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AGING IN QUARTZ CRYSTAL UNITS

INTRODUCTION

Any change in the characteristics of a device or component with time is called *aging.* Applied to quartz crystal units the term usually means a change in the resonant frequency of the unit, although other parameters, especially the motional resistance, may also change with time. But since the primary function of the crystal unit is to establish and maintain a constant frequency, the term aging is generally taken to imply a change of frequency. Changes in the equivalent motional resistance may influence the amplitude of oscillation in an oscillator circuit or the insertion loss in a filter network but have extremely small effect on the frequency in either case.

The causes of aging in quartz crystal units are many and the effects are complicated and varied. In the following paragraphs we discuss some of the causes and remedies.

AGING DUE TO SURFACE DETERIORATION

The lapped or polished surface of a quartz crystal consists of a layer of quartz which is in a strained condition. Evidence for this is readily obtained by x-ray diffraction. Figure 12.1 is a photographic record of the Bragg reflection from the (10.1) planes of a quartz surface which had been lapped with a 600-mesh SiC abrasive. The first exposure, at the top, was made with the crystal in the correct position for reflection of the Cu $K\alpha$ radiation. For the next exposure the crystal was rotated 2° away from the Bragg position. Successive exposures were made at increments of $\frac{1}{4}°$. It may be seen that reflec-

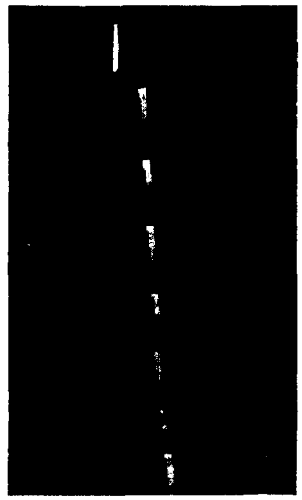

Fig. 12.1. Bragg reflection from a lapped-surface.

tion persists at the Bragg angle even when the crystal is rotated by $3\frac{1}{2}°$ from the Bragg position. This is interpreted to mean that some areas on the surface of the crystal are continually being brought into the Bragg position as the crystal is rotated. The more intense lines at the right in the picture are due to the Bremsstrahlung.

This phenomenon can be understood by considering the lapping operation which is actually a fracturing process. When a grain of abrasive is pressed against the quartz surface, cracks radiate from the point of contact. When cracks completely surround a particle of quartz, the particle falls off. However, at the time that the lapping process is terminated, many partially loosened particles remain. These particles are partially surrounded by boundaries at which the molecular bonds have been broken. Such particles are forced out of alignment with the main body of the crystal and a certain amount of energy is stored in the resulting strain. (The situation is not unlike that of having a piece of food lodged between two teeth, in which case the teeth are pushed out of their proper positions.) As time goes on the cracks continue to grow until they completely surround the particle, which may then fall from the surface. The particles thus dislodged form a dust on the surface of the blank which can be seen with the unaided eye by observing the surface at a glancing angle while dragging a probe across the surface. The size of the dust particles is roughly the same as that of the abrasive used in lapping the surface. The process is greatly accelerated by humidity and high temperatures and is accompanied by drastic increases in the frequency and resistance of the resonator. When the dust is removed by washing, the resistance of the unit returns to normal but the frequency is much higher than before. In extreme cases frequency changes of $0.1f^2$ or more may occur in a period of only a few days.[1]

This type of aging can be reduced somewhat by careful lapping and polishing and by protection from water vapor, but the only complete remedy is etching with HF or NH_4F_2 to relieve the strains causing the misorientation described above. The amount of etching required depends somewhat upon the type of lapping operation but is usually not less than about $0.5\,f^2$ for an AT-cut blank. The amount of etching required for any blank can be determined by making an "etching curve" as shown in Fig. 12.2. The crystal blank is etched under controlled conditions by fixed increments of time and the resulting frequency changes are recorded and plotted against the accumulated etching time. This graph shows that the etching proceeds very rapidly at first but later settles down to a (nearly) linear rate. The rapid initial rate is due to the fact that the chemical process

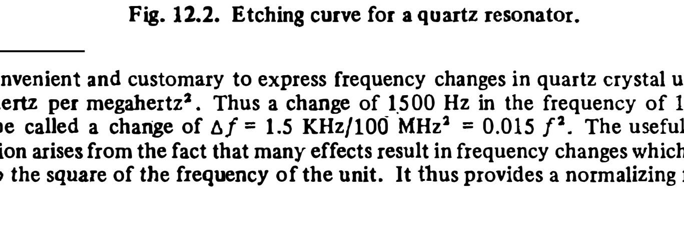

Fig. 12.2. Etching curve for a quartz resonator.

[1] It is convenient and customary to express frequency changes in quartz crystal units in units of kilohertz per megahertz^2. Thus a change of 1500 Hz in the frequency of 10-MHz unit would be called a change of Δf = 1.5 KHz/100 MHz^2 = $0.015\ f^2$. The usefulness of this convention arises from the fact that many effects result in frequency changes which are proportional to the square of the frequency of the unit. It thus provides a normalizing factor.

proceeds most rapidly at points of strain. Etching the quartz until the rate of frequency change with time is linear as indicated by the point *X* in Fig. 12.2 is sufficient to prevent this type of aging. X-ray diffraction photographs made of such etched surfaces show no evidence of strained quartz, but the slightest abrasion is sufficient to cause its return. It is interesting to note that it is not necessary to etch away all the quartz which is initially misaligned but only to relieve the strain by widening the cracks which were produced in the lapping operation. Electron micrographs clearly show the nature of the phenomenon.

AGING DUE TO SURFACE CONTAMINATION

A serious source of aging is contamination of the surface of the blank by volatile materials which may be present in the holder. These materials affect the frequency by loading (and unloading) the surface of the quartz blank. One very serious contaminant is the flux used to make the solder seal in many types of holders. For this reason a great deal of effort has been expended in developing holders which employ other types of seals such as cold welding and capacitance discharge and resistance welding. Each of these sealing methods presents problems of its own. Encapsulation in glass presents a particular problem due to excess heat, especially in miniature-sized units.

Other contaminants which have been identified as causes of aging are residues of volatile materials which are used in attaching the lead wires to the quartz plate and the lubricants used in drawing the metal cans which form the enclosure. Both these contaminants can be minimized by high-temperature baking in vacuum or in a hydrogen atmosphere.

The presence of a contaminating substance generally tends to cause a reduction of the frequency of a resonator, but the effect may be misleading. At any given temperature, equilibrium is eventually established within the enclosure. In this condition each surface is receiving and giving up contaminating material at a constant rate. However, any change in the temperature results in a new equilibrium condition with a different distribution of the contaminants and, in general, a change of frequency. A period of hours or days may be required for the unit to achieve stability at the new temperature. The same thing occurs if the drive level is changed, since this also results in a change in the operating temperature of the quartz piezoid.

The sensitivity of the frequency of a crystal unit to surface contamination can be appreciated by noting that the removal of a single layer of atoms from the surfaces of a 20-MHz AT-cut blank causes a frequency increase of some 100 Hz, or about 5 ppm (5×10^{-6}). Many units are specified to have aging rates of a few parts in 10^8 per year.

AGING ASSOCIATED WITH THE ELECTRODES

Most crystal resonators have thin metal electrodes deposited on the quartz. These electrodes serve two functions: they provide the means of applying the electric field to the quartz and they are used in making the final adjustment of the frequency of the resonator. Thus any changes in the mass of the electrodes resulting from chemical combination with other elements must result in a change in the resonant frequency. The most commonly used metals are silver, gold, and aluminum. Each metal presents a different aging problem.

Silver is used more than any other metal as an electrode material. A thin layer of chromium is often deposited on the quartz beneath the silver to improve adherence. Silver is not attacked by oxygen under ordinary conditions although it is attacked by O_3 or ozone. (The ozone produced by sparks probably contributes to the oxidation of silver contacts in switches.) However, silver is strongly attacked by sulfur and by the halides – fluorine, chlorine, bromine, and iodine. Chemical reaction with any of these and certain other elements results in a decrease in the frequency of the resonator.

Silver iodide is sometimes used in fabricating crystal units. The silver electrodes react instantly at room temperature with iodine vapor, producing a layer of silver iodide on the silver electrodes. The increased mass provides a simple and inexpensive method of adjusting the frequency. The silver iodide thus produced is very stable both physically and chemically and units made by this process can have very good aging characteristics. It is necessary, however, to ensure that no unreacted iodine remains in the enclosure, since subsequent chemical reactions may occur causing further frequency changes and aging. Because complete removal of the excess iodine is difficult, the iodine process is not favored for units with severe aging requirements.

Gold is also extensively used as an electrode material, especially in low-frequency resonators and in those demanding excellent aging characteristics. Gold has the advantage of being chemically inactive and also being easy to deposit. However, it does not adhere well to quartz and its high density and low electric conductivity make it undesirable with high-frequency resonators in which mass loading of the electrodes seriously degrades the performance of the device. Gold has other disadvantages, as we will see later.

Aluminum is commonly used as an electrode material, especially in high-frequency units. Aluminum adheres tenaciously to quartz because of the nature of the silicon to oxygen to aluminum bonding. The acoustic impedance of aluminum closely matches that of quartz, thereby minimizing the effects of acoustic reflection at the quartz-aluminum interface. However, aluminum reacts slowly with oxygen to form Al_2O_3, or sapphire. The result is that aluminum-plated units usually exhibit rather poor aging characteristics with the frequency decreasing roughly logarithmically with time for periods up to a year or more.

The main source of aging in aluminum plated units is the growth of the oxide layer on the electrodes. A newly created aluminum surface begins to oxidize immediately upon exposure to air. The oxide grows until it reaches a thickness of about 50 Å after which the growth substantially ceases. Under ordinary conditions several months is required for the oxide to reach its terminal thickness and the process cannot be accelerated much by increasing the temperature. Therefore, heat treatment of aluminum-plated units is largely ineffective in preventing aging of this type.

It is possible, however, to minimize and to virtually eliminate aging due to oxidation of the aluminum electrodes by the use of anodic oxidation.[2] In this process anodic oxidation is used to create an oxide layer which is initially thicker than the terminal thickness of the natural oxide layer. The thickness of the oxide film is proportional to the voltage used to produce it, thus providing a simple and useful

[2] See Method of Adjusting the Frequency of a Crystal Resonator and Reducing Ageing Effects, U.S. Patent 4,130,771, December 19, 1978. This patent discloses the procedure used in adjusting the frequency of an aluminum plated quartz resonator by means of anodic oxidation. See also Virgil E. Bottom, "A Novel Method of Adjusting the Frequency of Aluminum Plated Quartz Crystal Resonators." Proc. *30th Annu. Symp. Freq. Contr.*, June 1976, pp. 249–253.

method for adjusting the frequency while at the same time ensuring freedom from further oxidation.

Aluminum oxide or sapphire is highly inert to most chemical reactions and is physically very durable. The protection thus provided to the aluminum electrodes thereby virtually eliminates aging due to chemical reactions with the electrodes.

A particularly troublesome form of aging is characterized by the refusal of the crystal unit to operate at low drive levels after a period of storage. The phenomenon is known by several names, among which are "second level of drive," "hard starting characteristics," and "sleeping sickness." Typically, after a period of storage, which may be hours, days, or weeks, the crystal unit refuses to oscillate in a circuit that requires the unit to operate at low amplitude of vibration. The unit can often be revived by operating it in an oscillator that drives the unit at high amplitude after which it operates satisfactorily in the low-drive-level oscillator. However, after a period of storage the unit usually repeats the cycle.

The refusal of the unit to operate at a low drive level has been traced, in almost every instance, to failure of the electrode metal to adhere properly to the quartz. Microscopic examination of such units, after having been driven at high amplitude, shows pinholes in the plating where the metal has been thrown off. It is obvious that the electrode metal did not adhere properly to the quartz in these areas. The loose plating, while present, acts as a damping mechanism which reduces the Q of the resonator below the limit required for oscillation. In some cases the metal may have been deposited over a particle of dust, thus forming a blister.

The problem is most severe in crystal units employing silver electrodes applied by evaporation. It also exists with gold-plated units and much less frequently with aluminum-plated units. Unlike aluminum, neither gold nor silver adheres well to quartz and for this reason a thin layer of chromium is often deposited on the quartz before the gold or silver electrodes are deposited. Chromium, like aluminum, forms a SiO_2-oxide–metal bond. The gold or silver then adheres to the chromium instead of to the quartz.

In order to obtain good adherence between the evaporated metal and the quartz surface it is essential that the surface be "clean" and that the metal be deposited under proper conditions. It is difficult to define a clean surface since no surface except one prepared in a perfect vacuum is completely free of adsorbed atoms. But the surface on which the metal is to be deposited must be free of the organic materials which are present in every atmosphere. The subject of surface chemistry, including cleanliness, is too large to be pursued here. It may be said, however, that ultrasonic cleaning with detergents and boiling water followed by ultraviolet light irradiation produces surfaces to which evaporated metals adhere satisfactorily. It is necessary, in addition, to perform the evaporation in a vacuum system which is free of oil and at a pressure no greater than 10^{-6} torr.

AGING ASSOCIATED WITH PHYSICAL EFFECTS

The resonant frequency of a quartz resonator is usually influenced to some degree by any mechanical strain imposed on the piezoid. Consequently, any change in the static stress imposed on the piezoid results in a change in the resonant frequency. Mechanical stresses are imposed upon the AT-cut quartz plate by the mounting structure and by the electrodes, both of which in general have temperature coefficients of expansion different from those of quartz.

Unless great care is exercised in mounting the blank, the supporting leads may exert a tensile force or a bending moment or both on the blank. The frequency of the blank is determined to some degree by the strains resulting from these stresses. It is easy to demonstrate these effects by artificially imposing stresses on an oscillating plate.

All solids, except perfect crystals, undergo stress relaxation with time, especially at elevated temperatures. As the stresses in the mounting structures relax, the frequency of the resonator may increase or decrease depending upon the nature of the stress on the plate. In either case the result is aging.

Stress relaxation in the metal electrodes is a serious source of aging. The frequency of both AT- and BT-cut resonators is strongly affected by radial stresses in the plane of the blank. Thermal stresses associated with the different temperature coefficients of the quartz and electrode metal result in frequency perturbations. After a long time at a fixed temperature, the stresses in the metal relax; but when the temperature is changed, the process is repeated. This is one reason why a crystal unit often starts a new aging cycle when the operating temperature is changed.

It is well known that thin metal films undergo significant molecular rearrangement with time and that these effects are accelerated by high temperatures. Therefore, annealing is useful in minimizing the effects of electrode stresses. The thickness of the film, the metal used and the method of application, the surface to which it is applied, and the presence of intermediate metals all influence the amount of built-in stress, the relief of which causes frequency changes and aging.

The contribution of the electrodes to aging can be eliminated by using a design in which the quartz blank is suspended between conducting surfaces with an air gap between the quartz and the electrodes. However, mechanical problems associated with such designs and their high cost make them unattractive.

AGING ASSOCIATED WITH THE QUARTZ

No quartz crystal is perfect. Impurity atoms, interstitial atoms, lattice vacancies, and nonstoichoimetric ratios are always present in both natural and cultured quartz crystals. Each of these defects has a subtle effect on the elastic coefficients which determine the frequency of the resonator and therefore any change in the distribution of the defects in the crystal may result in aging. The degree of perfection varies from crystal to crystal, both in natural and cultured quartz. For example, the frequency of a BT-cut resonator made from some specimens of natural quartz may be decreased by as much as 0.02 percent by irradiation with x-rays, while a similar resonator made from a different specimen may show little or no change. Those plates which exhibit large frequency changes with radiation also become dark or smoky; those whose frequencies do not change remain uncolored. These phenomena are all understood, but this is not the place to discuss them.

The tendency to change frequency and to darken may be eliminated by "sweeping" (see page 24). Units which must withstand the effects of high radiation fields (such as satellite applications) are usually made from swept quartz. The redistribution of crystalline defects, either from a concentration gradient or an externally applied electric field may induce changes in the elastic coefficients and changes in the frequency or aging.

Relaxation of body strains in crystals resulting from crystalline imperfections can be accelerated by annealing at elevated temperatures, but annealing is a continuous process. Ultimately the distribution of stress effects approaches equilibrium at a given temperature. If the temperature is changed, a new distribution must be established, which is another reason why time is required for a crystal unit to reach frequency stability after a change of temperature.

AGING ASSOCIATED WITH HOLDER DEFECTS

Most crystal holders are back-filled with a dry gas, usually N_2. Often a small percent of He is added to facilitate leak testing with a mass spectrometer. In some units vacuum encapsulating is used and in certain units such as the IT- and SC-cuts, it is essential.

Every holder leaks. It is only a matter of degree. Leaks which permit oxygen, water vapor, and other gases to enter the enclosure may result in changes in the frequency of the device through a number of mechanisms. Exposure to water vapor of an AT- or BT-cut resonator which has been previously vacuum-baked results in a frequency decrease which may be as much as $0.01f^2$. This decrease in frequency is due to the adsorption of a monomolecular layer of water on the previously dehydrated surface. The process is reversible by vacuum-baking the unit again. Some long-term aging effects are doubtless due to this phenomenon.

Unless protected by anodic oxidation, aluminum electrodes may undergo further oxidation with attendant frequency decreases. To avoid further oxidation of aluminum films on which the oxide has not reached the terminal thickness, it would be necessary to remove all oxygen from the holder and prevent the entrance of more. Both of these are virtual impossibilities except with glass holders which have been thoroughly vacuum baked.

Chemical reactions between silver and atmospheric gases such as SO_2 cannot be disregarded as possible sources of aging. Considering the extreme sensitivity of a high-frequency quartz resonator to any mass added to or removed from its surfaces, it is not impossible that the vapor pressure of the various materials in the holder may make some contribution to the aging phenomena. But even if this effect is negligible, no doubt exists that the holder makes a significant contribution to the aging of some crystal units.

ACCELERATED AGING TESTS

As a general rule, aging effects are accelerated by increased temperatures and for this reason it is desirable that the operating temperatures of crystal units be as low as possible. But there is no way in which temperature exactly substitutes for time, nor vice versa. This is obvious if one considers effects such as melting solder or phase changes resulting in broken quartz. A given crystal may remain within specified limits for years at room temperature and fail in a few days at 100°C and instantly at 250°C.

Nevertheless, it is useful and customary to include accelerated aging tests as a part of the specification for a crystal unit. For example, Standard Specification MIL 3098 requires that the frequency of a unit not change by more than 5 ppm in 30 days at 85°C. Some commercial specifications require that the frequency remain within certain limits for a specified time and temperature. As an example, one specification for a 12.0-MHz unit requires that the frequency remain within ±50 Hz of the nominal frequency after 21 days at 120°C.

An accelerated aging test should reflect the use and environmental conditions to be imposed upon the unit. There is questionable value in specifying an accelerated aging test at 100°C for a unit which is to be used at room temperature. It may simply result in the rejection of units which would be quite satisfactory for the purpose and thereby increase the cost.

Aging tests may be made with the units operating or not, but it must not be concluded that the results will be the same. For an aging test to be conclusive, the unit should continuously operate at a fixed temperature and drive level. The frequency may be monitored continuously or checked periodically. Any interruption of the operating conditions will normally result in a discontinuity in the frequency-time curve for one or more of the reasons outlined above. In tests where accelerated aging is interrupted, the units must be maintained at a fixed temperature (say room temperature) for a fixed period of time before recording the frequency. Drive levels must also be standardized. It is unnecessary to emphasize the need for the best test equipment, including ovens and frequency standards in making aging tests. And care must be taken in interpreting the results.

METHODS OF MINIMIZING AGING OF QUARTZ CRYSTAL UNITS

Aging can probably never be eliminated in quartz crystal units, but certain steps can be taken to minimize the effects. The first step is obviously to isolate the cause of the aging. This is complicated by the fact that several sources are usually present simultaneously. It is not uncommon in an aging test for the frequency change to reverse direction as different aging effects predominate and often cancel each other. A high initial rate of aging does not necessarily indicate a long-term effect, nor vice versa.

Substantial decreases in frequency are most often associated with some type of contamination or with a leaking holder. In these cases scrupulous attention to cleanliness and rigorous leak testing are required.

Poor vacuum conditions in plating equipment including inadequate vacuum and contamination from pump oil are common sources. These problems are attacked by ensuring that vacuum pressures are maintained below 10^{-6} torr and by using vacuum systems in which oil is adequately trapped or not used at all.

It is not possible to specify a procedure which will ensure minimum aging in every case. It can be stated that the utmost attention to every detail of the production process is required, since aging may arise from almost any operation in the entire production process.

Nevertheless, a surprising degree of stability is achievable with quartz crystal units. Aging rates as low as 1 part in 10^{11} per day have been achieved. Such a quantity is a bit more comprehensible if it is recalled that the distance across the North Atlantic Ocean is about 5×10^8 cm. A change of 1 part in 10^{11} in this distance is some 0.005 cm. A hypothetical clock controlled by a crystal resonator whose frequency decreases by 1 part in 10^{11} per day would be losing one second per day after running for thirty centuries!