CONF-780596--2

NOTICE MN ONLY

PORTIONS OF THIS REPORT ARE ILLEGIBLE.
has been reproduced from the best available
copy to permit the broadest possible avail-
ability.

POLYIMIDE BONDED RESONATORS

R.L. Filler*, J.M. Frank**, R.D. Peters**, and J.R. Vig*

SUMMARY

Silver filled polyimide adhesives capable of withstanding operation at 350°C have been evaluated. These materials have been found to be compatible with the high temperature processes used in the fabrication of precision resonators. The adhesives are single component, soft pastes, which can be applied by the techniques used in conventional cement bonding.

The outgassing properties and lap shear strengths of three silver filled polyimide adhesives have been measured. The polyimides outgas substantially less than silver-filled epoxies. Polyimide bonded resonators in four-point ribbon mounts have survived 20,000g shocks with no apparent damage to the polyimide bonds. The average aging rate of a group of 22 MHz polyimide bonded high shock resonators has been measured to be 1.5×10^{-9} per day.

Key words

Polyimides, quartz-resonators, quartz, bonding, resonator, piezoelectric-crystals, frequency-control, frequency-standards, stresses, aging (materials), shock (mechanics), shock-resistance, outgassing, shear-strength, adhesives.

INTRODUCTION

This paper is a progress report on the development of ruggedized twenty-two Megahertz fundamental mode AT-cut quartz resonators. Various aspects of this development have been reported previously^{1,2,3,4,5}. These resonators are designed primarily for use in artillery delivered devices. At earlier symposia we described a ruggedized design, a key feature of which was nickel electrobonding⁴. In that ruggedized design a nickel rim was electroplated onto the quartz blank to provide both strength and a non-contaminating bond to the support structure. Although the Nickel electrobonding process did permit resonators to survive very high shock levels, the process was difficult to implement and control. In this paper, a high shock resonator design is described which

*US Army Electronics Technology and Devices Laboratory (ERADCOM) Fort Monmouth, NJ 07703
**General Electric Company, Neutron Devices Department St. Petersburg, FL 33733

no longer relies on the nickel electrobond.

There are three major features to this design. First, the resonators are enclosed in a ceramic flatpack^{6,7,8}. Second, the quartz blanks are 6.4 mm diameter, and are chemically polished⁹. The chemical polishing process has been the key to strengthening the blanks. This inherent strength has allowed the nickel electrobond to be eliminated. Third, the resonators are bonded to a four point support structure using an electrically conductive silver-filled polyimide adhesive. The blanks are carefully oriented such that the supports are 45° away from the XX' and ZZ' axes. Resonators fabricated with these features have both a low aging rate and a very high degree of resistance to levels of shock as high as 20,000g, the highest shock level tried so far. Due to the unique properties of polyimides, these resonators can withstand exposure to high temperatures, thus permitting the use of the high temperature processes commonly employed in the fabrication of high precision resonators.

The ceramic flatpack was described at the 30th Annual Frequency Control symposium⁹. The chemical polishing was described at the 31st Symposium⁹. This paper will concentrate on a discussion of polyimide adhesives.

POLYIMIDE

Polyimides are a class of heterocyclic organic polymers having a nitrogen atom in one of the rings. There are two basic kinds of polyimides,

differing in the method of final polymerization. The condensation type is produced by reacting two organics into a fusible polyamic acid. This polyamic acid is converted by heat into an infusible polyimide, with water being given off during the cure. The second kind of polyimide is the addition type. This type is formed from short, pre-imidized, polymer chain segments which are

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

polymerized thermally without the loss of volatiles. Polyimides, as a class have the highest resistance to temperature of all the plastics commercially available. The condensation type can withstand a temperature of 500°C for a short duration, and 350°C continuously. The addition type has a slightly lower resistance to high temperatures. Polyimides have relatively high tensile strength for thermoplastics, have an unusually low outgassing rate, and a very high resistance to ionizing radiation. To compare polyimides with a more familiar material, the following chart is a comparison of its properties with those of standard epoxies^{10,11}.

	POLYIMIDE	EPOXY
Tensile Strength	6-9 X 10 ⁷ Pa	3-9 X 10 ⁷ Pa
Elongation	4-9%	2-10%
Tensile Elastic Modulus	3.1 X 10 ⁹ Pa	2.4 X 10 ⁹ Pa
Compressive Strength	1.68 X 10 ⁸ Pa	1-1.4 X 10 ⁸ Pa
Flexural Yield Strength	10-16 X 10 ⁷ Pa	7-9 X 10 ⁷ Pa
Deflection Temp. (1.8 X 10 ⁶ Pa)	360°C	260°C
Water Absorption	0.3%	0.08-0.15%
Resistance to Solvents	Very Resistant	Attacked by some

FIG. 2

The tensile strength and elongation are seen to be about the same. The tensile elastic modulus of the polyimide is a little higher, and so are the compressive and flexural yield strengths. The deflection temperature, which is the temperature at which the first detectable softening occurs, is seen to be much higher for the polyimide. Epoxy has a lesser tendency to absorb water but is susceptible to attack by some organic solvents. It can thus be seen that polyimides are equal to or superior to epoxy in almost every mechanical and chemical property. Polyimides are especially useful for their ability to maintain mechanical properties over a wide range of temperatures including well into the cryogenic region. High temperature epoxies, in contrast, are generally quite brittle, have very poor thermal shock resistance, and outgas profusely as their temperature is increased above about 200°C.

The major disadvantage of using polyimide is related to its foremost advantage. To realize its full potential, a cure cycle with temperatures much higher than those used for epoxy must be employed. A second potential disadvantage is that polyimide, not unlike quartz, has an affinity for water. Care should be taken to keep the material dry after cure.

The three commercially available conductive polyimide adhesives have been investigated. All three are one component pastes which are suitable for use in automatic micro-dispensers. The cure cycles have been performed in an inert gas atmosphere to maintain cleanliness and to prevent excessive oxidation of the silver. The resonator blank is contaminated during the cure but the contamination is readily removed by a brief exposure to the UV/ozone cleaning procedure^{4,12,13}.

A serious problem with the use of epoxy adhesives in resonator fabrication has been the rather large rate of outgassing, especially, as the temperature is increased¹⁴. The use of polyimide has been explored by NASA for space applications where low outgassing is of critical importance^{15,16}.

According to one published study¹⁷, polyimide which has been vacuum baked at 300°C for 12 hours has an outgassing rate which is lower than that of baked Viton and is also lower than that of unbaked stainless steel. Polyimide valve seals are also listed in the current catalog of a major vacuum equipment manufacturer¹⁸ as a replacement for Viton. The polyimide seals are rated for better than 10⁻⁹ torr and a temperature of 300°C. These seals are also recommended for use in high radiation environments. According to the literature, polyimides are undamaged and actually increase in flexural strength after exposure to levels of radiation of up to 10¹⁰ rads¹⁰. Recently, some polyimide bonded resonators were tested for radiation hardness at Sandia Laboratories. The conclusion of the test was that the polyimide did not contribute to radiation induced frequency shifts at a dose level of 4.7 X 10⁴ rads¹⁹.

OUTGASSING STUDY

An outgassing study has been performed on the three different polyimide formulations, one condensation type²⁰ and two addition types. A conductive epoxy was also evaluated for comparison²¹. The epoxy selected was one reputed to have a very low outgassing rate. Drops of each material were placed on molybdenum strips. The volume of each drop was approximately the same as the volume of adhesive used in fabricating the 22 MHz resonators. There were about 300 drops of polyimide on a strip and 110 drops of epoxy (Fig. 3).

FIG. 3
TYPICAL OUTGASSING SAMPLE

	MASS OF MOLY STRIP	MASS OF UNCURED ADHESIVE	MASS OF CURED ADHESIVE
EPOXY	10.18650g	260.8 mg	249.4 mg
CONDENSATION	10.23279g	261.1 mg	188.6 mg
ADDITION I	10.17612g	261.6 mg	161.5 mg
ADDITION II	10.31115g	261.0 mg	178.9 mg

FIG. 4

The cure cycles recommended by the manufacturers for the polyimides was not followed but one was substituted which was selected to reduce outgassing. The cure cycle for the polyimide consisted of an initial bake for 20 minutes at 150°C. The purpose of this initial bake is to drive off the solvents. The second step is to bake for 20 minutes at 300°C. A temperature over 273°C is needed to initiate the imidization reaction in the condensation type of polyimide. The addition type has a wide time-temperature cure schedule and could be cured for a longer time at a lower temperature. The final step is a 350°C bake for 2 hours. The epoxy was cured at 150°C for 2 hours as per the manufacturers recommendation.

The 350°C temperature is the maximum continuous use temperature for the condensation type of polyimide. The polyimides were baked at this temperature in order to minimize subsequent outgassing. Outgassing is a result of diffusion from the bulk and desorption at the surface. The rate of outgassing is proportional to the amount of gas remaining in the sample. The diffusion and desorption rates increase exponentially with temperature. Therefore, the most efficient way to lower the ultimate outgassing rate is to bake out the material at as high a temperature as possible and thus diminish the reservoir of stored gas as quickly as possible.

The polyimide samples and a bare strip of Mo were analyzed at 350°C and 150°C. A sample was inserted into a bell jar, the jar was attached to a mass spectrometer inlet and evacuated for one hour. After the evacuation period, the temperature of the sample was raised to 350°C and the outgassing products from the sample were collected for a fifteen minute period. At the end of the collection period, the accumulated gases and vapors were analyzed and then pumped away. The collection, analysis and pumping were repeated every fifteen minutes for one hour.

At the end of one hour at 350°C, the sample was cooled to 250°C. After the cooling period, the temperature was raised to 150°C and the collection, analysis and pumping steps were repeated every fifteen minutes for one hour.

The silver epoxy sample and a bare moly strip were analyzed at 150°C using this same procedure.

The outgassing rate was obtained by subtracting the gas quantities evolved by a bare strip from the quantities evolved from the

adhesive sample on a strip. The net value was divided by the collection time and the sample mass to obtain the outgassing rate per unit mass.

The results are tabulated in fig. 5, and the total outgassing rates are plotted in figures 6 and 7. The most important difference between the epoxy and the polyimides is in the amount of condensable matter which is given off. There is no detectable outgassing of hydrocarbons by any of the polyimides at 150°C. Water, which is the major constituent of the gases released by the polyimide is outgassed at a rate of two orders of magnitude lower than that of the epoxy. The comparison is not completely valid because the polyimide was outgassed at 350°C whereas the epoxy was not, however, the epoxy cannot withstand a prolonged 350°C bake¹⁴.

No attempt was made to develop a cure schedule to minimize the epoxy outgassing. The epoxy data is listed only to provide a reference point.

The variation of outgassing rate with temperature indicates that at room temperature the condensation type polyimide should be the best. In fact, no detectable outgassing was observed at room temperature for the condensation type of polyimide, the one selected for use in the high shock resonators. The other samples were not checked at room temperature, however, it has been repeatedly documented that epoxies have substantial outgassing rates at 125°C²², and even at room temperature.

The outgassing rates of all the samples decreased with time, especially at elevated temperatures. An improved cure schedule could possibly be devised if even lower outgassing rates are required. For our high shock resonator, the cure schedule described above has been sufficient to permit us to meet the aging requirement which is 1 ppm per year.

LAP SHEAR STRENGTH

To compare the relative strengths of the four adhesives, a series of lap shear tests were performed. The samples were prepared by covering the first 1.2 cm (½ in.) at the end of 2.5 cm (1 in.) wide strip of aluminum with the adhesive under test. A matching strip of aluminum was then overlapped on the adhesive (Fig. 8). A uniform pressure was applied during the cure. The strips of aluminum were then attached to a tensile test machine and pulled along their length until separation occurred. All of the separations were due to cohesive failure

CONDENSATION POLYIMIDE AT 350°C								
Accumulative Time (Min.)	H ₂	CH ₄	H ₂ O	CO	N ₂	CO ₂	C ₆ H ₆	Total
15	5.5×10^{-4}	1.9×10^{-5}	2.6×10^{-3}	1.9×10^{-3}	2.1×10^{-3}	7.1×10^{-3}	1.9×10^{-4}	1.4×10^{-2}
30	2.8×10^{-3}	1.9×10^{-5}	7.8×10^{-4}	2.2×10^{-3}	1.5×10^{-3}	5.4×10^{-3}	1.3×10^{-4}	1.3×10^{-2}
45	3.2×10^{-3}	6.4×10^{-6}	3.5×10^{-4}	1.7×10^{-3}	8.3×10^{-4}	3.3×10^{-3}	7.8×10^{-5}	9.4×10^{-3}
60	2.6×10^{-3}	4.9×10^{-6}	2.1×10^{-4}	1.3×10^{-3}	7.3×10^{-4}	2.5×10^{-3}	4.9×10^{-5}	7.5×10^{-3}
ADDITION POLYIMIDE II AT 350°C								
15	6.1×10^{-4}	5.7×10^{-5}	1.4×10^{-3}	3.5×10^{-4}	1.5×10^{-3}	3.8×10^{-3}	2.6×10^{-5}	7.7×10^{-3}
30	2.2×10^{-3}	8.2×10^{-5}	9.8×10^{-4}	5.8×10^{-4}	4.5×10^{-4}	2.5×10^{-3}	3.7×10^{-5}	6.9×10^{-3}
45	2.2×10^{-3}	6.1×10^{-5}	9.5×10^{-4}	5.0×10^{-4}	1.5×10^{-4}	1.4×10^{-3}	2.6×10^{-5}	5.3×10^{-3}
60	1.9×10^{-3}	5.4×10^{-5}	8.2×10^{-4}	5.3×10^{-4}	1.6×10^{-5}	1.1×10^{-3}	2.0×10^{-5}	4.4×10^{-3}
ADDITION POLYIMIDE AT 350°C								
15	ND	ND	6.4×10^{-5}	7.3×10^{-5}	2.1×10^{-4}	6.5×10^{-4}	1.6×10^{-5}	1.0×10^{-3}
30	ND	ND	3.4×10^{-5}	3.7×10^{-5}	1.5×10^{-4}	5.5×10^{-4}	6.8×10^{-6}	7.8×10^{-4}
45	ND	ND	ND	1.8×10^{-5}	9.7×10^{-5}	2.4×10^{-4}	1.1×10^{-6}	3.6×10^{-4}
60	ND	ND	ND	6.6×10^{-6}	6.8×10^{-5}	1.1×10^{-4}	1.1×10^{-6}	1.9×10^{-4}
EPOXY AT 150°C								
15	4.1×10^{-4}	4.1×10^{-5}	1.5×10^{-1}	ND	4.4×10^{-4}	3.9×10^{-3}	5.2×10^{-5}	1.6×10^1
30	1.7×10^{-5}	2.3×10^{-5}	9.7×10^{-3}	ND	3.7×10^{-4}	4.7×10^{-3}	4.9×10^{-5}	1.5×10^{-2}
45	3.2×10^{-6}	2.0×10^{-5}	8.6×10^{-4}	ND	4.0×10^{-4}	4.0×10^{-3}	5.4×10^{-5}	5.3×10^{-3}
60	4.8×10^{-6}	2.3×10^{-5}	1.2×10^{-3}	ND	9.2×10^{-5}	1.8×10^{-3}	4.4×10^{-5}	3.0×10^{-3}
CONDENSATION POLYIMIDE AT 150°C								
H ₂	CH ₄	H ₂ O	CO	N ₂	O ₂	CO ₂	C ₆ H ₆	Total
15	9.7×10^{-7}	ND	2.5×10^{-5}	ND	1.2×10^{-5}	9.1×10^{-6}	2.5×10^{-6}	5.0×10^{-5}
30	9.7×10^{-7}	ND	2.5×10^{-5}	ND	9.3×10^{-6}	7.3×10^{-6}	1.9×10^{-6}	4.4×10^{-5}
45	9.7×10^{-7}	ND	1.9×10^{-5}	ND	1.2×10^{-5}	8.6×10^{-6}	1.9×10^{-6}	4.3×10^{-5}
60	8.3×10^{-7}	ND	1.7×10^{-5}	ND	9.8×10^{-6}	7.5×10^{-6}	1.9×10^{-6}	3.6×10^{-5}
ADDITION POLYIMIDE II AT 150°C								
15	1.0×10^{-6}	ND	9.8×10^{-5}	ND	5.3×10^{-5}	4.7×10^{-6}	3.7×10^{-6}	1.6×10^{-4}
30	7.2×10^{-7}	ND	8.0×10^{-5}	ND	4.2×10^{-5}	6.7×10^{-6}	2.6×10^{-6}	1.3×10^{-4}
45	5.8×10^{-7}	ND	4.8×10^{-5}	ND	3.9×10^{-5}	8.2×10^{-6}	2.0×10^{-6}	9.6×10^{-5}
60	5.8×10^{-7}	ND	3.7×10^{-5}	ND	3.9×10^{-5}	6.1×10^{-6}	1.5×10^{-6}	8.3×10^{-5}

FIG. 5
OUTGASSING RATES OF SILVER FILLED ADHESIVES
(torr cc min⁻¹ mg⁻¹)

ND = not detectable

ADDITION POLYIMIDE I AT 150°C									
	H ₂	CH ₄	H ₂ O	CO	N ₂	O ₂	CO ₂	Hydro-Carbon	Total
15	ND	ND	ND	ND	5.0×10^{-5}	1.5×10^{-5}	1.1×10^{-6}	ND	6.6×10^{-5}
30	ND	ND	ND	ND	4.7×10^{-5}	1.2×10^{-5}	2.3×10^{-6}	ND	6.2×10^{-5}
45	ND	ND	ND	ND	5.0×10^{-6}	1.3×10^{-5}	2.3×10^{-6}	ND	6.6×10^{-5}
60	ND	ND	ND	ND	4.0×10^{-5}	1.0×10^{-6}	1.1×10^{-6}	ND	5.2×10^{-5}

FIG. 5 cont'd
OUTGASSING RATES OF SILVER FILLED ADHESIVES
(torr cc min⁻¹ mg⁻¹)

ND - not detectable

FIG. 6

Total Outgassing Rates of Silver Filled Adhesives at 150°C. Sample A - Epoxy; Sample B - Addition Polyimide II; Sample C - Addition Polyimide I; Sample D - Condensation Polyimide.

in the adhesives. There was no sign of separation from the aluminum. The relative ranking of the lap shear strengths is consistent with those claimed by the manufacturers but the absolute values are consistently 50% smaller than those advertised. As we later discovered, the differences in absolute values are due to a difference in test procedure. The manufacturers placed a mylar spacer between the aluminum strips to prevent the adhesives from squeezing out and causing a decrease

FIG. 7

Total Outgassing Rates of Silver Filled Polyimide at 350°C. Sample B - Addition Polyimide II; Sample C - Addition Polyimide I; Sample D - Condensation Polyimide.

in bond area. In any case, however, these numbers by themselves are difficult to translate into practical terms. However, our shock tests at 20,000g indicate that these materials have sufficient strength for most resonator applications.

SHOCK TESTS

The shock tests were performed with an air gun and were designed to simulate the environment

FIG. 8
TYPICAL LAP SHEAR SAMPLE

experienced by a transmitter which is gun emplaced.

The transmitter receives three separate shocks. The first is at the initial launch from a 155 mm howitzer. The second shock takes place when the delivery vehicle is ejected from the launch projectile. The final shock, which like the second shock is in the opposite direction to the first, occurs when the transmitter hits the ground. This impact, incidentally, occurs without the aid of a parachute. The magnitude of the first shock has been varied from 7,000g up to 20,000g to stimulate different launch conditions. The following two shocks have been held constant at 5,000 g each. The durations of the shocks were approximately 2 msec at 20,000g and 2.5 msec at the 5000g level.

The shock tests were conducted on resonators with three different support structure designs. All of the units were fabricated using the condensation type of polyimide. A total of 40 units have been shock tested to date of which half were tested at 20,000g. All of the units have survived at all shock levels. The survivability success can be traced directly to the chemical polishing. The magnitude of the frequency change due to the shocks is directly dependent upon the mounting structure.

The first type of mounting structure shock tested is called the nickel-gold "C" Clip, (Fig. 10) & (Fig. 11).

This clip is formed from 50 micrometers by 750 micrometers (2 mil X 30 mil) gold ribbon. The formed gold ribbons are then electroplated with 25 micrometers (1 mil) of nickel to give the support structure strength. The height of each clip is 500 micrometers (20 mil). This type of mounting structure produces frequency vs. temperature characteristics which makes the resonators appear to have an angle of cut much lower than that measured by an x-ray goniometer³. This is due to the thermal expansion difference between the ceramic flatpack and the quartz blank causing

ADHESIVES	AVERAGE STRENGTH OF FIVE SPECIMENS (10 ⁶ Pa)
EPOXY ADHESIVE	9.87
CONDENSATION POLYIMIDE	3.64
ADDITION POLYIMIDE II	2.58
ADDITION POLYIMIDE I	0.99

FIG. 9
LAP SHEAR STRENGTHS

temperature dependent stresses. These stresses couple through the force frequency coefficient to produce rotations in the frequency-temperature characteristic. The shock induced frequency changes measured on crystal resonators with the nickel-gold "C" clip are about 8ppm at shock levels of 11,000g.

The second clip design is identical in form to the nickel-gold "C" clip but is made of 25 micrometers (1 mil) thick molybdenum ribbon. These resonators have an apparent angle of cut near the x-ray measured angle.

The third clip design is the most interesting. It is called the moly "L" clip (Fig. 10 & 12). It is nothing more than an inverted "L". A dab of polyimide is placed on each of the four shelves and the crystal blank is placed on the dabs. Another dab of adhesive is applied to the top side of the blank so as to join up with the first dabs. The resulting structure is basically a molded polyimide clip. The two 5000g shocks are in the direction which would tend to pull the crystal blank away from the supports. The higher level first shock is in the opposite direction. No evidence of polyimide bond failure has been seen in this design or in either of the other two designs.

The average shock induced frequency change in resonators with Moly clips is about 1.9 ppm for shock levels up to 11000g. The frequency change is about 4.2 ppm for shocks of 20,000g. These figures represent averages. In all cases, the frequency shifts have been under 10 ppm. Many of the units had shock induced frequency shifts of less than 1 ppm.

We attribute the shock induced frequency change to a change in the mounting stress pattern due to a deformation of the clips. The resonators with the smallest amount of mounting stress, as measured by the degree of rotations of the

FIG. 10

FIG. 11
"C" CLIP

FIG. 12
"L" CLIP

frequency-temperature characteristic have the smallest amount of sensitivity to shock. The typical shift in apparent angle in nickel-gold clip resonators is about 4 minutes. The corresponding shift in resonators with moly clips is about 1 minute, interestingly, in the opposite direction. The important requirements for a high shock mounting structure are that it not apply undue stress to the crystal blank, and that it be strong enough not to permanently deform under the loading experienced during shock.

It should be emphasized that the inherent shock resistance of the quartz blank is provided by the chemical polishing. An epoxy bond would most likely work as well as a polyimide bond. However, since these ruggedized resonators must also have low aging, the polyimide is preferred because it allows the use of high temperature processing.

AGING

The aging rate was measured on a group of ruggedized polyimide bonded resonators. Some of these resonators had the earlier nickel-gold "C" clip support structures, the others had moly clips. The data for the moly clip resonators is only for the initial aging rate. The fabrication sequence for these resonators consist of first applying moly-gold contact spots to the crystal blanks. The blanks are then mounted in the clips with the polyimide making the electrical and mechanical contact.

The assembly is placed in an inert gas oven and the adhesive is cured. The units are UV/ozone cleaned and then loaded into the electrode deposition vacuum chamber. The rough plating of the gold

electrode is performed with the resonators at a temperature of 325°C. Final frequency plating is done in the same vacuum system after the resonators cool down to room temperature. The final step in the sequence is to seal the flatpacks with a gold to gold diffusion bond. The seal is made at a temperature of 300°C and at a pressure of less than 5×10^{-7} torr.

The sealing process for these resonators had to be performed in a separate vacuum system, which meant that they were exposed to the atmosphere after electroding. Also, the nickel-gold "C" clip resonators are known to have large mounting stresses which lead one to believe that the aging results do not represent the lowest rates achievable with polyimide bonding.

The aging measurements were carried out at a constant temperature of 85°C. The average aging rate from day 68 to day 97, for 20 Ni-Au "C" clip resonators, is 1.5 parts in 10^9 per day, with the worst being 3.9 parts in 10^9 per day. Several of the resonators are aging less than the sensitivity of the measurement, which is about 1.6 parts in 10^{10} per day. The aging for 10 moly clip resonators has been measured for 21 days. The average initial aging rate is 6.1 parts in 10^9 per day. The range of rates is from 8.0×10^{-10} /day to 1.3×10^{-8} /day. These results would be respectable even for low shock, two point mounted resonators. It should be reiterated that these are results for four point mounted resonators which have been shown to be capable of surviving 20,000g shocks. It is strongly suspected that stress relief in the support structure is the significant aging mechanism in these resonators.

CONCLUSIONS

The conclusion derived from the evaluation of polyimide bonded resonators is that this material is preferable to both nickel and epoxy for bonding. Further study is required to determine if it can compare with thermo-compression bonding.

Future plans include a repositioning of the mounting locations of the four clips to coincide with the minimum force-frequency directions for 4 point mounts recently derived²³. This repositioning should serve to improve both the aging rate and the magnitude of the shock induced frequency change. The performance of two point mounted resonators will also be measured to determine the lowest aging rates achievable with polyimide bonding.

A continuation of the outgassing study is in progress. The performance of an epoxy which has been baked at higher temperatures will be evaluated.

ACKNOWLEDGEMENTS

The authors would like to thank Mr. T.M. Mason, GEND, for performing the outgassing study.

REFERENCES

1. M. Bernstein, "Quartz Crystal Units for High G Environments", Proc. 25th Annual Symp. on Freq. Control, US Army Electronics Command, Fort Monmouth, NJ, p. 125-133 (1971), National Technical Information Service Accession NR AD 746211
2. W. D. Lawrence, "Frequency Control Requirements for Remote Sensor Systems", Proc. 26th Annual Symp. on Freq. Control, p. 113-119 (1972), NTIS Accession NR AD 771043.
3. J. M. Stanley, et al, "Frequency Control Devices for High Stability Remote Transmitters", Proc. 26th Annual Symp. on Freq. Control, p. 120-131 (1972), NTIS Accession NR AD 771043.
4. J. R. Vig, J. W. LeBus, R. L. Filler, "Further Results on UV Cleaning and Ni Electrobonding", Proc. 29th Annual Symp. on Frequency Control, p. 220-229, (1975); copies available from Electronic Industries Association, 2001 Eye Street, NW, Washington, DC, 20006.
5. R. L. Filler, J. R. Vig, "The Effect of Bonding on the Frequency vs. Temperature Characteristic of AT-Cut Resonators", Proc. 30th Annual Symp. on Frequency Control, p. 264-268, (1976), See ref. 4.
6. J. R. Vig, E. Hafner, "Packaging Precision Quartz Crystal Resonators", US Army Electronics Command, Fort Monmouth, NJ 07703, TR ECOM-4134, NTIS Accession NR AD 763215 (1973).
7. P. D. Wilcox, G. S. Snow, E. Hafner, J. R. Vig, "A New Ceramic Flatpack for Quartz Resonators", Proc. 29th Annual Symp. on Freq. Control, p. 202-219, (1975), See ref. 4.
8. R. D. Peters, "Ceramic Flatpack Enclosures for Precision Quartz Crystal Units", Proc. 30th Annual Symp. on Freq. Control, pp. 224-231, (1976), See. ref. 4.
9. J. R. Vig, J. W. LeBus, R. L. Filler, "Chemically Polished Quartz", Proc. 31st Annual Symp. on Freq. Control, p. 131-143, (1977), See. ref. 4.
10. J. Agranoff, Editor, "Modern Plastics Encyclopedia", Vol. 53, No. 10A, McGraw-Hill, (1976)
11. C. A. Harper, Editor, "Handbook of Plastics and Elastomers", McGraw-Hill, (1975).
12. J. R. Vig, C. F. Cook, Jr, K. Schwidtal, J. W. LeBus, E. Hafner, "Surface Studies for Quartz Resonators", Proc. 28th Annual Symp. on Freq. Control, p. 96-100, (1974), See ref. 4.
13. J. R. Vig, J. W. LeBus, "UV/Ozone Cleaning of Surfaces", IEEE Trans on Parts, Hybrids, and Packaging, Vol. PHP-12,4, (1976), p. 365-370.

14. See e.g. - J. J. Licari, B. L. Weigand, K. L. Perkins, "Material Requirements and Process Controls for Epoxy Adhesives Uses in Hybrid Microcircuits", Proceedings of the ECOM Hybrid Microcircuit Symp., US Army Electronics Command, Fort Monmouth, NJ, P. 173-187, (1976).
15. R. M. Kurland, G. L. Brown, J. F. Thomasson, J. T. Bevans, W. P. Bell, "Properties of Metallized Flexible Materials in the Space Environment", Final Report, Dept of the Air Force, HQ, Space and Missile Systems Org., (1978), SAMSO TR-78-31 - NTIS Accession ADB 024667.
16. D. H. Buckley, "Friction and Wear Characteristics of Polyimide and Filled Polyimide Compositions in Vacuum (10^{-10} mm Hg)", National Aeronautics and Space Administration, NASA - TN D3261 (1965).
17. L. I. Maissel, R. Glang, "Handbook of Thin Film Technology", McGraw-Hill Book Company, NY (1970).
18. Varian Associates/Vacuum Division, 611 Hansen Way, Palo Alto, CA 94303, Model No. 951-0036.
19. T. Young, Sandia Laboratories, Private Communication, (May 1978).
20. Ablebond 71-1, Ablestik Laboratories, 833 West 182nd St., Gardena, CA 90248.
21. Ablebond 773-6, Ablestik Laboratories, See ref. 20.
22. See e.g. - W. A. Campbell, Jr., R. S. Harriott, J. J. Park, "An Outgassing Data Compilation of Spacecraft Materials", NASA, NASA Reference Publication 1014, (1978).
23. A. D. Ballato, "Four-Point Mounting Configuration for Resonators Subjected to Severe Environments", USAECOM, Fort Monmouth, NJ 07703, TR-ECOM 4544 (1977), To Be Published: "Force-Frequency Compensation Applied to Four Point Mounting of AT-cut Resonators - IEEE Trans. Sonics and Ultrasonics, Vol. SU-25, 4, (1978).

ENTERED

Send column of text line on first page only.