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RESONATORS**

T. J. Young
D. R. Koehler
R. A. Adams

Sandia Laboratories

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RADIATION INDUCED FREQUENCY AND RESISTANCE CHANGES IN ELECTROLYZED HIGH PURITY QUARTZ RESONATORS*

T. J. Young, D. R. Koehler, R. A. Adams
Sandia Laboratories
Albuquerque, New Mexico 87185

ABSTRACT

This paper describes radiation induced frequency and resistance changes in precision 5 MHz AT-cut quartz resonators fabricated from electrolyzed, high purity quartz. It includes a description of the radiation measurement methods, transient and steady-state data, and the results of thermal modeling. It is concluded that SARP[†] opt 1 and Premium-Q quartz may be pure enough as grown that 1) the usual frequency time dependent recovery characteristic of $t^{-1/2}$ is not observed; 2) without electrolysis, the impurity levels are nevertheless high enough to cause a significant decrease in Q for a short time following a pulse of ionizing radiation; 3) electrolysis can further reduce radiation response so that impurity effects are no longer significant; and 4) the transient radiation response in electrolyzed quartz is primarily thermal in nature.

[†] Sawyer Research Products, Inc., Eastlake, OH

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Introduction

The response of quartz crystal oscillators to ionizing radiation has been attributed primarily to impurities in the quartz crystals. According to the model, ionizing radiation interacting with the impurities causes changes in the elastic properties and Q of the crystal which result in both transient and steady-state changes in oscillator frequency. King and Sander¹ found, for both natural and electronic grade synthetic quartz, a typical frequency recovery characteristic of $t^{-1/2}$ with an offset of a few ppm at one second after exposure to a short pulse of ionizing radiation.

The objective of the present work is to minimize radiation induced frequency and Q changes in precision 5 MHz AT-cut quartz resonators. These changes are thought to be due primarily to interstitial monovalent cations associated with substitutional aluminum atoms in the SiO₂ lattice which become mobile upon interacting with ionizing radiation. One technique for the reduction of impurities in quartz is high temperature electrolysis (sweeping). In the sweeping process, an electric field applied along the optic axis moves impurities through the bulk material to electrodes applied to the face of the quartz bar. This process is carried out at high temperature to increase cation mobility. In the work reported in this paper, SARP optical grade and Premium-Q material were fabricated into precision 5 MHz, AT-cut resonators for evaluation of radiation effects. Data were taken on both transient and steady-state response to ionizing radiation.

Although the unswept material shows transient effects attributable to impurities sufficiently great to shut our test oscillator off for several seconds, swept material does not cease oscillation (within the measurement time resolution of 0.1 seconds and within the same test oscillator) and exhibits frequency changes of the order of only a few parts in 10^8 after exposure to a 2×10^4 rads (Si) ionizing pulse.

The transient radiation effects in the swept, high purity quartz can be described, with good agreement, by a lumped thermal model of the resonator structure and associated oven. In addition to the crystal and oven thermal properties, the associated temperature control circuitry has been included in the model. For pulse radiation dose levels of the order of 10^4 to 10^5 rads (Si), the resonator geometry and the supporting structure determines the early time response while oven effects show up at later times in the frequency transient.

¹ Resonators fabricated by Frequency Electronics, Inc., New Hyde Park, NY, and western Electric Co. Inc., North Andover, MA

Experimental Details

Since the objective of this work was to minimize radiation induced frequency and Q changes by improving the purity of the quartz material, high purity synthetic quartz was used as the starting material. In the work reported here, optical grade and Premium-Q stones were purchased from SARP and swept at Sandia. The swept quartz, as well as unswept quartz from the same stones, was then fabricated into 5 MHz, 5th overtone, AT-cut crystal resonators and sealed in evacuated metal enclosures.

Two types of radiation testing were done on these resonators, one group of tests to determine steady-state response to radiation and another group to determine transient response. To measure steady-state changes, the resonators were first measured in a transmission line as shown in Figure 1. This allowed determination of the resonator resistance, R_s , and Q. These data were taken at room temperature. Frequency measurements were made in a Pierce oscillator at 350 K in an oven which provided ± 0.1 K temperature control. The standard deviation of these frequency measurements was estimated to be $\pm 2 \times 10^{-8}$. One resonator of each material or sweeping condition was first measured in this apparatus, exposed to 10^5 rads, measured, exposed to 10^6 rads, measured, exposed to 10^7 rads, and measured again. Time between exposure and subsequent measurement was typically one day. The radiation source for these exposures was a 112 kCi ^{60}Co array at the Sandia Laboratories Gamma Irradiation Facility.

For the transient measurements, the resonators were stabilized at their high temperature turn-over point (350 K) in proportionally controlled double ovens** which provided milli-degree temperature control. The radiation source for these measurements was the Sandia Laboratories Hermes II Facility, a 10 MeV, 70 ns pulse width electron beam source operated in the bremsstrahlung mode. Output frequency of the oscillator was measured directly and the series resistance determined through an oscillator AGC voltage as indicated in Figure 2. Lead collimators were used to minimize exposure to the oscillator and oven control circuitry. The crystal, oscillator, and oven were doubly shielded to avoid electrical noise and EMP. Triaxial cables were used for the oscillator output signals and a shielded twisted pair provided input power. Frequency was recorded at 0.1 second intervals from approximately 5 seconds before to several hundred seconds after the radiation pulse with a resolution of approximately 2 parts in 10^9 . AGC voltage was also recorded over this time span and later converted into resonator series resistance. As an experiment to determine any radiation induced circuit effects, the oscillator, without crystal resonator, was driven externally through a radiation pulse with no effect on output amplitude being measurable. Circuit effects were also evaluated by 1) exposing the circuit and resonator to the full

** Model FE2637B, Frequency Electronics, Inc., New Hyde Park, NY

dose, 2) exposing the resonator to the full dose while shielding the circuit, and 3) exposing the circuit to the full dose while shielding the resonator. In all cases, the results were those appropriate for the resonator dose and apparently unaffected by circuit dose (except for the first few microseconds required for the semiconductors to recover from their radiation effects).

Experimental Results

Typical characteristics of the resonators used in this work are indicated in Table I. All optical grade quartz data are from bars from a single stone; similarly for Premium-Q. A frequency aging rate of $< 6 \times 10^{-11}$ per day was measured on one of these resonators. Figures 3 and 4 show steady-state changes in frequency and resonant resistance resulting from the ^{60}Co irradiations. These data are shown for unswept and swept optical grade and Premium-Q quartz and for partially swept Premium-Q material. The results show a frequency shift of opposite sign for the two types of quartz with some indication of improvement due to sweeping.

Transient frequency data were taken on resonators representing the same conditions as above. Figure 5 shows the transient frequency response of the Premium-Q quartz which was unswept, partially swept, and swept. The unswept material caused the oscillator to shut off ($R_s \geq 600$ ohms) for 3.5 seconds, whereas the partially swept material did not shut off but did experience a large positive transient. The swept material showed neither shut-off nor a positive transient. The response of this latter material is typical of swept quartz in this resonator structure and even and is thought to be thermal in nature rather than due to impurities as will be discussed later.

In Figure 6, we present data for the unswept and swept optical grade quartz as well as for unswept optical grade quartz previously exposed to 10^7 rads at the ^{60}Co source. The swept versus unswept comparison follows as before. However we also see that the previously irradiated unswept material behaves similarly to the swept material. This radiation stabilization characteristic was typical for all material which did not exhibit the swept characteristic. It is thought that the large dose traps the impurities in these materials such that they are unable to participate in the transient response. Although this might seem to be a useful technique to minimize the transient radiation response, it is probably of limited utility because the annealing behavior of the trapped impurities suggests that the stabilization will become less effective with time.

Response Modeling

When crystal resistance changes occur in an oscillator, concomitant frequency changes are also observed due to resistance dependent frequency effects.² Oscillator frequency dependence on resistance is a

function of the quartz crystal parameters as well as the circuit phase characteristics and is therefore different for different resonator and oscillator combinations. Such a dependence is shown in Figure 7 where the experimental frequency versus resistance data for one of the test oscillators is plotted. Transient resistance data were taken on a resonator which showed a positive frequency transient characteristic and are shown in Figure 8. Correction of the frequency measurements for the transient resistance changes leads to the conclusion that the positive frequency transients in the partially swept and unswept material are due to transient resistance changes in the quartz which are associated with impurities. The swept material shows no observable transient resistance changes and is therefore thought to contain a negligible amount of these impurities.

The transient frequency changes observed after pulse irradiation are therefore the results of a composite of effects stemming from elastic modulus changes, resistance changes, and temperature changes in the quartz and resonator structure. A thermal model of the quartz crystal resonator to describe the radiation-induced temperature effects has been constructed⁵ to explain the frequency transient observed in the swept synthetic quartz resonators. The modelling takes into account the thermal characteristics of the various components of the resonator structure and approximates them in a lumped element description. The frequency changes in this model are assumed to stem from the time changing temperature in the active region of the quartz crystal. The various elements in the resonator structure are heated instantaneously by the radiation pulse to characteristic temperatures dependent upon the material and mass of the element. Subsequent equilibration of this non-homogeneously heated system yields the time changing temperature of the crystal.

Although Holland⁴ has calculated the frequency change associated with a non-uniform heating of the crystal resonator in the thickness direction, transient frequency changes associated with a time changing temperature ambient had been observed as early as 1950 by Warner et. al.⁶ and attributed to radial crystal temperature gradients or to crystal-electrode stresses. The empirical characterization of this effect was given by the expression

$$\frac{df}{f} = A \frac{dT}{dt}$$

where $A = 15 \text{ ppm}/^{\circ}\text{C}/\text{sec}$ for a 5 MHz 5th overtone AT resonator and dT/dt is the time rate of change of ambient temperature.

We have empirically determined the proportionality constant to be $26 \text{ ppm}/^{\circ}\text{C}/\text{sec}$ when the frequency change is expressed in terms of the time-changing temperature at the oscillating quartz boundary. The experiments consisted of perturbing the oven temperature set-point of

an oven stabilized oscillator and observing the frequency change and temperature change as a function of time.

The thermal model for these precision AT-cut resonator and ovens is shown in Figure 9. The frequency change is a function of the active region temperature and its rate of change given by

$$\frac{\Delta f}{f} = A \frac{dT}{dt} + g(T)$$

where $g(T)$ is the static frequency-temperature characteristic. With a three point mounting configuration, the quartz was partitioned into a central vibrating zone and four annular quadrants. Heat flow to the oven assembly was possible along the three mechanical supports. Heat flow in the thickness direction of the quartz is neglected since its characteristic time is less than 0.1 second. This model includes the resonator structure and the oven, with their thermal properties, and the oven temperature control characteristic. The physical dimensions and thermal properties of the various parts of the resonator structure and oven have been used to calculate the values of the lumped elements. For small temperature rises, the oven will maintain constant control, but if the incident radiation pulse is sufficiently large, the attendant temperature increase can turn off the oven. Under this condition the resonator structure will cool until the temperature reaches the oven control region where proportional oven heating again takes place.

Figure 10 displays the results obtained with the present thermal model in comparison with the experimental data. The effects of oven set temperatures relative to crystal turnover temperature are shown in Figure 11. The impact of a given energy deposition and temperature rise is such as to cause a positive offset in the transient frequency response when operated above the upper turnover temperature. Dose dependence is accurately described by the model as shown in Figure 12.

A 4 MHz fundamental resonator with a two point mounting structure in a ceramic enclosure^{6,7} was also irradiated. The thermal model of this structure is shown in Figure 13. The mounting clips are of gold and the active zone is approximately ten times smaller than for the 5 MHz unit. This configuration gives rise to radiation-induced frequency changes greater than for the 5 MHz unit at early times by about two orders of magnitude. The calculated response using the same proportionality constant as for the 5 MHz resonator and the experimental data shown in Figure 14 are again in good agreement. The calculated effect of resonator structure material is also shown in Figure 14 where the mounting clip material has been changed to nickel. A long term relative frequency change of 60×10^{-8} occurs due to thermal equilibration of the resonator in the absence of an oven.

Conclusions

High purity synthetic quartz as represented by SARP Premium-Q and optical grade material appears to be sufficiently pure as grown that the $t^{-1/2}$ transient frequency recovery characteristic is not observed. There is some evidence that the optical grade material may be somewhat better, but it is not known whether the differences represent growth conditions or typical stone-to-stone variations. Without sweeping, resistance changes are still large enough to stop these test oscillators for several seconds. Partial sweeping reduces the resistance changes such that the oscillator continues to operate, but large positive frequency transients are observed. More complete sweeping reduces resistance changes to the point that they are no longer observable. This is believed to be an indication of very low active impurity content.

The transient frequency response of swept quartz in precision AT-cut resonators appears to be primarily thermal in nature. A thermal model written in terms of temperature and its rate of change which includes the resonator structure and associated oven, if any, provides a good description of the transient frequency response. The model appears to be successful over a range of doses and for different resonator structures.

Transient frequency shifts no greater than a few parts in 10^8 after an ionizing pulse of 2×10^4 rads can be achieved in precision AT-cut resonators using swept synthetic quartz. Since no impurity effects are observable, this would appear to represent a limit as to how far the radiation response in resonators using this crystal cut and resonator structure can be reduced. Further improvements will require changes in crystal cut to minimize the effects of thermal stresses or changes in resonator structure. Both are presently under evaluation.

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TABLE I

<u>Material</u>	<u>Sweeping</u>	<u>R_s (ohms)</u>	<u>Q</u>
Optical Grade	Unswept	140	2.0×10^6
Optical Grade	Swept	115	2.6×10^6
Premium-Q	Unswept	106	2.5×10^6
Premium-Q	Swept	104	2.7×10^6

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Figure 1 Transmission Line Test Set

Figure 2 Block diagram of data recording system for measuring oscillator frequency and equivalent crystal resistance as a function of time following a short-duration radiation exposure.

Figure 3 Radiation-induced steady-state frequency changes

Figure 4 Radiation-induced steady-state resonant resistance changes

Figure 5 Transient frequency changes in Premium-Q quartz following a pulse of radiation

Figure 6 Transient frequency changes in optical grade quartz following a pulse of radiation showing the effect of prior irradiation

Figure 7 Experimental frequency-resistance calibration for test oscillator

Figure 8 Resistance transients following a pulse of radiation

Figure 9 Lumped-element thermal-model of resonator and oven structure in equivalent electrical form

Figure 10 Frequency transient following pulse irradiation

Figure 11 Dependence of frequency transient following pulse irradiation on quartz operational temperature

Figure 12 Dependence of frequency transient following pulse irradiation on radiation dose

Figure 13 Lumped-element thermal-model of ceramic enclosure resonator structure in equivalent electrical form

Figure 14 Frequency transient following pulse irradiation for ceramic enclosure resonator-structure