RESEARCH AND DEVELOPMENT TECHNICAL REPORT

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PRECISION SINGLE SIDEBAND CRYSTAL UNITS

FINAL REPORT

By

Raymond K. Hart

JULY 1974

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Atlanta, Georgia
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PRECISION SINGLE SIDEBAND CRYSTAL UNITS

Final Report

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ABSTRACT

This report is concerned with the systematic investigation of various cleaning and processing techniques which are used to assemble high precision single sideband (SSB) quartz resonators. The final requirement is to be able to produce crystal units which will meet a strict aging requirement of $2 \times 10^{-10}$/week, when measured at the upper turning point of the crystal unit after a stabilization period of 4 weeks.

The specific aspects of resonator fabrication that have been investigated during this study are several wet-cleaning processes for preparing quartz surfaces, the sputter-ion cleaning of quartz and the composition profiles and impurities associated with both the quartz surface and the copper electrodes.

Analyses of the prepared resonator components were carried out by Auger electron spectrometry (AES), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and high energy electron diffraction (HEED).

Both chemical and sputter-ion cleaning methods were employed in the fabrication of complete SSB crystal units, with the sputter ion cleaning process being performed in the final fabricating chamber. Aging data from these units are presented and the effects of processing variables on resonator aging are discussed.
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I. INTRODUCTION

A. Statement of the Problem

Precision single sideband (SSB) crystal units having properties not generally available at the present time are required for the next generation of SSB radio equipment. The units must neither age more than $\pm 2 \times 10^{-10}$/week nor deviate more than $\pm 1 \times 10^{-8}$ from the original frequency when subjected to thermal cycling between -55°C and +85°C. Moreover, these units must oscillate at their fundamental frequency rather than at an overtone because the resonators will be used in temperature compensated oscillators (TCXO); overtone units have too high an inductance ("stiffness") for TCXO operation.

Other requirements such as minimum Q and frequency-temperature behavior are important, but they can be more easily met than either the aging or the frequency deviation requirement. The problem then is how to improve the long term aging and frequency deviation (sometimes called retrace) due to thermal cycling.

B. Approach to the Problem

The dependence of quartz aging on various fabrication variables can only be effectively determined on resonators that have been fabricated under precisely controlled conditions. A recent innovation is to carry out the final part of the fabrication process, i.e., plating, baking and sealing, in the same environmental chamber.

Before the quartz wafers are placed into the fabrication chamber, they are mounted onto crystal headers and thoroughly cleaned by the action of suitable chemical agents, such as chrome/sulfuric acid or $\text{H}_2\text{O}_2/\text{NH}_4\text{OH}$ mixtures. Unfortunately, the "cleaned" quartz surfaces carry adsorbed and absorbed water, gas, and perhaps cleaning chemicals, into the fabricator. Even with these materials on the quartz surface, resonators having an aging rate of less than $10^{-8}$/week can be fabricated(1).

It is logical to assume that the removal of extraneous surface materials, before the plating and sealing processes are accomplished, will allow resonators of improved performance to be made. A method that has been successfully applied to the cleaning of surfaces in controlled environments is sputter-ion cleaning. This method employs a focused beam of gas ions (usually an inert gas such as argon) which is accelerated toward the target surface by a potential difference of a few kilovolts.

During this project we have made a study of the sputter-ion cleaning process, as applied to quartz resonators, and an ion cleaning capability has been incorporated into the final resonator fabrication chamber.

Extensive use has been made of Auger electron spectrometry (AES) to characterize surfaces of resonator components that have been cleaned by either chemical, and/or ion bombardment, methods.
Other supplementary analytical methods, such as reflection high energy electron diffraction and scanning electron microscopy, have also been employed in this work to further characterize both the chemical and physical nature of exposed surfaces of resonator components.

The analyses of residual gases in the resonator fabrication chamber before, during, and after electrode plating were obtained, and these data were used in conjunction with both AES and resonator aging data to evaluate the fabrication processes that have been employed in this work.
II. SPATTER ION CLEANING—THEORETICAL CONSIDERATIONS

Any material surface that cannot be cleaned in the controlled environment of the final fabricating unit will, without exception, carry surface adsorbates. Their effect on resonator frequency will naturally be varied with some materials having substantial influence, while others may only have very limited influence. Irrespective of the degree to which they influence the frequency stability of the resonator, it is desirable to remove these substances from the resonator components.

Ion beams are presently the most popular means for in situ cleaning of materials that have previously been subjected to thorough cleaning by conventional chemical or mechanical processes. The principles of the ion-sputtering process have recently been discussed by Kaminsky (2,3) and Sigmund (4). When a solid surface is bombarded with particles that can impart enough energy to the target atoms as to exceed their displacement energy (between 20 and 30 eV), then these target atoms will be ejected from their lattice positions. The actual sputtering process can either be chemical or physical in nature, though physical sputtering is by far the more common of the two processes.

In physical sputtering, the maximum energy transfer during a collision between the incoming ion and target atom is simply

$$E_{\text{max}} = \frac{4M_o M_1}{(M_o + M_1)^2} \cdot E_o$$  \hspace{1cm} (1)

where $M_o$ and $M_1$ are the respective masses of incident particle and target atom, and $E_o$ is the beam energy. If $E_{\text{max}}$ exceeds the displacement energy of the bombarded atom, then this atom will be displaced.

The range of beam energies used for ion cleaning surfaces is usually of such a magnitude that the incoming particle has only sufficient energy to distort the electron cloud of the stationary atom, and the collision is like "hard spheres" colliding. This interaction gives rise to a screened coulomb collision for which the required beam energy can be determined from the following:

$$E_A = 2E_R Z_o Z_1 (Z_o^{2/3} + Z_1^{2/3})^{1/2} (M_o + M_1)/M_1$$  \hspace{1cm} (2)

In this equation $E_R$ is the Rydberg energy of hydrogen (13.68 eV) and $Z_o, Z_1$ the respective atomic numbers of beam particle and target atom. For beam energies between the sputtering threshold energy and $E_A$, there is a general increase in the sputtering yield with energy. With beam energies above $E_A$, the sputtering yield remains at near maximum and does not change drastically with beam energy. Calculated values of $E_A$ for a few gases incident upon silicon and quartz are given in Table I.
Table I. Limiting Energies, $E_A$ for a Number of Gas Ions Incident Upon Silicon and Quartz

<table>
<thead>
<tr>
<th>Bombarding Ion</th>
<th>$E_A$, keV</th>
<th>SiO₂ Target</th>
<th>Si Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen (8)</td>
<td>11.6</td>
<td>8.2</td>
<td></td>
</tr>
<tr>
<td>Neon (10)</td>
<td>16.7</td>
<td>16.8</td>
<td></td>
</tr>
<tr>
<td>Argon (18)</td>
<td>50.1</td>
<td>59.6</td>
<td></td>
</tr>
<tr>
<td>Xenon (54)</td>
<td>485.1</td>
<td>526.4</td>
<td></td>
</tr>
</tbody>
</table>

*Average values for $Z$ and $M$ were used.

An important point to remember is that in sputter-ion cleaning only the immediate surface atoms are of interest. Thus, the beam energy should be kept low enough to produce a reasonable sputtering yield yet not give rise to deeply implanted gas ions. An empirical range-energy relationship has recently been formulated by Nielsen (5) for energetic ions in materials, from a unified theory for nuclear stopping by Lindhard and his associates (6,7). The range (total pathlength) of an ion into a solid can be represented by

$$R(A) = \frac{60E_o (\text{keV})M_1M + M_1}{GZ_1M_0(Z_o/Z_1)^{2/3} + Z_1^{2/3})^{1/2}}$$

where $G$ is the target atom density.

The straight line distance beneath the surface, i.e., projected range ($R_D$), that an ion travels can be obtained by dividing the $R$ values by $(1+M_1/3M_0)$. Calculated $R_D$ data for a few ions in silicon and quartz are plotted in Fig. 1. With the adsorbed contaminants accounting for no more than a monolayer thickness at the surface, argon beam energies of 1 to 2 keV should not penetrate more than about 20 Å into the quartz. Experience has shown that at these relatively low energies (1-2 keV) the removal rate of most contaminants and resonator construction materials is sufficiently rapid to complete the process in a few minutes.
III. EXPERIMENTAL WORK

A. Introduction

It would have been highly desirable to carry out all our physical fabrication and systematic surface analyses in the one fabricating chamber. However, this was not possible, and thus it was necessary to carry out the various investigations that were undertaken during the contract in several different items of equipment.

During the first half of the contract period, investigations were largely of an analytical nature, with work in the areas of AES, HEED and SEM predominating.

With the delivery of two sputter-ion guns, the fabrication of sputter-ion cleaned quartz resonators was commenced. This work occupied much of the second half of the contract period. The finished surfaces of resonator components could not be analyzed in situ, so it was necessary to carefully follow the ion cleaning procedure that was used in the Auger electron spectrometer. Unfortunately, the ion cleaning conditions in the AES and fabrication chamber were not identical since geometrical considerations prevented a similar placement of the ion guns in the two systems.

B. Apparatus and Procedures

1. Auger Electron Spectrometry

During the first half of this contract, two different types of AES systems were used to characterize resonator surfaces. At the beginning of the contract only a retarding-grid electron spectrometer (8) was available. Investigations of evaporated copper electrodes were initiated in this instrument. This work was later transferred to the new cylindrical-mirror electron spectrometer (CMES), which became available about a third of the way through the contract, and all the AES analyses of uncoated quartz were carried out on the CMES unit.

It was found that the retarding grid-type spectrometer suffers excessively from charging problems when insulating materials are being examined. On the other hand, it was found that charging of bare quartz surfaces could be either eliminated or suitably controlled in the fast recording CMES unit by careful control of the electron beam voltage during the viewing period.

A general view of the Georgia Tech CMES instrument is shown in Fig. 2. The primary electron beam voltage is variable from 0 to 5 keV, and the focussed beam (about 10 microns) can be electronically scanned over a 0.5 x 0.5 cm square section of the specimen. The irradiated section of the specimen can be imaged on a TV type display, by using signals derived from either specimen current or secondary electrons collected in an electron multiplier (F in Fig. 2). The cylindrical mirror analyzer (9,10) has a 42.3° acceptance angle and a 10° window. A europium doped calcium fluoride
scintillator detects the transmitted (energy analyzed) electrons, and a photomultiplier (H) converts the photon current into an electrical signal. The sample (M), which is usually mounted on a type HC36/U crystal header can be rotated about an axis perpendicular to both the gun and analyzer axes. The sputter ion gun (L) is located opposite the analyzer, so the specimen has to be rotated through 90° for ion cleaning. Unfortunately, with this arrangement it is not possible to simultaneously bombard the specimen with ions and analyze the emitted Auger electrons. This spectrometer normally operates in the 10^-10 torr range, and because of its compact size, the specimen turn-around time is of the order of an hour.

2. Ion Cleaning System

An important segment of this research project was to study the effect of ion cleaning on quartz surfaces. Initially, a Physical Electronics Industries (PHI) Model 04-131 sputter-ion gun was obtained and installed in the cylindrical mirror electron spectrometer. With this arrangement, the effectiveness of sputter-ion cleaning in removing surface contamination on quartz was determined. Later in the program additional funds were made available for the purchase of another sputter-ion gun. When both guns were on hand, they were mounted in the fabricating unit in such a way as to enable both sides of the quartz to be cleaned, but not simultaneously since only one ion gun supply was available and power had to be switched from one gun to the other.

The geometrical arrangement of the two guns in the fabricating chamber was not the most desirable because the minimum gun-to-specimen distance that we could employ was 11.5 cm. At this distance the minimum beam diameter at focus is larger than the quartz wafer, so wafer, posts and other surfaces inside the chamber were exposed to ions during the sputter-ion cleaning process.

The vacuum system containing the CMES and the ion gun contains neither HEED nor LEED, thus structural damage to the quartz during sputter-ion cleaning was determined in a separate HEED system. Atmospheric contamination during transfer to our HEED system was not considered a problem since the HEED technique is largely insensitive to monolayer adsorption of gases.

3. Residual Gas Analysis

Residual gases in the fabricating chamber were analyzed just before, during and then after the electrode-plating operation with a Finnigan Model 400 quadrupole mass spectrometer. When measuring static or slowly fluctuating pressures spectral data were recorded on a X-Y pen recorder, since the elapsed time for a complete scan was ~ 6.5 minutes. During rapid pressure excursions, such as when the vapor source heaters were outgassed and the copper charge melted, the mass spectra of residual gases were monitored with an oscilloscope and photographically recorded. The instrument sensitivity at fast scan rates is, however, quite poor and only the more prominent responses were displayed.

4. Quartz Resonator Fabrication and Measurements

The basic fabricating chamber used for the plating, baking and
sealing resonator components into finished resonators has been described in a previous report (1). Also described in the cited report is the testing equipment which we used to obtain resonator aging data.

Before quartz wafers could be ion cleaned in the fabricating chamber, the cold-weld die support structure had to be modified. This modification consisted of attaching the evaporator support yoke, see Fig. 3, to the central post which also holds the upper section of the cold-weld die.

During sputter-ion cleaning the movable components of the fabricating system are located in the positions shown in Fig. 3. At the conclusion of the sputter-ion cleaning process, the evaporator yoke and associated hardware are lowered until the evaporators are in line of sight with the quartz wafer. The mask/shutter unit is also moved into the shutter position at this time. Once the copper evaporation has commenced, the electrode mask is positioned about the crystal, and the plating continued until wafer is resonating at frequency. The mask-shutter unit is withdrawn for the final baking and sealing operations.

An external view of the fabricating chamber is shown in Fig. 4, giving the positions of the two ion guns, the shutter activating mechanism and the residual gas analyzer.

Due to an oversight on our part, we have not previously mentioned the bakeout procedure for the fabricating chamber. This unit is given a mild bakeout to about 100°C in the early stage of each pumping cycle, i.e., with the pressure at about 10⁻⁶ torr.

A typical sequence of events for the fabrication of 5 MHz quartz resonators is as follows:

a) Mount ten wafers in a Teflon carrier, clean in chrome-sulfuric acid, rinse with deionized water (DIW) followed by methanol and dry in a stream of warm air. Etch for one minute in a saturated solution of ammonium bifluoride; rinse in DIW, then methanol.

b) Load into mask and plate the bonding tabs (Cu+Au) on both sides of each quartz wafer in diametrically opposed positions. Figure 5 shows the positions of the bonding tabs and electrodes for a typical 5 MHz resonator; the electrode dimensions were selected on the basis of 1) the principal region of oscillation is centrally located and about 3/16 inch in diameter for a 2.5 diopter, plano-convex, 5 MHz wafer and 2) the wide portion extending to the edge gives enhanced electrical continuity where it overlaps the bonding tabs.

c) Mount each wafer in an HC-36/U holder base using tab-clip supports. Apply AZ-111* photoresist to the regions' bonding sites where no plating is desired, and electrobond the exposed metal with nickel(11). The electrolyte is held at 55°C ± 5°C during plating which is carried out over a 45 to 60 minute period with a 5 mA current. Nickel is deposited to about 0.00075 inches in thickness. The photoresist is easily removed with acetone and the assembly recleaned as in (a) above,

*Shipley Co., Inc., Newton, Massachusetts.
and then stored in a vacuum desiccator.

d) Final cleaning of the base assembly, including the mounted quartz wafer, and cap was initially done with chrome-sulfuric acid, followed by distilled water and methanol rinses, and warm air dried. Recently, the cleaning of these parts has been carried out in a solution of \( \text{H}_2\text{O}_2 + \text{NH}_4\text{OH} \) (9/1 by volume), held at about 80°C. At this temperature the solution effervesces vigorously and continues to do so until all the \( \text{H}_2\text{O}_2 \) is decomposed. The cleaned object is then rinsed with DIW and spin dried. Polysiloxane coatings, when used, were applied at the conclusion of the final cleaning of the mounted quartz wafer.

e) Copper vapor sources* are each loaded with 6 inches of 0.020 inch diameter copper wire**. The wire is first cut into 6 inch lengths and cleaned by 1) vapor degreasing in trichloroethylene, 2) electrocleaning in a trisodium phosphate solution (19 g per liter), 3) ultrasonic rinsing in a solution of MICRO R)**, and then 4) rinsing in DIW, methanol and drying with warm air. The wire is then cut into 1/2 inch lengths and fed through the vapor hole into each of the tantalum sources.

f) When the fabricating chamber pressure reaches \( 10^{-8} \) torr, or lower, the ion gun degassing procedure is started using first filament current only, then filament current and the outgas mode of operation. For the actual sputter-ion cleaning of the quartz surfaces, a beam voltage of 950 V, a focus voltage of 900 V, emission current of 30 mA are employed. The beam current is then set at 2 \( \mu \text{A} \) by adjusting the argon pressure in the chamber to about \( 10^{-4} \) torr.

g) Electrode plating is commenced when the pressure is in the low \( 10^{-9} \) torr range; a pressure rise of about one order of magnitude during plating is typical. After the base pressure has been reached the sequence of events is as follows:

1) With the two sections of the cold-weld die almost closed, heat the die to the selected temperature (usually between 150 and 250°C). The quartz heating rate is shown by Fig. 6; a minimum of 5 hours is required to bring both the die and mounted quartz wafer to temperature.

2) Degas the vapor sources, premelt the copper, evaporate a small amount, and then lower the source temperature from about 1200°C to about 950°C. The graph in Fig. 7 shows how the source temperature varies as a function of source current. The source temperature is measured with an optical pyrometer.

3) Open the die by raising the upper section containing the holder cap and position the electrode mask which is manipulated by an external magnet. Increase the source current to about 90 amps. The crystal usually starts oscillating

---

* R. D. Mathis, Part No. S17A-.005Ta.
** Materials Research Corporation MARZ Grade (99.999%).
*** International Products, Inc., Trenton, N. J.
after a plate-back of about 10 kHz. The frequency is then monitored until the plate-back is about 25 kHz for copper-plated, 5 MHz wafers. Typically, the plating time is two minutes; shorter times are possible with higher source current.

4) The plating mask is then retracted and the die lowered to the position used in g(1) above. An exception to this step is sputter-ion cleaning of the Cu plated wafer; in the latter case the die is raised higher than for plating and each previously degassed sputter ion gun operated alternately for approximately 5 minute periods of time, using the parameters given above. During the ion cleaning process the fabricating chamber is backfilled with argon.

5) Bake resonator components and die for at least 5 hours, usually overnight, then seal the resonator container by cold-welding at the bakeout temperature.

6) Open the fabricating chamber to nitrogen and retrieve the sealed unit as quickly as possible from the hot die.

h) Most resonators are relocated in the 62°C aging oven within 30 minutes of sealing and the first frequency measurement is usually taken a few hours later. The methods used for measuring the frequency of the resonator and for calibrating the in-house secondary frequency standard have been described elsewhere (1).

Specimens for AES and other experiments were fabricated in exactly the same way as were the resonators, except they were not sealed into cans. After preparing these specimens, they were allowed to cool to room temperature before the plating system was brought to atmospheric pressure with nitrogen, opened, and the specimen quickly transferred to the required analytical instrument.

5. Additional Apparatus

A number of analytical instruments have been used on this project on an as-needed basis. These are 1) a Cambridge Stereoscan Mark IIIa scanning electron microscope; b) an Acton MS-64 electron probe micro-analyzer, c) an RCA-EMU-3F electron microscope with high resolution electron diffraction attachment, and d) a Phillips EM-200 electron microscope.
IV. EXPERIMENTAL RESULTS

A. Quartz Surfaces

1. Composition

All the investigations of quartz that are reported in this section regarding AES data from quartz surfaces were performed in our cylindrical mirror electron spectrometer (CMES), which has been described in Section III,B,1. Most of this work involved the determination of the chemical nature of quartz surfaces and the investigation of the experimental parameters that will allow reliable data to be obtained from non-conducting surfaces.

The quartz wafers were mounted on HC-36/U cold-weld type bases with tab clips grasping the edge of each wafer. Each wafer was given the customary one minute etch in saturated ammonium bifluoride before mounting. Both of the tab clips were either grounded or electrically biased at some potential opposing the primary electron beam during AES examination. The best bias potential was found to be about -100 volts.

Charging effects which result from electron bombardment of insulating materials can usually be avoided if the surface is sufficiently smooth and is not composed of electrically isolated particles (12). This is essentially the condition of the "as cleaned" quartz surface before sputter-ion cleaning, and may be why we do not observe charging effects with chemically cleaned surfaces. Since we remove very little quartz with our sputter-ion cleaning procedure, as verified by frequency measurements and electron microscopic examination, charging of sputter-ion cleaned quartz has to be ascribed to changes in surface electrical properties.

Before investigating the sputter-ion cleaning quartz wafers, several wet cleaning methods were investigated. These methods included chrome-sulfuric acid, $\text{H}_2\text{O}_2 + \text{NH}_4\text{OH}$ (9.1 ratio) heated to effervescence, rinsing in water or methanol and vapor degreasing in trichloroethylene. Figure 8 shows the type of Auger electron spectra that were obtained from a perfectly clean quartz surface, using $\text{H}_2\text{O}_2 + \text{NH}_4\text{OH}$ as the cleaning agent, and a surface containing only a trace of carbon after cleaning in $\text{CrO}_3 + \text{H}_2\text{SO}_4$. Although our experience with $\text{H}_2\text{O}_2 + \text{NH}_4\text{OH}$ as a cleaning medium is more limited than our experience with $\text{CrO}_3 + \text{H}_2\text{SO}_4$, the results appear to favor the performance of $\text{H}_2\text{O}_2 + \text{NH}_4\text{OH}$.

AES data obtained by the chemical cleaning techniques mentioned above as well as the effect of vacuum heating on surface composition resulting from atmospheric exposure and sputter-ion cleaning are given in Table II.

The carbon-free surface of specimen SI-6 was recleaned in $\text{CrO}_3 + \text{H}_2\text{SO}_4$, rinsed in deionized water and spin dried. Reexamination by AES showed the addition of a small carbon peak. One can theorize that the source of this carbon was either the cleaning solution, or the atmosphere to which the specimen was exposed for a few minutes. An example of contamination by atmospheric exposure is given in the S-8 data, Table II. Thus, it would appear that airborne carbonaceous compounds react with clean quartz surfaces.
to produce a small equilibrium concentration of surface carbon.

The effect of substituting a methanol rinse for spin drying appears to slightly increase the surface carbon content, to about the same degree as observed by atmospheric exposure.

We also decided to reevaluate the effect of trichloroethylene on surface cleanliness, since previous results (1) from copper plated quartz resonators indicated the presence of carbon and chlorine. The immersion of a chemically cleaned quartz wafer, see SH-1 in Table II, into room temperature trichloroethylene apparently has very little, if any, effect on a clean quartz surface. A small amount of carbon was observed when this specimen was exposed to trichloroethylene vapor at 85°C (VDG). Also, a small amount of chlorine appears to be picked up by the quartz from the hot vapor.

**TABLE II. SUMMARIZED RESULTS OF AES ANALYSIS OF QUARTZ WAFER SURFACES**

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Si</th>
<th>Cl</th>
<th>C</th>
<th>O</th>
<th>Σ?*</th>
<th>O/Si</th>
<th>C/Si</th>
<th>C/O</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>SI-6</td>
<td>32</td>
<td>-</td>
<td>68</td>
<td>-</td>
<td>2.1</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>H₂O₂+NH₄OH</td>
</tr>
<tr>
<td></td>
<td>42</td>
<td>5</td>
<td>53</td>
<td>-</td>
<td>1.3</td>
<td>.12</td>
<td>.09</td>
<td>.09</td>
<td>Cr₂O₃+H₂SO₄</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>6</td>
<td>63</td>
<td>-</td>
<td>2.1</td>
<td>.20</td>
<td>.09</td>
<td>Methanol</td>
<td></td>
</tr>
<tr>
<td></td>
<td>41</td>
<td>5</td>
<td>55</td>
<td>-</td>
<td>1.3</td>
<td>.12</td>
<td>.09</td>
<td>Atmosphere-50 hr.</td>
<td></td>
</tr>
<tr>
<td>SH-1</td>
<td>19</td>
<td>16</td>
<td>65</td>
<td>-</td>
<td>3.4</td>
<td>.84</td>
<td>.25</td>
<td>Cr₂O₃+H₂SO₄</td>
<td></td>
</tr>
<tr>
<td></td>
<td>23</td>
<td>13</td>
<td>63</td>
<td>-</td>
<td>2.7</td>
<td>.57</td>
<td>.21</td>
<td>235°C-30 min.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>7</td>
<td>68</td>
<td>-</td>
<td>2.7</td>
<td>.28</td>
<td>.10</td>
<td>Ion beam-10 min.</td>
<td></td>
</tr>
<tr>
<td>SH-2</td>
<td>19</td>
<td>-</td>
<td>81</td>
<td>-</td>
<td>4.3</td>
<td>-</td>
<td>0</td>
<td>Cr₂O₃+H₂SO₄-tap water</td>
<td></td>
</tr>
<tr>
<td></td>
<td>37</td>
<td>-</td>
<td>63</td>
<td>-</td>
<td>1.7</td>
<td>-</td>
<td>0</td>
<td>Trichloroethylene</td>
<td></td>
</tr>
<tr>
<td></td>
<td>31</td>
<td>2</td>
<td>60</td>
<td>-</td>
<td>1.9</td>
<td>.23</td>
<td>.12</td>
<td>VDG</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Carbon film</td>
<td></td>
</tr>
<tr>
<td></td>
<td>41</td>
<td>10</td>
<td>49</td>
<td>-</td>
<td>1.2</td>
<td>.24</td>
<td>.20</td>
<td>Ion beam-10 min.</td>
<td></td>
</tr>
<tr>
<td>S-8</td>
<td>26</td>
<td>5</td>
<td>15</td>
<td>54</td>
<td>2.1</td>
<td>.58</td>
<td>.28</td>
<td>Cr₂O₃+H₂SO₄-bakeout</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>5</td>
<td>65</td>
<td>-</td>
<td>2.2</td>
<td>-</td>
<td>0</td>
<td>Ion beam-10 min.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>21</td>
<td>5</td>
<td>49</td>
<td>20</td>
<td>2.3</td>
<td>.23</td>
<td>.10</td>
<td>Atmosphere-94 hr.</td>
<td></td>
</tr>
</tbody>
</table>

Note: these results are normalized to Σ divisions = 100.

*Sum of unidentified peaks.
Attention was next focussed upon the effect of vacuum heating on chemically cleaned surfaces. The quartz wafers used in these experiments were mounted in the usual way on HC-36/U bases and in addition, they had an evaporated nichrome heater on one side and a temperature sensing thermistor near one edge. A temperature vs input power calibration curve was obtained with the mounted wafer in a $10^{-6}$ environment. This curve is shown in Fig. 9.

From wafers which had been heated to temperatures between 200 and 250°C a slight decrease in the carbon response was observed, see SH-1 data in Table II. What was more noticeable, however, was the decrease in the O/Si ratios. These compositional changes could be attributed to the removal of adsorbed water. It is interesting to note that the O/Si ratio from sample SH-1 after heating is the same as after ion beam cleaning.

For the sputter-ion cleaning of quartz wafers an ion beam energy of 950 eV was used, with the argon pressure at $5 \times 10^{-5}$ torr, and the exit face of the gun was positioned at a distance of 4 cm from the target. Beam currents of about 10 μA were used and the beam was focussed to cover an area in the center of the quartz wafer about 0.5 cm in diameter.

The AES results from argon-ion cleaned surfaces show that this technique is effective in reducing the carbon concentration on quartz, either to zero or very close to it.

The failure to remove chlorine in the case of sample S-8 was unexpected. A plausible explanation is that this response which has been credited to chlorine may actually be a charging artifact. As mentioned beforehand, the smaller O/Si ratio that is obtained in spectra from both heated and ion cleaned quartz indicates that most, if not all, water is removed from the surfaces.

2. **Morphology**

During the process of this work we subjected quartz resonator surfaces to various treatments used in the preparation of resonators, and then subjected these surfaces to electron optical examination. The techniques we used in these examinations included high energy electron diffraction (HEED), transmission electron microscopy (TEM), and scanning electron microscopy (SEM).

The first series of experiments were directed towards evaluating the texture of unetched and etched surfaces of polished quartz wafers. Two polished quartz wafers were selected from the ECOM wafers which we received on May 8, 1973. Both were cleaned in chrome-sulfuric acid, rinsed and dried in a stream of warm air. One of the wafers was immediately subjected to reflection electron diffraction examination. The other was etched for one minute in a saturated solution of ammonium bifluoride, rinsed and then dried in a stream of warm air before examination by HEED.

The results are shown in Figs. 10 and 11. On viewing these two patterns it is quite obvious that the etched surface contained virtually no material which gives rise to diffuse scatter. One can conclude that a one minute etch, which will remove between 150 and 200 Å of quartz, is sufficient to remove any distorted quartz remaining after polishing, and to expose the true crystallinity of the quartz.
A one minute etch was shown by electron microscopic examination to produce only a mild roughening of the quartz surface. The degree of roughness is shown in Fig. 12 whereas the as-polished surface did not contain any features that could be observed by scanning electron microscopy.

Since very minute features (<100 Å) can only be observed by transmission electron microscopy, we decided to replicate the surfaces of a few other wafers and examine them by TEM. All the examined as-polished surfaces remained featureless, but when we examined replicas from these surfaces after etching quite a few features were observed. The various types of features are shown in Fig. 13. Besides an occasional scratch, there were fissure-like defects and conglomerations of hemispherical features, which varied in size between about 100 Å and 10,000 Å (1 micron). These last two features were only seen on several specimens and it was concluded that they resulted from poor quality quartz used to make these particular wafers.

B. Copper Surfaces

1. Composition

Experiments were carried out on both evaporated copper electrode surfaces and chemically etched bulk copper specimens. Most of the surface characterization work was performed in the retarding-field electron spectrometer. Several of the early results were later checked by looking at similarly prepared specimens in the CMES unit, and the copper surfaces obtained from a few additional experiments were also evaluated in the CMES instrument.

The general AES results are summarized in Table III. As suspected from the residual gas analyses, evaporated copper surfaces do appear to contain more carbon than do quartz surfaces which have been exposed to the same environment. A typical carbon response from a freshly evaporated copper surface (after transfer from evaporator to spectrometer) is shown in Fig. 14. The corresponding carbon response, normalized to $E_{\text{divisions}} = 100$, from an adjacent free quartz surface was only about 20 divisions.

The presence of carbon on "clean" copper surfaces is not restricted to evaporated material, since it was detected in all the spectra that were obtained from copper surfaces.
TABLE III. SPECTRAL LINE RESPONSES FROM COPPER AFTER VARIOUS TREATMENTS

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Cu</th>
<th>S</th>
<th>Cl</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>C/Cu</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>XP-3</td>
<td>8</td>
<td>2</td>
<td>4</td>
<td>81</td>
<td>2</td>
<td>3</td>
<td>10.1</td>
<td>evaporated Cu</td>
</tr>
<tr>
<td></td>
<td>83</td>
<td>3</td>
<td>14</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.2</td>
<td>evaporated Cu ion cleaned-10 min.</td>
</tr>
<tr>
<td>Cu-2</td>
<td>15</td>
<td>16</td>
<td>6</td>
<td>28</td>
<td>5</td>
<td>30</td>
<td>1.9</td>
<td>bulk Cu, cleaned in CrO$_3$+H$_2$SO$_4$ and rinsed in methanol</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>8</td>
<td>4</td>
<td>42</td>
<td>3</td>
<td>34</td>
<td>4.7</td>
<td>cleaned as Cu-2 above and exposed to lab air for 48 hrs.</td>
</tr>
</tbody>
</table>

Note: these results are normalized to $I_{\text{divisions}} = 100$.

Even ion cleaning did not completely remove carbon from evaporated copper, so it is highly probable that carbon is included in the copper deposit during its deposition. However, adsorption of the carbonaceous material after evaporation cannot be entirely ruled out.

Copper surfaces also appear to have a greater affinity for other elements which form copper compounds, such as sulfur, chlorine and oxygen, than do quartz surfaces. These elements, with the possible exception of sulfur, are fairly readily removed from the copper by ion cleaning. Since the concentration of sulfur actually appears to show a slight increase on freshly exposed copper surfaces, after successive sputter-ion cleaning steps, it appears that sulfur is distributed throughout the copper.

At this point we decided to continue experiments involving the sputter-ion removal of successive layers of copper, with the aim of determining the chemical distribution of elements, particularly carbon and sulfur, throughout evaporated copper electrodes. Using a freshly prepared resonator, the central portion of one copper electrode was sputter-ion removed in successive steps down to bare quartz. From the AES spectra we obtained from the various levels throughout the copper it was readily apparent that carbon, chlorine and sulfur were present in significant quantities. The sulfur/carbon ratio was observed to decrease from 0.72 at the original surface to 0.53 at about halfway through, and finally to 0.35 on the exposed quartz substrate.

A difficulty which exists in the interpretation of compositional changes resulting from sputter-ion removal of material is the uncertainty in the manner in which sputtered material is distributed within the spectrometer. This
may, in part, account for the rather large sulfur peak recorded from an un-
sputtered zone of the copper surface at the end of sputter-ion removal of cop-
per from an adjacent zone.

These data show that concentration gradients of carbon and sulfur exist
across the copper film; the source of these contaminants, as well as others,
such as chlorine, is of vital importance to this work. The occurrence of
carbon is expected in small quantities, even in ultrahigh vacuum systems,
from the residual carbonaceous gases, e.g., CO, CO₂, CH₄ etc. However, the
only source of sulfur is 3 ppm in the copper stock used in the metallization
of the quartz wafers. In previous work we have shown that chlorine can come
from solvents used in cleaning resonator components prior to metallization.
Our present cleaning procedure, using hydrogen peroxide and DIW rinses,
excludes all chlorine-bearing solvents. Regular distilled water contains
parts per billion chlorine, and when used to rinse surfaces this concentra-
tion may well be enough to give an AES response if it is preferentially
adsorbed on a particular surface.

Possible contributions of sulfur and chlorine from residual gases in the
fabricating chamber are discussed later.

An indication of the reactivity of copper surfaces with foreign matter
which comes into contact with them can be gained from the spectral data shown
in Fig. 15. These data were obtained from a freshly prepared copper surface
and after this surface had been exposed to laboratory air for 48 hours. The
growth of the carbon response is almost 6 times greater than that observed
with similarly prepared and exposed quartz surfaces.

2. Morphology

During this work a detailed study was not made of either the struc-
ture or texture of vacuum deposited copper electrodes. From previous reports
in the literature it can be assumed that room temperature deposits will be
randomly oriented polycrystalline. At elevated temperatures, especially in
the vicinity of 200°C one would expect either large grained or single crystal
copper overgrowth, showing a certain degree of epitaxial relationship to the
quartz substrate.

Some of our copper electrodes were examined by SEM after various amounts
of copper were removed by the sputter-ion technique. These examinations re-
vealed that the copper deposits have a mosaically textured grain structure,
see Fig. 16, with the individual crystallites ranging in size from about
1 to 3 microns. Before sputter-ion etching, the copper surfaces were very
smooth and textureless. This observation was a little unexpected as it had
been assumed that metallizing a heated (about 200°C) quartz single crystal
surface would produce a large amount of epitaxial growth. Apparently the
misfit between the structure of an A-T cut quartz surface and the preferred
copper growth habits are too large for epitaxy to occur.

It should be pointed out that sputter-ion removal of metal to trim the
resonator to frequency (before encapsulating it) will produce an etched
surface of higher surface area than the as-deposited surface. The etched
surface may lead to enhanced adsorption of contaminants.

C. Residual Gas Analysis

The residual gas atmospheres in the plating system were analyzed as described in Section III-B-3. The results of the analyses are given in this section. The plot shown in Fig. 17 was recorded at a base pressure of \(2.0 \times 10^{-9}\) torr, before any fabricating activities were started. The principal constituents of the residual gas atmosphere in the fabricating system were water vapor, carbon monoxide, carbon dioxide and hydrocarbons \(\text{CH}_4, \text{C}_2\text{H}_6, \text{C}_3\text{H}_8\). Increasing the instrumental gain by a factor of 10 revealed numerous peaks, one or two divisions above the background, which can be ascribed to cracking patterns of heavier hydrocarbons.

The next step was to heat the two series-connected Ta vapor sources, each loaded with 6 inches of 0.020" dia copper wire. Figure 18 shows the gas fractions present when the evaporant sources were heated by the passage of 75 A through them (temperature \(\sim 960^\circ\text{C}\)); the pressure rose very rapidly from the base of \(2.0 \times 10^{-9}\) torr to about \(1.5 \times 10^{-7}\) torr. The pressure then dropped sharply to \(1.5 \times 10^{-8}\) torr before starting a slow rise, reaching \(7 \times 10^{-8}\) torr at the end of the 6.5 minute recording period. The effect of this pressure increase appeared to result only in the increase in the partial pressure of the major components, which have already been identified.

During the 6.5 minute recording time the pressure rose from \(7 \times 10^{-8}\) to \(2.5 \times 10^{-7}\) torr. The major gas present is shown to be water, with the minor constituents being CO, CO_2, and CH_4. The reason for the pressure rise during the long period of source heating is most likely outgassing from adjacent parts of the system and from the chamber walls which become warm from radiant heating.

The system was cooled to room temperature, with the pressure dropping to \(1 \times 10^{-9}\) torr, before continuing with the next step, which was to melt the copper in the tantalum source. The source current was set at 100 A (\(\sim 1200^\circ\text{C}\)) and the recording of Fig. 19 commenced. Initially, the pressure rose to \(8 \times 10^{-9}\) torr as the source current rose to a value above 100 A without a change in voltage, indicating that the copper charge had melted. The source current was then reduced to 75 A until the shutter could be opened; the plating "smears" if the shutter is moved while the sources are at the evaporation temperature. The spectrum shown in Fig. 19 was then recorded at the same sensitivity setting as used to record Fig. 18. The major constituent of the residual gas appears to be H_2O; however, when CO and CO_2 were scanned the source current was 75 A rather than 100 A. The scanning time was \(\sim 6.5\) minutes during which time the pressure decreased to \(2 \times 10^{-8}\) torr. The shutter was then opened and the quartz wafer plated on both sides with copper in the previously described electrode pattern. The plating time was one minute, about normal for a 25 kHz plateback at 100 A source current. The resonator was not oscillated during plating.

At the end of the one minute evaporation the data shown in Fig. 20 were recorded. The initial pressure was \(5 \times 10^{-8}\) torr but decreased rapidly and reached \(3 \times 10^{-9}\) torr after the 6.5 minute recording period.
The pictures taken of oscilloscope traces during the actual evaporation gave essentially the same information as the pen recordings but with less resolution. Only the H$_2$O, CO, and CO$_2$ peaks were significant in these photographs, each response increasing from the beginning through the middle to the end of the one minute evaporation period.

The residual gas atmosphere in the retarding grid spectrometer was also analyzed, to ascertain whether or not the chlorine and sulfur responses during AES analysis of copper came from that source. Typical spectra were similar to that shown in Fig. 17, except the hydrogen peak was about 60 divisions in height. At mass numbers 32 and 35 only trace peaks about 2 divisions in height were observed. Since oxygen occurs with sulfur at M/e = 32 and hydrocarbon fractions at M/e = 35, it can safely be said that the presence of sulfur and chlorine in the gas phase is marginal and in any case below the detectable limit (about 5 x 10$^{-14}$ torr for N$_2$ with unit resolution). All the peaks occurring in spectra from the AES spectrometer could be identified with either water or carbon containing gases or fragments.

D. Quartz Resonator Measurements

1. Introduction

After installation of the two sputter-ion guns in the resonator fabrication chamber two experiments were made to determine both their electrical performance and their efficiency.

a. Ion Beam Experiments. Figure 21 shows the variation of ion current, measured between a plated quartz target and ground, with argon gas pressure in the fabricating chamber. Because of the low ion currents produced by this system, it was decided to operate the ion guns at the highest practical beam current, consistent with stable operating conditions. These conditions were obtained with a gas pressure of 10$^{-5}$ torr and a beam current of 2 μA.

The operating parameters for the sputter-ion guns during resonator fabrication for aging studies were the following:

- Beam voltage ($E_B$) 950 V
- Focus voltage ($E_F$) 900 V (ADJ. for I$_{B,max}$)
- Emission current 30 mA
- Beam current 2 μA
- Argon pressure 1 x 10$^{-4}$ torr
- Time Variable ranging from 5 to 20 min.
b. Cleaning and Sputtering Efficiency of Plated and Unplated Quartz. The effect of argon ion bombardment on bare quartz specimens was determined by AES and reported previously in section IV-A-1; the effect of ion sputtering on plated resonators in the resonator fabrication system was also investigated. Table IV shows the range of positive frequency changes that were obtained. The approximate mass of Cu removed from each side of the quartz wafer can be determined by the fact that the nominal plateback for 2000 Å thick Cu electrode on 5 MHz wafers is ~ 1.25 ppm/Å/side; thus the total amount of Cu removed is less than approximately 100 Å. The beam-on times during resonator fabrication were shorter than those given in Table IV. Each side of the crystal was alternately exposed to an ion beam for a number of five minute periods of time.

2. Quartz Resonator Fabrication

The system for resonator plating, baking and sealing without venting has been described previously (1). Two modifications during this project were: 1) provision for the cold-weld die to be raised as well as lowered, allowing certain operations such as heating before plating and 2) attachment of the vapor source yoke to the die raising and lowering mechanism so the sources could be moved up to clear the line-of-sight path between the ion guns and the quartz target.

These modifications were not completely successful; the cold-weld die started binding badly on the two remaining guide pins when the second modification was added partly because one of the three guide pins had been removed in order to clear a path between the quartz and one of the vapor sources. Reliable operation was restored by removing the die-raising feature of modification No. 1 in the preceding paragraph. Even so, the die shows evidence of excess wear and will soon need refacing and new guide pins.

3. Long-Term Aging Measurements

The aging data of crystal units assembled during the first half of the project were reported in R&D Technical Report ECOM-0172-1 (January, 1974)**. Fifteen selected resonator units were sent to ECOM during November, 1974 and the rest phased out to make room in the constant temperature oven for recently assembled units. Thus this report covers only units fabricated during the second half of the project.

We prepared three groups of resonators during the second half of this contract, using variable fabrication techniques as the most important parameter. Following the mounting and chemical cleaning processes carried out on the quartz wafers before they are placed in the fabricating chamber, as described in section III-B-4, the crystals were either 1) ion cleaned, plated, baked and sealed, 2) plated, ion cleaned, baked and sealed, or 3) plated, baked and sealed.

The aging data obtained from the first group were quite poor, as shown in Fig. 22. This figure shows the average aging rate data which were obtained from five resonators. The maximum and minimum variations from this average aging rate are shown in vertical bars through each sampling point.

*These specimens were preterminated with Cr+Au bonding sites and electrode-bonded in HC-36/U holders. No driving electrodes were present, however.

**Copies available from National Technical Information Service, Springfield, Virginia; Accession No. AD774284.
<table>
<thead>
<tr>
<th>Exposure No.</th>
<th>Specimen No.</th>
<th>Gun Position</th>
<th>Sputtering Time Min.</th>
<th>Sputtering Current 1(\mu)A</th>
<th>(\Delta F) PPM</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>Right</td>
<td>20</td>
<td>1</td>
<td>Low</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Both sides of target @ ground.</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>Right</td>
<td>20</td>
<td>1</td>
<td>+54</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Right side target only grounded.*</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>Right</td>
<td>20</td>
<td>1</td>
<td>+84</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Experiment No. 2 repeated.</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>Left</td>
<td>20</td>
<td>1</td>
<td>+33</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>Left</td>
<td>20</td>
<td>1</td>
<td>+60</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Experiment No. 4 repeated.</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
<td>Right</td>
<td>30</td>
<td>2</td>
<td>+32</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>2</td>
<td>Left</td>
<td>30</td>
<td>2</td>
<td>+134</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>2</td>
<td>Left</td>
<td>30</td>
<td>2</td>
<td>+103</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Experiment No. 7 repeated.</td>
</tr>
<tr>
<td>9</td>
<td>2</td>
<td>Right</td>
<td>30</td>
<td>2</td>
<td>+43</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Experiment No. 6 repeated.</td>
</tr>
</tbody>
</table>

* This grounding procedure also applies to exposures 3 through 9.
The data obtained from several additional units were not included in Fig. 22 because their high negative aging rates were suspected as being due to leaking containers; this was before we realized that this fabrication sequence produced high negative aging.

The averaged aging data from ten units in the second group of units fabricated in the sequence described above are shown in Fig. 23. The aging slope is now positive and the rate is in the $10^{-9}$/week range after 30 days at 62°C.

The third group, also consisting of ten units and which were fabricated in the plate-bake-and-seal sequence, aged as shown in Fig. 24. The aging data recorded in Fig. 23 show the lowest aging rate that was obtained from the three sequential options. Also, the data spread from resonators made by the third option was the lowest we measured, a fact not apparent from the graph because of the sensitive frequency scale.

Pertinent data for each crystal unit fabricated during the second half of the project are given in Table V.
TABLE V. CRYSTAL UNITS FABRICATED FOR AGING MEASUREMENTS

<table>
<thead>
<tr>
<th>Unit No.</th>
<th>Source</th>
<th>Diameter (inch)</th>
<th>Final Cleaning</th>
<th>Oxidizer</th>
<th>Rinse</th>
<th>Dry</th>
<th>Electrode Preparation</th>
<th>Plating Time (Min)</th>
<th>Bakeout Time (Hours)</th>
<th>Bakeout Temp (°C)</th>
<th>Rs (Ω)</th>
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<td>7.0</td>
<td>200</td>
<td>3.0</td>
<td>1.13</td>
<td>&quot; 15 min/side&quot;</td>
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*Also applies to cap and base of HC-36/U holder.

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<th>Rinse</th>
<th>Dry</th>
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<td>Ion cleaned quartz 5 min/side</td>
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</table>

*Also applies to cap and base of HC-36/U holder.
V. DISCUSSION

A considerable portion of the time allotted to this contract was spent investigating the sputter-ion cleaning process as applied to quartz wafers and other resonator components. Of particular interest in this work was the effect this cleaning method had on the long-term aging of SSB quartz resonators, and the comparison between it and the more conventional chemical cleaning methods that are used during resonator fabrication.

The results of this investigation show that under the experimental conditions we used, the short term aging of sputter-ion cleaned resonators was inferior to chemically cleaned units, although their long term aging, i.e., after about the first 30 days at temperature, is generally better than $10^{-8}$/week. This performance is comparable with the better quality chemically cleaned units that we have made, but is two orders of magnitude poorer than the best units that we have made; especially those units in which the quartz surfaces were coated with a polysiloxane before plating.

Perhaps it is unwise to draw any definite conclusions as to the effectiveness of sputter-ion cleaning in preparing SSB quartz resonators, since the results that have been obtained from this work were not obtained under optimum conditions. A fabricating system is required in which the ion sources can be located at a close enough position as to permit the ion beams to be focused onto specific areas of the quartz resonator and its enclosure vessel. In our experiments the enclosure vessel was not sputter-ion cleaned. Such an arrangement would reduce the problem we faced of adjacent metal components being sputtered by the ion beams and the deposition of some of this sputtered metal onto the "cleaned" quartz. Another problem that has to be faced if the metal surfaces of the resonator are bombarded with gas ions is the entrapment of the ion-beam gas in the metal. Recent experiments (14) have shown that implanted argon is only slowly removed from bombarded metals, such as copper, gold, nickel, etc., which are used in resonator fabrication. On the other hand, low energy (i.e., 1000 eV) argon ions are only retained in the quartz lattice for a very short time (seconds), even at room temperature.

The predominantly negative aging characteristic which was exhibited by our sputter-ion cleaned resonators could quite possibly be related to this property that metals have to absorb argon. One explanation of negative aging is that the inertia of the crystal is changing due to electrode separation from the quartz. If this process is in fact occurring in our resonators, it could be the result of poor adhesion between the quartz surface and plated electrodes. This situation could result from having a thin layer of poorly adhering metal, containing entrapped argon, on the quartz surface prior to electrode plating. This material would originate from the sputtered support posts, etc., during the sputter-ion cleaning process.

Another source of negative aging is a gain in weight by absorption of gas onto the active region of the quartz wafer. This gas could well be argon which has escaped from previously bombarded metal components. This absorption/desorption process is expected to continue until an equilibrium condition is reached.
One interesting aspect of including sputter-ion sources in the final fabricating chamber is that they can be used to trim the frequency of the plated wafer. The frequency adjustment is accomplished by sputtering copper from the plated electrodes in controlled amounts. However, from the preceding discussion, this capability may be of dubious advantage, since the sputtering process will almost certainly add argon to the copper electrodes. The loss of entrapped argon could account for the positive aging shown in Fig. 23, which gives aging data from resonators which were bombarded with argon ions after the electrodes were deposited.
VI. CONCLUSIONS AND RECOMMENDATIONS

Preliminary experiments using the sputter-ion cleaning method on quartz resonators have shown that the method is capable of improving the cleanliness of both the copper and the quartz surfaces beyond that possible with more conventional cleaning methods. With ion beam energies of about 1000 eV the amount of material that is removed from a quartz surface appears to be regulated by surface conductance. After the conducting surface contaminants are removed, the quartz becomes almost a perfect insulator and the resulting charge buildup deflects the oncoming ions to nearby conducting materials.

Once strongly bound water, or hydroxyl, is removed from quartz either by heating or ion bombardment, the quartz surface acts as if it is relatively immune to contamination by materials that would readily contaminate it when in its hydrophilic state.

The evaporated copper electrodes appear to be more surface active than does the quartz surface. There is evidence that carbonaceous materials in the residual gas atmosphere at the time of plating are included in the deposited copper. Also, materials such as sulfur, chlorine, and possibly water, which react chemically with copper appear in larger concentrations on the copper than on the quartz.

The aging data that have been obtained from sputter-ion cleaned quartz resonators have not come up to the performance level that has been obtained from resonators that have been prepared in the conventional way. This may be due largely to experimental parameters that were used in the present experiments.

In future work employing sputter-ion cleaning the experiments should be designed so as to optimize the various parameters involved. Should sputter-ion cleaned resonators fail to show a marked improvement over chemically cleaned units, then supplemental neutral beam sputtering should be investigated. If these combined cleaning techniques still fail to produce resonators with superior aging properties, the application of photon irradiation may prove to be a suitable alternative method.
VII. ACKNOWLEDGEMENTS

The author of this report wishes to express his appreciation to the following persons for conducting the various experimental tasks and for their inputs to this report: Dr. John L. Carden, Mr. James R. House and Mr. Larry A. Phillips for the Auger electron spectrometric studies, Mr. Walter H. Hicklin for resonator fabrication and frequency data, also Mr. Larry H. Glassman and Mr. James W. Johnson for the electron optical studies.
VIII. REFERENCES


Fig. 1. Calculated projected ranges, $R_p$, of various ions in quartz and silicon as a function of ion energies.
Fig. 2. Sectional view of scanning Auger electron spectrometer.
Fig. 3. Exposed view of top section of quartz resonator fabricating equipment. The yoke carrying the two evaporators and the bakeout heater are attached to the top die section, which can be raised vertically 1.5 inches.
Fig. 4. View of the quartz resonator fabricating equipment, showing location of the two ion guns, the residual gas analyzer and the shutter.
Fig. 5. Diagram of mounted quartz resonator assembly. The crystal is 0.528 in diameter, and the copper electrodes are 0.187 in wide and approximately 2000 Å in thickness.
Plateback ~ 25 kHz

Fig. 6. Frequency vs time graph for a typical unit during plating and 200°C bakeout.
Fig. 7. Ta source temperature and total source power vs source current.
Fig. 8. Auger electron spectra from quartz wafer SI-6 cleaned with a) H$_2$O$_2$ + NH$_4$OH, and then with b) CrO$_3$ + H$_2$SO$_4$. 

$E_b = 2$ keV

$V_{Sp} = -75$ V

Grazing angle = 30°
Fig. 9. Heater power vs temperature calibration curve for heated samples.

Specimen SH-1
$R_H = 34 \, \Omega$
Fig. 10. Kikuchi-line electron diffraction pattern from a quartz wafer surface cleaned in chrome-sulfuric acid, rinsed in water and alcohol and then dried in warm air.
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Fig. 18. Analysis of residual gas in electrode plating system during degassing of both Ta vapor sources at -960°C. Pressure: variable (see text); recorder sensitivity: 50 mV/inch.
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Fig. 20. Analysis of residual gas in fabrication system immediately following a one minute evaporation of copper onto quartz surface. Pressure variable.
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Fig. 22. Aging data for argon ion cleaned quartz resonators, averaged over 5 units. The vertical bars indicate the data spread at each sampling point. These data are compared with the best aging rate that we have obtained from a non ion cleaned resonator.
Fig. 23. Average aging and data spread for ten resonators plated with Cu, ion cleaned, baked and sealed.
Fig. 24. Average aging and data spread for ten resonators plated, baked and sealed.
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This report is concerned with the systematic investigation of various cleaning and processing techniques which are used to assemble high precision single sideband (SSB) quartz resonators. The final requirement is to be able to produce crystal units which will meet a strict aging requirement of $2 \times 10^{-10}/\text{week}$, when measured at the upper turning point of the crystal unit after a stabilization period of 4 weeks.

The specific aspects of resonator fabrication that have been investigated...
during this study are several wet-cleaning processes for preparing quartz surfaces, the sputter-ion cleaning of quartz and the composition profiles and impurities associated with both the quartz surface and the copper electrodes.

Analyses of the prepared resonator components were carried out by Auger electron spectrometry (AES), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and high energy electron diffraction (HEED).

Both chemical and sputter-ion cleaning methods were employed in the fabrication of complete SSB crystal units, with the sputter-ion cleaning process being performed in the final fabricating chamber. Aging data from these units are presented and the effects of processing variables on resonator aging are discussed.