THE EFFECTS OF SURFACE CONTAMINATION
ON THE NOISE AND DRIVE-LEVEL SENSITIVITY
OF PIEZOELECTRIC RESONATORS

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The effects of surface contamination on the short-term instabilities and drive-level sensitivities of piezoelectric resonators are explored. A plausibility argument is presented to show that the adsorption and desorption of surface contamination may be a significant contributor to short-term instabilities.

Although high drive levels produce high velocities and accelerations at resonator surfaces, the extra kinetic energy imparted directly to contaminant molecules by the high drive levels is shown to be negligible compared to the adsorption/desorption energies of the contaminant molecules of concern. Since adsorption/desorption rates depend exponentially on temperature, and since the increased dissipation caused by high drive levels raises the resonator's temperature, surface contamination can influence a resonator's drive level sensitivity via thermal effects.
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INTRODUCTION

It is safe to say that every resonator in existence has contaminated surfaces. It is only a question of how contaminated the surfaces are, not if the surfaces are contaminated.* That adsorbed contamination is a significant contributor to aging is well known. It is also well known that surface contamination prior to plating has a significant influence on the properties of the thin films that are used for the electrodes. The purpose of this report is to explore the effects, if any, of surface contamination on short-term instabilities (i.e., noise) and on the drive-level sensitivity of piezoelectric resonators.

*Even at $10^{-9}$ torr, the number of molecules hitting a resonator's surface is such that, if all the molecules that collide with the surface stick, an atomic layer of contamination forms in about 1000 seconds (~ 17 minutes.) Moreover, even if it were possible to keep a resonator's surfaces perfectly clean during fabrication: since all metals, glasses, epoxies, etc. outgas, the resonator's surface would start to be contaminated immediately upon sealing.
THE EFFECT OF SURFACE CONTAMINATION ON RESONATOR SHORT-TERM STABILITY

Short-term stability (i.e., noise) is among the least well-understood resonator phenomena. Factors that have been recognized to contribute to short-term instability include: Johnson noise, temperature fluctuations, vibration, acoustic losses (i.e., Q), noise originating from interfaces between the electrodes and the quartz plate and between the mounting structure and the quartz plate, and noise due to the oscillator circuitry.

Another source of noise is resonator surface contamination, i.e., the fluctuations in the number of adsorbed contaminant modules. Consider, for example, a resonator that is a million atomic layers thick (i.e., about 0.5 mm thick). An atomic layer of (quartz-equivalent) contamination will then lower the frequency by $1 \times 10^{-6}$. If the resonator active area is $1 \text{ cm}^2$, then, for a $5 \times 10^{-8} \text{ cm}$ contaminant molecule spacing, there will be $4 \times 10^{14}$ contaminant molecules contributing to the frequency lowering. Since contaminant molecules have a finite lifetime on a surface (the average lifetime depends on the adsorption energy) the number of adsorbed molecules will fluctuate. In order to account for frequency fluctuations of $1 \times 10^{-13}$ to $1 \times 10^{-12}$, the number of contaminant molecules would have to fluctuate by $1 \times 10^{-7}$ to $1 \times 10^{-6}$ atomic layers (in the same averaging time). These numbers
appear to be reasonable because, in statistical physics, the normalized fluctuations in a large number \( N \) of objects are typically on the order \( 1/\sqrt{N} \). For example,\(^1\) if the average gas density in a \( 1 \text{ mm}^3 \) volume of a large volume of gas is \( N \), then the density fluctuation (rms deviation from the average) in the \( 1 \text{ mm}^3 \) volume is \( \sqrt{N} \). The same results hold for the "shot effect," i.e., the thermionic current noise in a vacuum tube. If \( n_0 \) is the average number of electrons emitted per unit time, then the rms fluctuation in \( n_0 \) is \( \sqrt{n_0} \). (The excess spectral density of the shot noise has \( 1/f \) dependence.\(^2\))

Assume that we are dealing with only one type of contaminant molecule, and only one type of adsorption site on the resonator, and let

\[ \begin{align*}
N_a & \quad \text{number of adsorption sites in the active area of the resonator,} \\
N_c & \quad \text{number of contaminant molecules in the resonator enclosure,} \\
E_{rc} & \quad \text{resonator-to-contaminant-molecule binding energy (i.e., the desorption energy),}
\end{align*} \]
$E_{cc} =$ contaminant molecule to contaminant molecule binding energy when neither is adsorbed on the resonator,

$E_{rcc} =$ binding energy of a second layer contaminant molecule.

For simplicity, let us assume that $E_{cc} \approx E_{rcc} \approx 0$ and let us consider the three cases: $N_c << N_a$, $N_c \approx N_a$, and $N_c >> N_a$. It can be readily seen from the following qualitative arguments that the three cases can contribute to short-term instabilities in very different ways.

Case I: $N_c << N_a$

When $N_c << N_a$, the probability that an adsorption site is occupied depends on $N_c/N_a$, and the time of occupation at a given site depends on $E_{rc}$. There are many available sites for each contaminant molecule; so, whenever a contaminant molecule collides with the resonator surface, on the average, it will stick for a finite time that is a function of $E_{rc}$. 

4
Case II: $N_c = N_a$

When $N_c = N_a$, the lifetime of a molecule on an adsorption site will be the same as in case I. However, since nearly all adsorption sites are occupied nearly all of the time, once a molecule desorbs, it will take many collisions with the surface before it is readSORBED. Therefore, the fluctuations in the number of occupied sites will, clearly, be different from those in case I.

Case III: $N_c >> N_a$

When $N_c >> N_a$, for each desorbing molecule there are many others available to take its place; therefore, all adsorption sites will be occupied nearly all of the time. The frequency fluctuations due to surface contamination fluctuations will be smaller than those mentioned in cases I and II, i.e., a "dirty" resonator is likely to be less noisy than a partially contaminated resonator (everything else being equal).

The relationship between contamination-induced noise and contamination level, for constant $E_{rc}$ and measurement time, is likely to be as shown in Fig. 1. Similarly, for a constant $N_c/N_a$, the relationship between contamination-induced noise and $E_{rc}$ will be somewhat as shown in Fig. 2. The scales are to be
Figure 1. Contamination-induced noise vs. contamination level.

Figure 2. Contamination-induced noise vs. desorption energy.
determined by performing the necessary experiments or statistical calculations.

The curve in Fig. 1 crosses the origin because, of course, if there is no contamination, there will be no contamination-induced noise. For \( N_c >> N_a \) (case III), the noise will be low, but finite.

In Fig. 2, when \( E_{rc} = 0 \), the lifetimes of contaminant molecules on the resonator surface will be zero. Therefore, the noise will be very small, but finite, due to the impacts of the molecules. When \( E_{rc} \) is very large, the lifetimes of adsorbed molecules will be very long; therefore, the fluctuations in the number of adsorbed molecules will be very low. Figure 3 shows the relationship of lifetime to adsorption energy and temperature for a simple adsorption process \(^3\) (\( E_d = E_{rc} \) for our problem). At 25°C, for example, the lifetimes range from microseconds to about the age of the universe as \( E_{rc} \) ranges from 10 kcal/mol to 45 kcal/mol. For many of the commonly occurring contaminant molecules, \( E_{rc} \) is in the 10 to 30 kcal/mol range (e.g., for H\(_2\)O, CO\(_2\), CH\(_4\), O\(_2\), N\(_2\), etc.)

There exist some experimental results that tend to indicate that "dirty" resonators can be less noisy than "clean" resonators. For example, several years ago the author's laboratory supplied a
Average residence time of molecule on a surface, $T = T_0 \exp(Ed/rt)$, $T_0 \sim 10^{-13}$ sec

<table>
<thead>
<tr>
<th>$E_d$ Kcal/Mol</th>
<th>$-50^\circ C$</th>
<th>$25^\circ C$</th>
<th>$100^\circ C$</th>
<th>$300^\circ C$</th>
<th>$350^\circ C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>$6 \times 10^{-4}$ sec</td>
<td>$2 \times 10^{-6}$ sec</td>
<td>$7 \times 10^{-8}$ sec</td>
<td>$6 \times 10^{-10}$ sec</td>
<td>$3 \times 10^{-10}$ sec</td>
</tr>
<tr>
<td>20</td>
<td>50 DAYS</td>
<td>50 sec</td>
<td>$5 \times 10^{-2}$ sec</td>
<td>$4 \times 10^{-6}$ sec</td>
<td>$10^{-6}$ sec</td>
</tr>
<tr>
<td>30</td>
<td>$10^9$ YRS</td>
<td>30 YRS</td>
<td>$10$ HRS*</td>
<td>$3 \times 10^{-2}$ sec</td>
<td>$3 \times 10^{-3}$ sec</td>
</tr>
<tr>
<td>40</td>
<td>$10^{19}$ YRS</td>
<td>$6 \times 10^8$ YRS</td>
<td>$900$ YRS**</td>
<td>$3$ MIN</td>
<td>$10$ SEC</td>
</tr>
<tr>
<td>45</td>
<td>$10^{23}$ YRS</td>
<td>$3 \times 10^{12}$ YRS</td>
<td>$6 \times 10^5$ YRS</td>
<td>$4$ HRS</td>
<td>$10$ MINS</td>
</tr>
</tbody>
</table>

*Monolayer per 10 hrs $\rightarrow \sim 1$ ppm per day

**Monolayer per 900 yrs $\rightarrow \sim 10^{-9}$ per year

Figure 3. Thermal Desorption - average residence time of contaminant molecule vs. temperature and desorption energy.
number of ceramic flatpack-enclosed, fundamental-mode, AT-cut resonators to Bendix Corp. for use in the development of the Tactical Miniature Crystal Oscillator (TMXO). These resonators had been fabricated under superclean conditions (UHV, high-temperature processing, etc.) The resonators had excellent aging, but were noisy, typically in the 10^{-11} range at 1 sec. One memorable resonator (No. CR186) was superlow-noise, i.e., it was more than 10X better than most of the rest. Bendix used this resonator as a standard, i.e., they measured the noise of other resonators against No. CR186. Later, the performance of this resonator degraded significantly; a radioactive tracer leak test showed this resonator to have a small leak!

Similarly, Parker had reported a few years ago\textsuperscript{4,5} that SAW delay lines fabricated with (RTV) silicone adhesives (which outgas) had significantly better noise performance, but significantly poorer aging, than SAW delay lines fabricated under superclean conditions.

Parker showed that "delay lines which have been thoroughly cleaned and hermetically sealed are the noisiest, while devices which have a very thin layer of silicone material are the quietest." Furthermore, he showed that, for RTV mounted delay lines, immediately after the RTV was cured, the noise level dropped; it
decreased 6 dB during the first three days. It decreased an additional 4 dB upon a 16-hr, 90°C bake, which, presumably, caused further outgassing. When the same devices were subsequently cleaned by UV/ozone, the noise levels increased to their original value! Unexplained, though, is another of Parker’s findings, i.e., that surface treatments on SAW resonators had no observable effect, even though the resonators had lower 1/f noise levels than the delay lines.

From the foregoing findings, the following conclusions can be drawn:

1. Rigorous calculations need to be performed on "real" contamination models to verify the above qualitative arguments and to ascertain that the magnitude of the effect is not negligible compared to other noise sources. The model should take into account that, in general, several types of contaminant molecules and surfaces are present in the resonator enclosure, and that $\text{ErCC} \neq 0$.

2. To minimize surface-contamination-caused noise, resonators should be either very clean or very dirty, but not in between.
3. Since making and keeping resonators atomically clean is very difficult, developing methods of minimizing the fluctuations in surface contamination levels without causing excessive aging or other adverse effects is another approach that one might explore. Such methods might include: the modification of the adsorption properties of the resonator surface (e.g., with silanes); the deposition of an atomic layer, or a few atomic layers, of tightly adhering, nonadsorptive (e.g., Teflon-like) material. An interesting possibility would be to deposit a single molecular layer of a temperature-stable material, such as a polyimide. A recent paper showed that it was possible to deposit a monolayer of polyimide with the Langmuir-Blodgett technique. The resulting film was stable to 400°C.

4. If contamination is a significant noise source, the short-term stability should, then, be temperature dependent, e.g., the short-term stability of an SC-cut resonator at the lower and upper turnover temperatures should not be equal.

5. One can investigate the effect experimentally by, for example, measuring the short-term stability with a reflectometer while an unsealed resonator is exposed to different pressures of different gases in a vacuum system.
DOES HIGH-DRIVING A RESONATOR HAVE A SIGNIFICANT EFFECT ON THE ADSORPTION/DESORPTION OF SURFACE CONTAMINANTS?

The aging and short-term stability of oscillators can be affected by resonator drive level. The effects are not fully understood. Increasing the drive level increases the displacements and accelerations of particles at the resonator surfaces. At high frequencies, especially, particle accelerations can be on the order of $10^6$ g. That high driving can remove particulate contamination from resonator surfaces is well known. Is it possible that these high accelerations also affect adsorption and desorption phenomena at the resonator surfaces? The following simple, "back-of-the-envelope"-type calculation may answer this question.

The displacement of a tightly adhering contaminant molecule on a resonator's surface is given by

$$x = k \sin (2\pi ft),$$

where $k$ is the amplitude of vibration and $f =$ frequency of vibration. The velocity and acceleration are then given by

$$\dot{x} = 2\pi fk \cos (2\pi ft)$$

$$\ddot{x} = -(2\pi f)^2 k \sin (2\pi ft).$$

According to Adachi et al., 7 for example, for a typical resonator and for a reasonable driving current (e.g., 1 mA), the
amplitudes of vibration are on the order of 100 Å to 300 Å. Therefore, if

\[ f = 10 \text{ MHz and } k = 160 \text{ Å,} \]

then,

\[ \dot{x}_{\text{max}} = 2\pi fk \approx 10^2 \text{ cm/sec} \]

and,

\[ \ddot{x}_{\text{max}} = (2\pi f)^2 k \approx 6 \times 10^8 \text{ cm/sec}^2 \approx 6 \times 10^5 \text{ g.} \]

The kinetic energy per unit mass of adsorbed molecule is

\[ \frac{\text{K.E.}}{\text{unit mass}} = \frac{1}{2} v^2 = \frac{10^4 \text{ cm}^2}{\text{sec}^2} = \frac{10^4 \text{ ergs}}{\text{gm}}. \]

A typical adsorption energy is 20 kcal/mol. Since 1 kcal = 4.2 \times 10^{10} \text{ ergs}, and 1 mol = 6.02 \times 10^{23} \text{ molecules}, 20 kcal/mol = 10^{-12} \text{ erg/molecule}. If a contaminant weighs 60 gm/mol, then

\[ \frac{\text{K.E.}}{\text{unit mass}} = 10^{-18} \text{ erg/molecule.} \]

Also, the average thermal energy of a molecule at room temperature is 1/40 eV; since 1 eV = 1.6 \times 10^{-12} \text{ ergs}, the average room temperature energy = 4 \times 10^{-14} \text{ ergs}. Therefore,

\[ \frac{\text{K.E.}}{\text{adsorption energy}} \approx 10^{-6}, \]

\[ \frac{\text{K.E.}}{\text{ave. thermal energy}} \approx 10^{-3}. \]
Consequently, the kinetic energy due to drive is negligible. Whether or not a resonator is vibrating, the level of drive will not produce a significant effect on adsorption/desorption phenomena. Of course, the energy deposited in the resonator by high drive levels raises the resonator's temperature, and that will affect the adsorption/desorption of surface contaminants.

SUMMARY AND CONCLUSIONS

The effects of surface contamination on the short-term instabilities and drive-level sensitivities of piezoelectric resonators have been explored. A plausibility argument has been presented to show that the adsorption and desorption of surface contamination may be a significant contributor to short-term instabilities.

Although high drive levels produce high velocities and accelerations at resonator surfaces, the extra kinetic energy imparted directly to contaminant molecules by the high drive levels is shown to be negligible compared to the adsorption/desorption energies of the contaminant molecules of concern. Since adsorption/desorption rates depend exponentially on temperature, and since the increased dissipation caused by high drive levels raises the resonator's temperature, surface contamination can influence a resonator's drive level sensitivity via thermal effects.
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