. Apparently, the heat treatment has changed the quartz properties so that the resultant displacement is a combination of shear and compressional displacements. Since the slope of the fired (7.3 MHz) is less than the unfired (5.0 MHz) device, the shear component has diminished.

To investigate the nature of the structural change suggested by the network analysis, X-ray rocking curve analysis was performed on the unbaked and fired and quenched QCMs. The QCMs were etched to

remove the metal electrodes; the results are shown in Figures 5a and b. The pattern obtained for the unbaked sample (Figure 5a) shows a single sharp peak with a full width half max (FWHM) thickness of approximately 10 arc seconds or 0.1°, which is at the limit of the

Figure 4. Plot of the network analysis of the as-received (5.0 MHz) and quenched quartz resonators (7.3 MHz) measured with various alcohols in contact with the surface.

instrument's resolution. The extreme narrowness of the peak indicates the high order and perfection of the as-received crystal. The incident beam energy is listed in the figure for each sample. The x-ray pattern shown in Figure 5b was acquired for the fired and quenched crystal and is very different from the pattern of the unfired crystal. A higher incident power was required to evaluate this sample and the number of counts reaching the detector was greatly reduced. The peak is much broader, and secondary peaks appear to be present in the pattern. The FWHM of the broadened peak is 360 arc seconds or 0.36°. The higher incident energy required, as well as the broadening of the peak, suggest the order of the single crystal structure has been disturbed by the rapid processing.

The above results document that rapid thermal processing causes crystal damage, even though neither SEM, TEM nor optical microscopy revealed surface cracks or twin formation in the fired and quenched sample. For comparison, quartz crystals were heated and cooled at varying rates, then characterized using a network analyzer. For the crystal which was heated and cooled at a slow rate, the resonant frequency remained at 5.0 MHz, with no evidence of crystal damage as indicated by a 7.3 MHz response. In contrast, samples heated slowly then air quenched, as well as samples heated rapidly then slowly cooled, had a 7.3 MHz response indicating the importance of heating rate, as

opposed to the temperature reached in causing crystal damage.

Figure 5. X-ray rocking curve results for AT-cut quartz, as received (a) and fired at 400°C for 20 minutes (b).

Discussion

Crystal damage is thought to arise from shear stresses induced by thermal gradients created across the crystal during rapid heating and/or cooling. In the heat treatment, the samples were placed individually into a preheated furnace while sitting on edge in a slot of an alumina boat. In this configuration, radiative heat transfer is the primary heating mechanism for the crystal.

Figure 6 schematically illustrates the thermal gradient created within the crystal and its effect. As the sample is heated or cooled, the surface will be heated or cooled faster than the center, creating a temperature differential (Fig. 6a), and a shear stress within the crystal results (Fig. 6b). The thermal expansion coefficient of AT cut quartz is 1.4×10^{-5} [2], thus the stress within the crystal due to the thermal gradient will be quite high. When the level of strain within the crystal exceeds the

damage threshold, permanent changes (damage) to the crystal structure result (Fig. 6c). The damage threshold is the energy required to break bonds within the material, or cause a rotation of the tetrahedra. The pure shear mode of the quartz is a result of the perfect ordering of the crystal and the alignment of the particular plane. When this order is disrupted, a compressive mode emerges.

Figure 6. Schematic representation of the effect of thermal strain on the quartz crystal.

The liquid test results indicate that heat treatment has induced conversion from pure shear displacement to displacement that includes a surface-normal component. The reproducible change in resonant frequency from 5 to 7.3 MHz is consistent with the conversion from shear waves to higher velocity compressional waves. These results suggest that the crystal structure has been altered or damaged by the heat treatment.

Structural changes induced by heat treatment were examined using x-ray analysis. The broadening of the x-ray rocking curve peak can be explained by a number of phenomenon within the crystal structure, including the presence of micro-cracking at the surface, the existence of twins in the crystal and the presence of amorphous or disordered regions within the crystal. Analysis of the crystal surface by SEM, TEM and optical microscopy did not reveal the presence of micro-cracking. The existence of subsidiary peaks in the rocking curve pattern might be due to sub-grains within

the single crystal[3]. Sub-grains in the single crystal α -quartz may indicate the presence of twinned micro-domains. There are a number of twin types that occur in α -quartz. Dauphiné twins are formed α -quartz when the orientation or tilt of the silica tetrahedra in the basal plane rotates in response to an applied stress[4]. This transition occurs without the breaking of bonds, and thus no reconstruction of the crystal is required. The evidence of the subsidiary peaks, however, is not conclusive, as various experimental conditions may cause subsidiary peaks in the pattern. The presence of twinning within the crystal could not be confirmed by either TEM (for micro-domains) or optical microscopy (for macro-domains).

Another mechanism that would relieve strain of the crystal is the formation of amorphous regions, the local disordering of the crystal structure. The presence of amorphous regions is difficult to verify. Evidence of amorphous regions (suggested by a broadening of the peaks in the pattern) is not discernible in an x-ray diffraction pattern until the volume percent of the amorphous material is greater than 5%. Amorphous regions within the crystal would be visible by viewing the lattice fringes of the crystal in the TEM, but this analysis could not be done due to the instability of the sample under the electron beam.

Though the exact nature of the crystal damage could not be ascertained, it is clearly demonstrated that rapid thermal processing of the quartz crystal in the sensor fabrication process has a deleterious effect on the structure of the crystal and leads to changes in the acoustic mode excited. Crystal damage due to thermally-induced stresses are avoided if the sensor are heated and cooled at slower rates.

Summary

The rapid heating and cooling of quartz resonators result in the generation of a surface normal displacement component. The emergence of the surface normal component is caused by damage to the crystal microstructure, which results from thermal gradients induced during the rapid thermal processing. Slower heating and cooling rates avoid the generation of this damage to the crystal structure, as indicated by the lack of the surface normal component.

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