The Investigation of the Potential of a Crystal Oscillator with Attached
Porous Silicon Adsorber Device for Gas Analysis

by

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Abstract

This investigation explored the potential of a slab of porous silicon mounted onto a quartz crystal to detect various gas species or measure gas pressures for a given gas species. The pore sizes of the porous silicon are such that they should allow gas molecules to enter the silicon and thus change the mass of the silicon by a slight amount. This small mass change affects the frequency of oscillation of the quartz crystal which can be detected by a frequency counter. The strategy exploits the almost unique properties of the two materials: quartz crystal and porous silicon.

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I. INTRODUCTION

Porous Silicon is a morphologically unique form of crystalline silicon that was discovered during early attempts to electropolish the material [1,2]. Anodic dissolution of silicon in concentrated $HF:H_2O$ solutions yields a low density layer that contains a large number of small pores. The final density of the porous layer depends upon both the anodic current density and the doping level of the silicon crystal [3]. The density values between 40 and 70% of the silicon density and pore radii between 20 and 100 Å can be obtained by varying the electrochemical conditions of preparation [4]. A very unique property of porous silicon is its high surface area along with its low density creating a high surface to volume ratio as is illustrated in the sample calculations of Appendix A.

One potential application for porous silicon is in forming thin layers of single crystal silicon on insulator for VLSI applications. Devices built using this technology have a high speed performance which is very desirable for VLSI applications. Porous silicon may be oxidized at high rates and low temperatures without macroscopic volume change. Application of such oxidized porous silicon regions to dielectrec isolation has been extensively pursued in Japan [5,6].

Another potential application for porous silicon, and the one pursued in this investigation, is its potential to be used in conjunction with a crystal oscillator to detect the prescence of different gasses or different pressures of a given gas. The principle involved is the same as that in

thickness monitors which are so commonly used in electronic device fabrication to monitor small thicknesses of metal evaporated on to a wafer. As the metal is evaporated onto the wafer, it is also evaporated onto a quartz crystal. This mass loading of the quartz produces a change in its resonant frequency. The use of quartz-crystal oscillators to determine small quantities of deposited matter was first explored by Sauerbrey and Lostis. The crystal oscillator monitor utilizes the piezo-electric properties of quartz. A thin crystal wafer is contacted on its two surfaces and made part of an oscillator circuit. If a small mass is added to either one or both sides of the wafer, it may be assumed that the original crystal surfaces remain antinodes of vibration and the effect of mass loading on the frequency may be derived mathematically. Graphs according to these mathematical derivations are shown in Figure 1 [7]. A thin wafer of porous silicon can be mounted onto a quartz crystal in an oscillator circuit and then be slightly mass loaded by the adsorbtion of a gas. A frequency change according to this mass loading can then be observed.

II. EXPERIMENTAL

A 3.58 MHZ crystal was chosen because it is in a suitable frequency range for mass loading with porous silicon and because it is widely used and therefore inexpensive and easy to obtain. The next step was to find and build a crystal oscillator circuit for the specfied crystal. The one decided upon is shown in Appendix B along with some calculations pertaining to it. Once this circuit was constructed with a "clean" crystal,

"clean" meaning no porous silicon attached, it was tested for frequency stability by monitoring the frequency with a Monsanto counter accurate to 8 decimal places. The next step was to get the crystal to oscillate with the porous silicon attached. According to calculations (Appendix C) from the graphs shown in Figure 1, the crystal could only be loaded with about 4 or 5 μm of porous silicon and still oscillate, but the thinnest porous silicon available was about 10 μm. In addition to this problem an adhesive, which also adds mass to the crystal, had to be used to mount the porous silicon onto the quartz crystal. After the porous silicon was mounted to the quartz crystal using a very dilute solution of black wax, it was put through an etching process to thin the porous silicon. Through this method it finally oscillated. The next step was to inject a gas and see if the frequency decreased as expected due to the mass loading of the gas molecules being adsorbed into the pores of the porous silicon. A vacuum set-up in the Institute of Solid State Electronics Laboratory was used for this process. The crystal oscillator circuit was placed in the vacuum's glass bell jar and evacuated to a relative vacuum pressure of 5×10^{-6} torr. This evacuation process was performed to evacuate the pores so that they would be free to adsorb the gas when injected. After the evacuation was complete, the system was vented with pure Nitrogen gas from a relative vacuum pressure of 0 inches of Mercury (in. Hg) to about 29 in. Hg in increments of 5 in. Hg. At each increment, frequency readings were taken, again using the Monsanto counter. The sample was evacuated again and the process repeated to see if the values were the same each time. A "clean" crystal was put through the whole process to make sure that any observed frequency changes were due to the porous

silicon and not the crystal itself.

III. RESULTS AND DISCUSSION

The results of evacuating and then filling with Nitrogen gas can be seen in the graphs of Figures 2, 3 and 4. Figure 2 is the result of a crystal with porous silicon mounted on one side. As the Nitrogen was injected the frequency decreased almost linearly. As the circuit was again evacuated the frequency increased as expected, but did not follow the same path. The circuit was injected with Nitrogen a second time and again the frequency decreased, but didn't follow either of the earlier two paths. The total frequency change observed here is about 50 Hz over a pressure difference of about 30 in. Hg. Figure 3 is the result of a second crystal with a little bit less porous silicon mounted on it than on the first crystal. It also exhibits a linear decrease in frequency over the same pressure range. The total frequency change observed for crystal two is about 36 HZ. Notice that the total frequency change for the crystal with less porous silicon is less than that of the crystal with the greater amount of porous silicon. Figure 4 is the same data for a "clean" crystal. This is how each crystal should perform without the porous silicon mounted. Although the frequency does decrease a little with gas injection, the change, about 10 HZ, is much smaller than for the crystals with porous silicon. Therefore, most of the frequency change is due to the porous silicon. Also, the paths are approximately the same for each direction of pressure change, indicating that the hysterisis affect seen in the other two crystals is due to the porous silicon. Figure 5 shows how the frequency is not very stable when the crystal oscillator circuit with

porous silicon is exposed to air.

IV. CONCLUSION

The potential of using porous silicon in conjunction with a crystal oscillator to detect the prescence of different gasses or different pressures of a given gas has been investigated and useful results obtained. It was originally thought that a very inexpensive digital pressure gauge or gas analyzer could be made from the principles in this experiment. The results for this are actually inconclusive, they indicate that it is plausible, but not likely. What has been shown is that the porous silicon crystal oscillator does produce the expected affects.

Now that the desired results have been obtained with the crude model used for the results in this report a more sophisticated porous silicon-quartz crystal sample could be built. This would include using porous poly silicon instead of single crystalline silicon. The porous poly silicon could cover the entire crytal surface where the single crystalline silicon can not as well as be more uniformly doped. The process, however, for making and mounting the porous poly silicon is much more difficult. Also, another step would be to provide a reference crystal, one without porous silicon, during the experiment as shown in Figure 6. This would omit any frequency change due to the quartz crystal and thus we could be sure that all the frequency change was due to the porous silicon. For further analysis different gases such as Methane, Oxygen and water vapor could be used to explore how the porous silicon behaves when exposed to different gases. From these results it might be found that

different gas species could be determined with the methods presented in this paper. Not shown in the results of this paper is that a very large frequency change occured when the device was evacuated for the first time. We believe that this may be due to the evacuation of water molecules. If this is true, the device could potentially be used as a humidistat.

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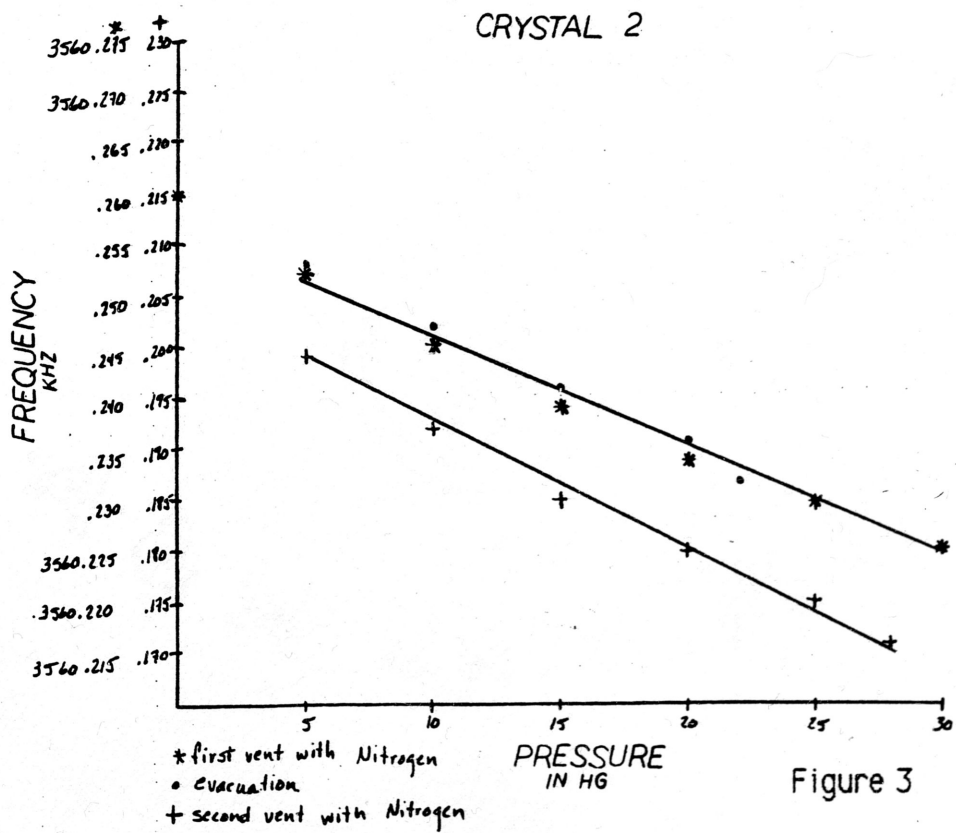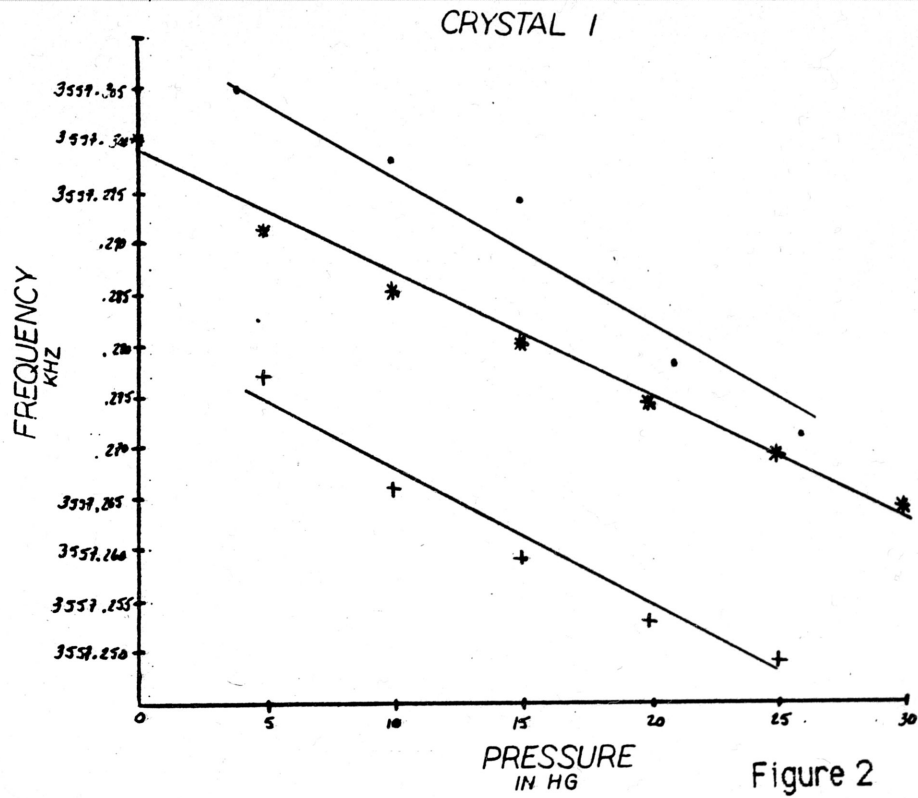[7] <u>Handbook of Thin Film Technology,</u> p. 1-109 (1970).

Figure 1

CRYSTAL 1

FREQUENCY
KHZ

PRESSURE
IN HG

Figure 2

CRYSTAL 2

FREQUENCY
KHZ

PRESSURE
IN HG

Figure 3

* first vent with Nitrogen
• evacuation
+ second vent with Nitrogen

BLANK CRYSTAL

FREQUENCY (KHZ) vs PRESSURE (IN HG)

* first vent with Nitrogen
○ evacuation
☆ second vent with Nitrogen

Figure 4

FREQUENCY (KHZ) vs TIME (SEC)
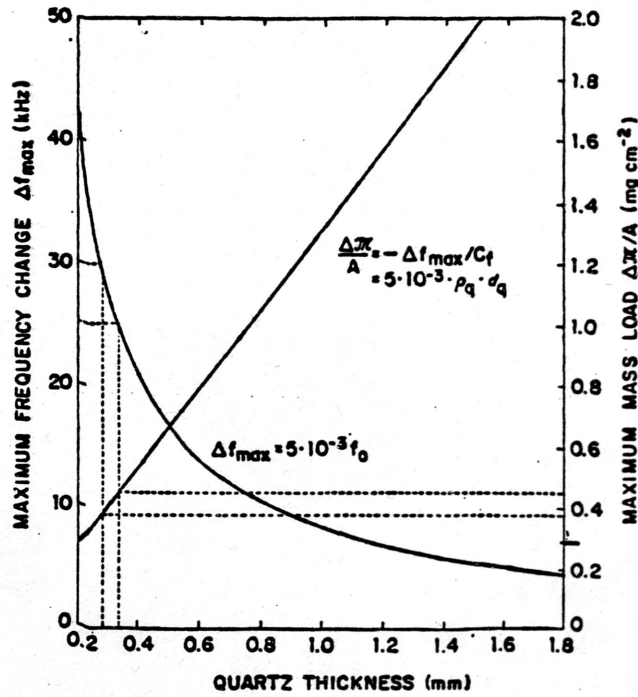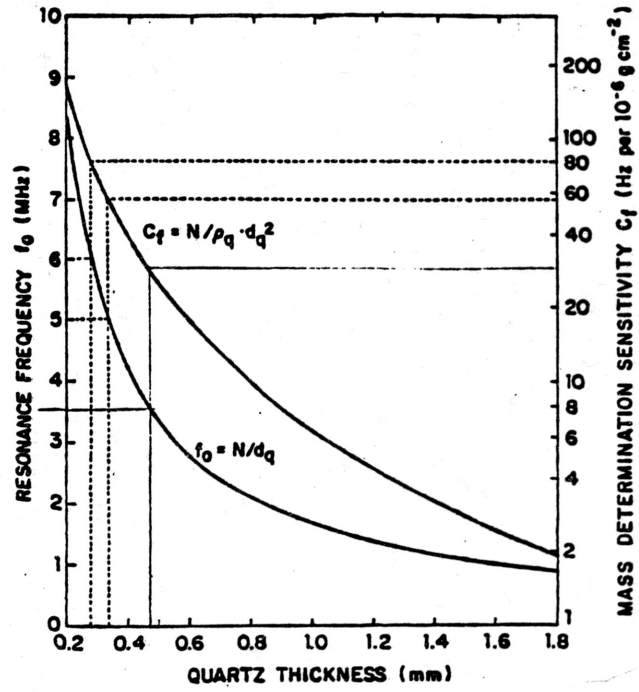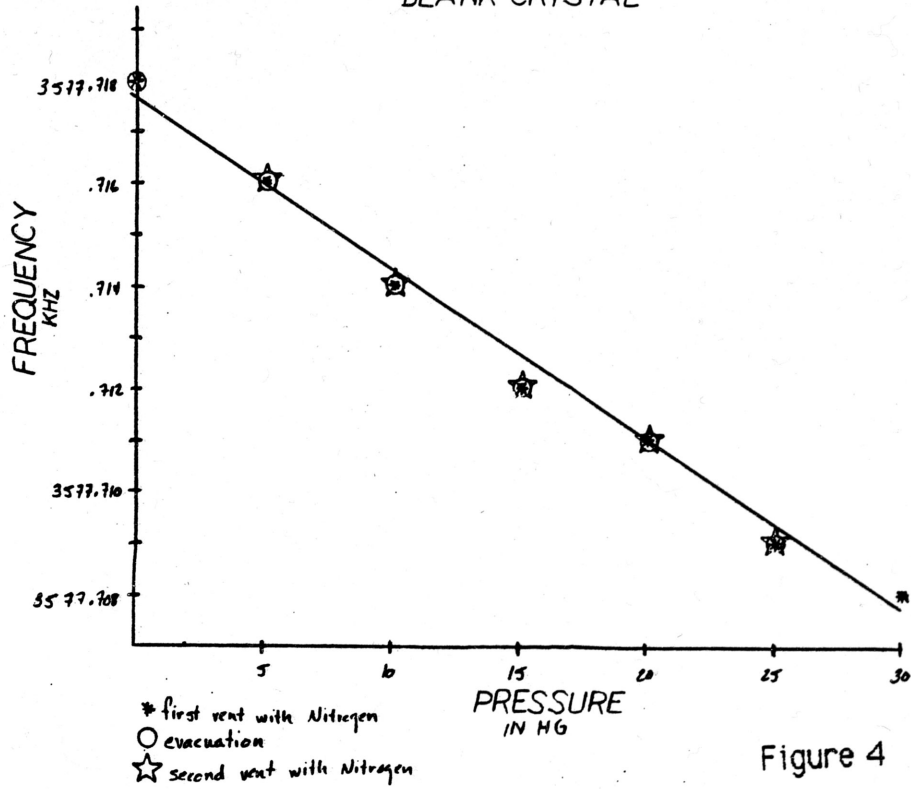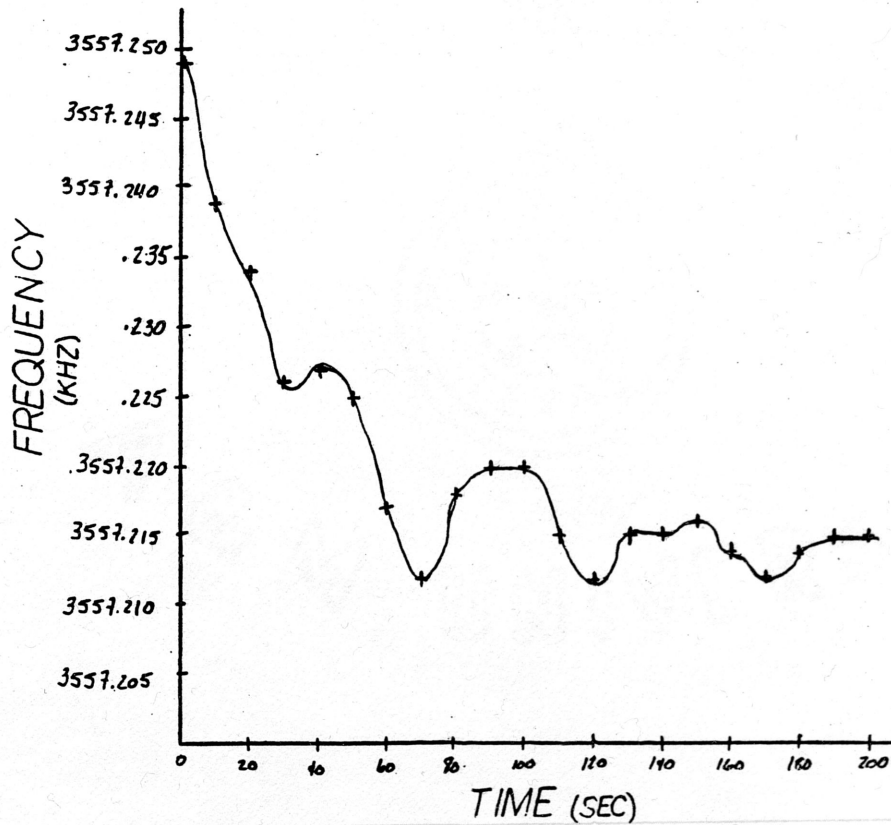
Figure 5

Quartz Crystal with Porous Silicon

Oscillator Circuit

frequency 1 (f1)
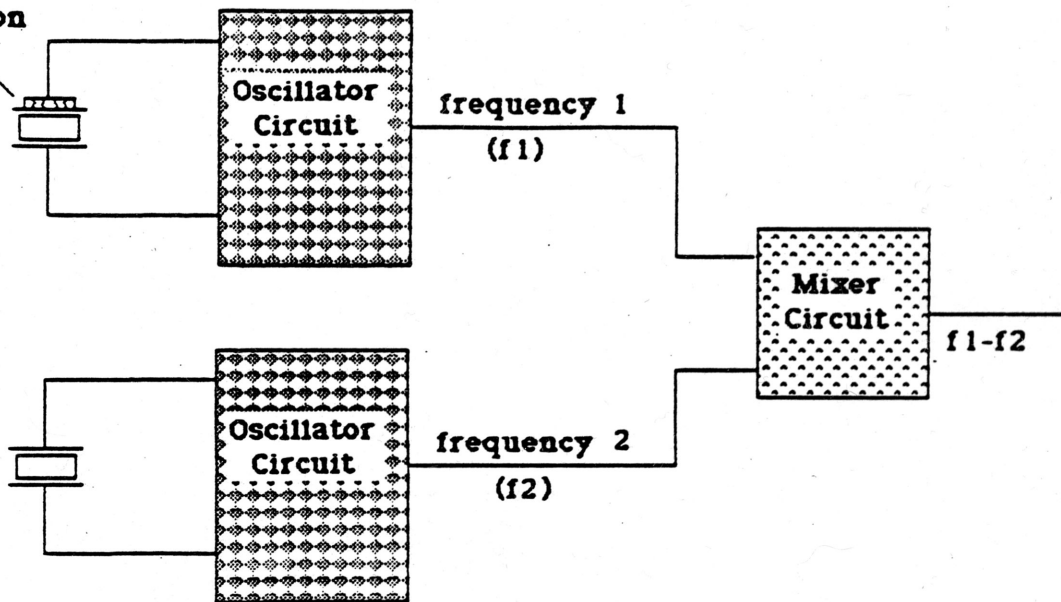
Oscillator Circuit

frequency 2 (f2)

Mixer Circuit

f1-f2
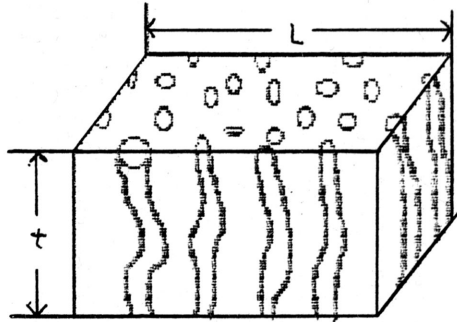
Figure 6

Appendix A

What is the total surface area of a film of thickness, t, density, ρ_p, and pore diameter, d? The density of normal silicon is ρ.

volume of 1 cylinder:
$$\frac{\pi d^2 t}{4}$$

number of cylinders :
unit surface area
$$\frac{N}{L^2}$$

"missing" mass of one cylinder:
$$\frac{\rho \pi d^2 t}{4}$$

"missing" mass of N cylinders:
$$\frac{N\rho\pi d^2 t}{4}$$

"missing" mass:
$$\rho L^2 t - \rho_p L^2 t = \frac{N\rho\pi d^2 t}{4}$$

$$N = \frac{4(1 - \rho_p/\rho)L^2}{\pi d^2}$$

surface area of single pore: $\quad \pi dt$

surface area of all pores: $\quad N\pi dt = \dfrac{4(1 - \rho_p/\rho)L^2 \pi dt}{\pi d^2}$

$\dfrac{\text{total surface area}}{\text{apparent surface area}} \qquad \dfrac{4(1 - \rho_p/\rho)t}{d}$

$\dfrac{\text{total surface area}}{\text{density}} \qquad \dfrac{4(1/\rho_p - 1/\rho)L^2 t}{d}$
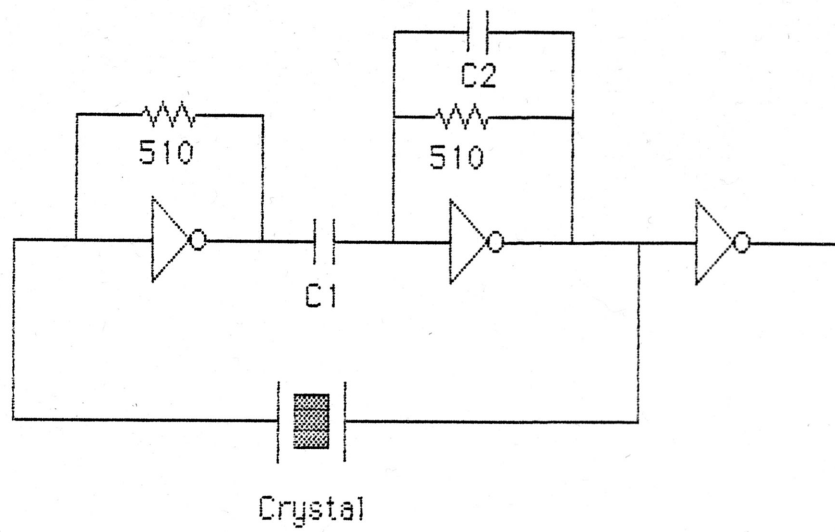
Example: $\rho_p = 0.5$, $\rho = 2.33$ gm/cm^3, $\rho_p = 1.165$ gm/cm^3, $t = 100$ µm, $d = 50$ A, $L = 4$mm

$$\dfrac{\text{total surface area}}{\text{apparent surface area}} = 40{,}000$$

$$\dfrac{\text{total surface area}}{\text{density}} = 5{,}493.6 \text{ cm}^5/\text{gm}$$

Appendix B

Crystal Oscillator Circuit

$$X_{C1} \rightarrow 0$$

$$X_{C2} = 510 \text{ ohms} = 1/\omega C2 = 1/2\pi f C2 \Rightarrow C2 = 86pF @ 3.58 \text{ MHz}$$

Appendix C

Calculations for determining the amount of mass loading the quartz
crystal with attached porous silicon can take.

For: density of quartz = 2.65 g/cm^2
thickness of porous silicon = t_{ps}
density of normal silicon = 2.33 g/cm^2
resonant frequency: f_0 = 3.58 MHZ

$$\text{quartz thickness: } d_q = \frac{N}{f_0} = \frac{1.67\times10^6 \text{ Hz mm}}{3.58\times10^6 \text{ Hz}} = 466.5 \text{ } \mu m$$

mass load: $\Delta m/A = 5\times10^{-3} \rho_q d_q = 0.618113$ mg/cm^2

Consider a slab of porous silicon 4mm x 4mm:

Area of porous silicon: A_{ps} = 16 mm^2

mass load: Δm = 0.098898 mg

$$\frac{\text{density of porous silicon}}{\text{density of normal silicon}} = \frac{\rho_p}{\rho} \approx = 0.5$$

volume of porous silicon: $V_{ps} = A_{ps} t_{ps} = 16 \text{ mm}^2 t_{ps}$

mass of porous silicon: $m_{ps} = (\rho_p/\rho)\rho V_{ps}$

$\Delta m = m_{ps}$
$V_{ps} = 8.4891\times10^{-5}$ cm^3
$t_{ps} = 5.3057$ μm