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A Research on Integrated-Circuit
Sensors for Gas Chromatography

Contract Number NAS 2-6491
Final Report

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ABSTRACT

Fabrication of a miniature gas chromatograph column using integrated circuit technology has been studied and found to be feasible. A bonding problem of forming a strong, gas tight seal between two wafers of silicon has prevented the completion of the column design. Continuing research using tin or a chromium-gold bond promises to overcome the problems of using the proposed gold-eutectic bond. Specifications for the miniature gas chromatograph column are: a spiral capillary column of semi-circular cross section, 30μm radius, and a total length of 6.9 meters etched into a silicon structure 50 mm in diameter and 0.625 mm thick.

MINIATURE GAS CHROMATOGRAPH COLUMN

Introduction

This is a final report on the work done under the NASA contract NAS2-6491 at the Stanford Integrated Circuits Laboratory. Under this contract, the feasibility of fabricating a miniature gas chromatograph column out of silicon by state of the art integrated circuit processing techniques was to be studied.

Research to date has developed a promising fabrication process, and has exposed the more severe problems associated with the fabrication of a miniature gas chromatograph column. The approach taken was to etch a long channel in a wafer of silicon and form a closed capillary column by bonding a flat cover plate over the channel. Basic integrated circuit fabrication techniques of mask making, photolithography, and silicon etching were used to chemically mill the proposed channel. As of the expiration date of this contract, the processing step of bonding an etched silicon wafer to another cover wafer was not fully developed. A variation of the proposed silicon-gold-silicon bond has been used to successfully bond a column, but inherent problems of channel blockage require a different bonding approach to be used.

This project is continuing under NASA grant NGR05-020-543. As was intended with this contract, completed columns will be furnished to NASA for testing as soon as the bonding problem is solved. Under the larger NASA grant, this miniature gas chromatograph column is to be an integral part of a complete gas chromatography system including a compatible detector and gas valving mechanisms. At present, development of both the miniature column and the detector looks promising.

Design

To achieve both good utilization of wafer area and laminar flow characteristics in the column, a spiral configuration was chosen for

the channel. A spiral groove was to be etched into a flat silicon wafer approximately 50 mm in diameter. The total length of the channel is determined by the desired groove width, the width of the isolation mesa between grooves, and the outside diameter of the silicon wafer to be used. Figures 1 and 2 are plots of the relationship of total channel length to the diameter of the wafer used, with groove separation as a parameter. From these curves, spirals of two sizes were designed with the following dimensions:

	Long Spiral	Short Spiral
Groove Width	80-100 um	200 um
Mesa width	45-25 um	40-50 um
Inner radius	5 mm	3 mm
Number of turns	96	40
Length	6.7 m	2.1 m

For both designs, an approximate spiral geometry was achieved by using two sets of concentric semicircles offset from each other by one half the center-to-center groove spacing.

Two rubylith masks of the long spiral were cut, one by the semicircle approximation method here at Stanford, and the second by a computer controlled cutter at Lockheed. The rubylith cut at Stanford was used in making a 20 to 1 reduction, high resolution photographic mask for the long spiral, and a 14 to 1 reduction was made of the rubylith cut for the short spiral mask. When calculating the required dimensions of the rubylith mask, the effects of the silicon etch were taken into account. Isotropic etchants horizontally undercut oxide masks by an amount approximately equal to the vertical depth of the etch. Hence the channel width on the high resolution mask must be the desired etched channel width minus twice the etch depth. Figure 3 shows photographs of the masks used in the photolithography step.

Prior to the column design, an etch study was performed to determine what could be expected of the silicon etchants. Figure 4 summarizes the results of the study. An anisotropic etchant (KOH) gave the expected triangular groove profile and the isotropic etchant

($HF-HNO_3$) yielded groove profiles that varied from the expected "bath tub" profile to one that was semi-circular. This variation is attributed to the effect of a narrow mask opening restricting the circulation of fresh etchant to the exposed silicon surface, i.e., it was a function of geometry, the ratio of HF to HNO_3, and agitation.

Based on the above study, the isotropic etchant was selected for its independence on crystal orientation and the ability to achieve semi-circular groove profiles. For both spiral designs, a 10% HF - 90% HNO_3 etchant was used. Etch times on the order of 8 minutes resulted in a semi-circular groove for the long spiral with a depth of 30 microns (figures 5 and 6). Note, for the same etch conditions, the short spiral with a mask opening five times greater than that of the long spiral had a profile that is more "bath tub" like because of the better circulation of etchant.

To minimize alignment problems, the exit and entry ports were drilled in the etched spiral wafer instead of the top cover wafer as was originally proposed. A Gulton Industries ultrasonic cutter, model U-602, was used with a 30 mil diameter tool to cut through the 12 $\pm$ 2 mil thick wafer. Care has to be taken to avoid introducing hairline fractures in the wafer during ultrasonic cutting. Such fractures tend to split the wafer during the high temperature bonding step which follows.

The most formidable problem$ encountered was that of bonding the cover wafer to the etched spiral wafer. The proposed method was to utilize the silicon-gold eutectic bond at 377°C A 1000 Å gold layer was evaporated on both wafers, followed by 2 mi ons of gold electroplated on the cover wafer. The two wafers were held in contact and heated to 400°C. This bonding method failed because sufficient force could not be applied to the wafers to provide the necessary intimate contact between the gold surfaces at all points. As an alternative method, the same silicon-gold system was used, but the bonding temperature was elevated to 1100°C, slightly above the melting point of gold. In this case the gold melted and wet both surfaces. A very strong bond resulted, but channel blockage occurred. A silicon-gold eutectic composition was found to be blocking the channel. It was determined that since the bonding temperature was approximately

700 C° above the eutectic temperature, a sufficient quantity of silicon was being recruited into the gold melt (approximately 60% silicon and 40% gold) and that the volume of the melt was sufficient to block the channel. A variation of this bonding method allowing only a short exposure to high temperature has produced the only working column thus far. This was with the short spiral with an extra large channel. Other bonding techniques currently under investigation are those of using tin as the bonding metal (requiring a bonding temperature of only 232°C), and of using a barrier metal such as chromium between the gold and silicon to prevent the recruiting of silicon into the gold melt.

Currently, stainless steel tubes are being epoxied onto the wafers as exit ports. Figure 7 shows a completed column with tubes. In the future, after the bonding technique has been perfected, the tubes will be brazed on during the bonding process.

Conclusion

The major problem encountered in the fabrication of the spiral columns in silicon has been in achieving a strong, airtight bond of the cover wafer to the etched spiral wafer without blocking the 80 micron diameter, semi-circular channel. We are optimistic that a satisfactory bond will be achieved using the low temperature tin process or with the gold-silicon barrier plane process to prevent the gold-silicon eutectic mix. Though, only the short spiral with a wide channel has been successfully fabricated, perfection of the bonding technique should facilitate fabrication of the longer, smaller bore columns.

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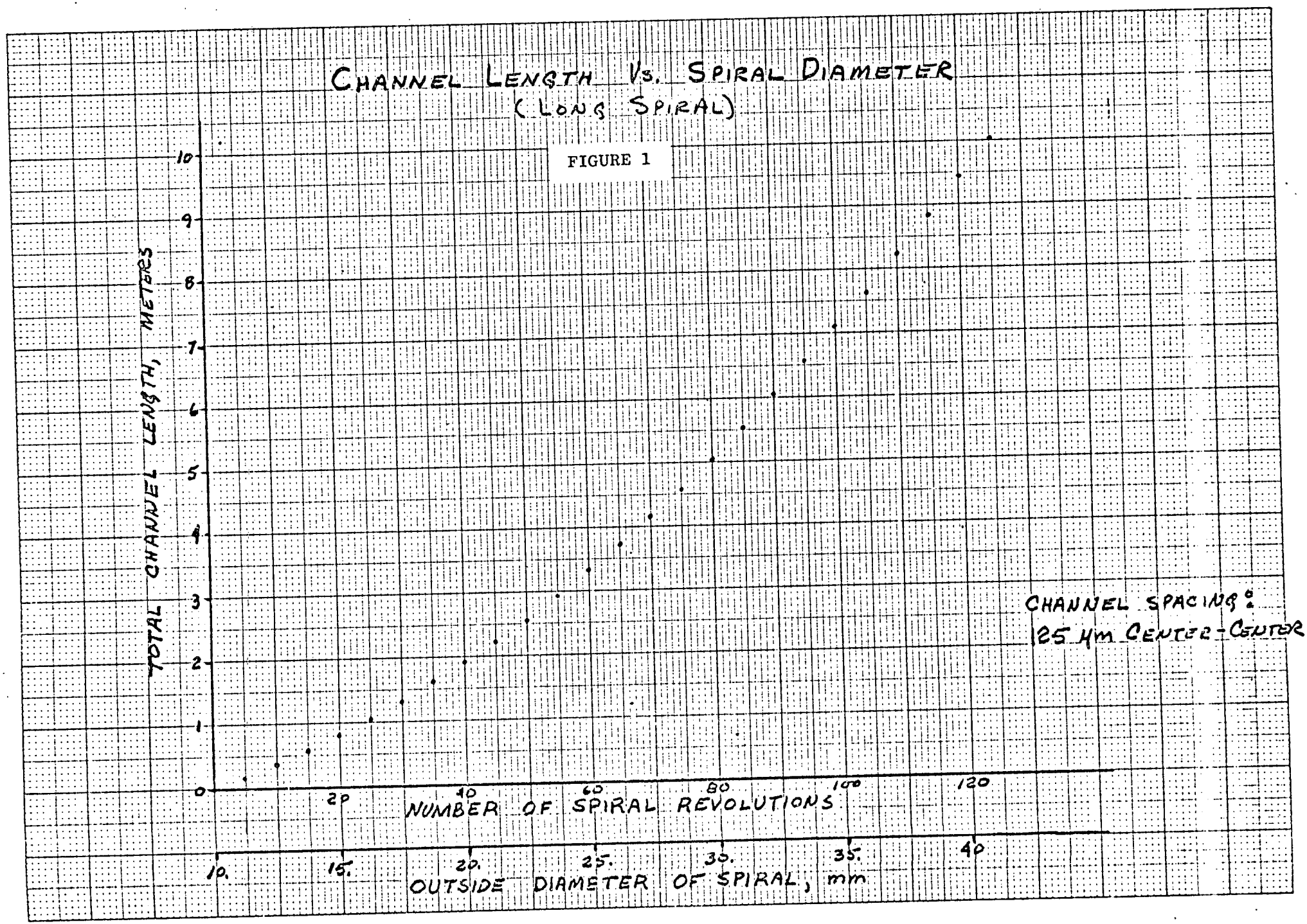

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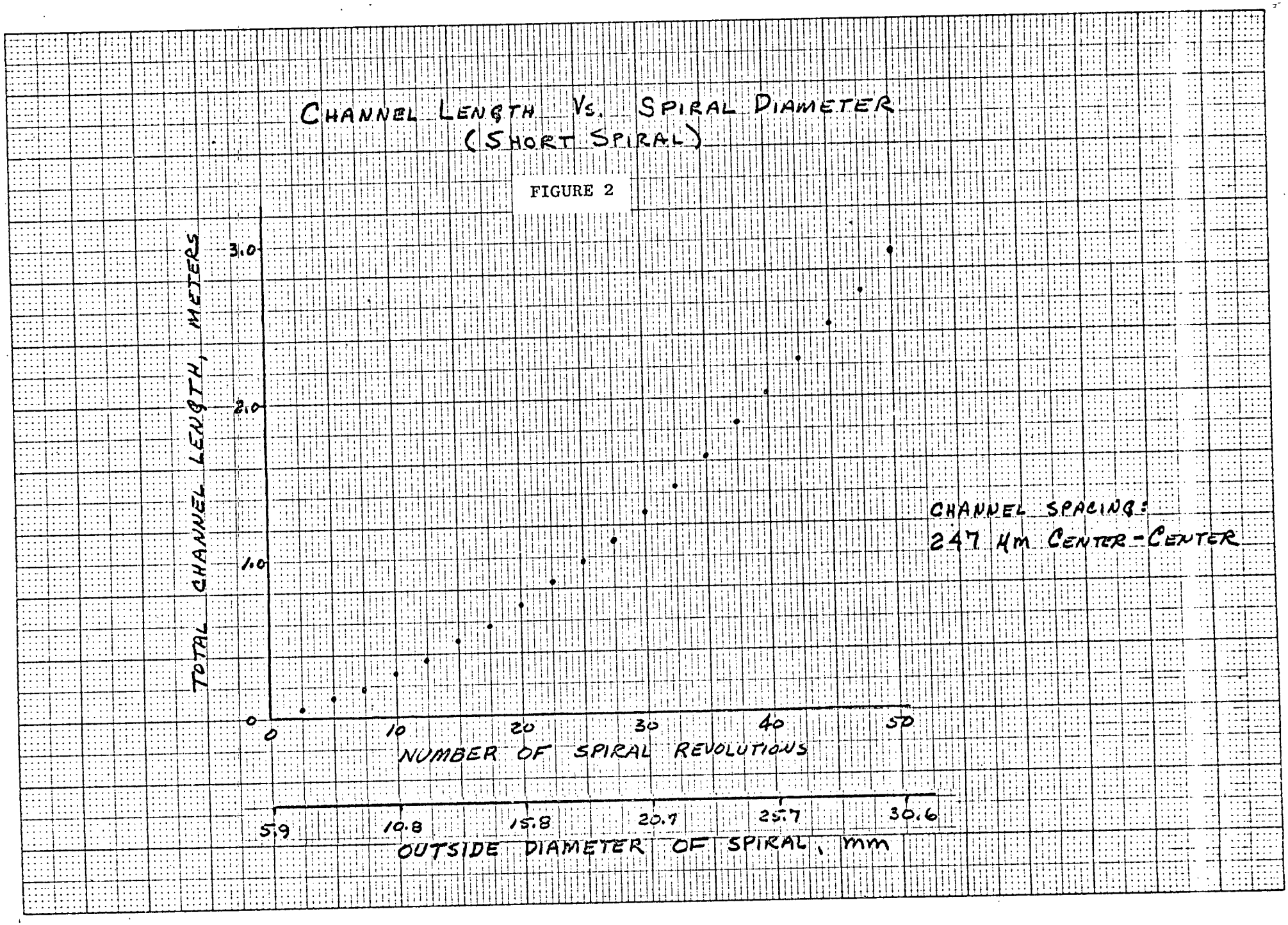

FIGURE 2

FIGURE 3

High resolution masks used in the photolithography process, both long & short spirals.

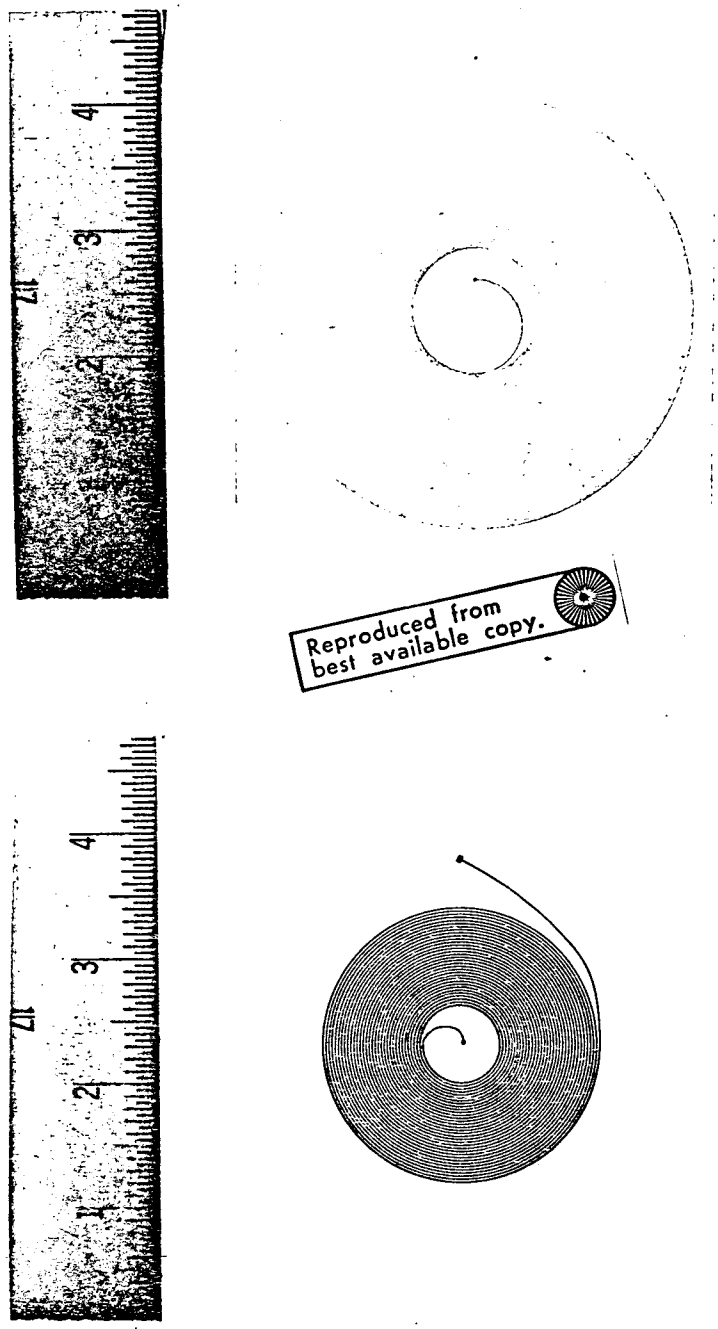

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FIGURE 4

Groove profile study of anisotropic and (2) isotropic etchants.

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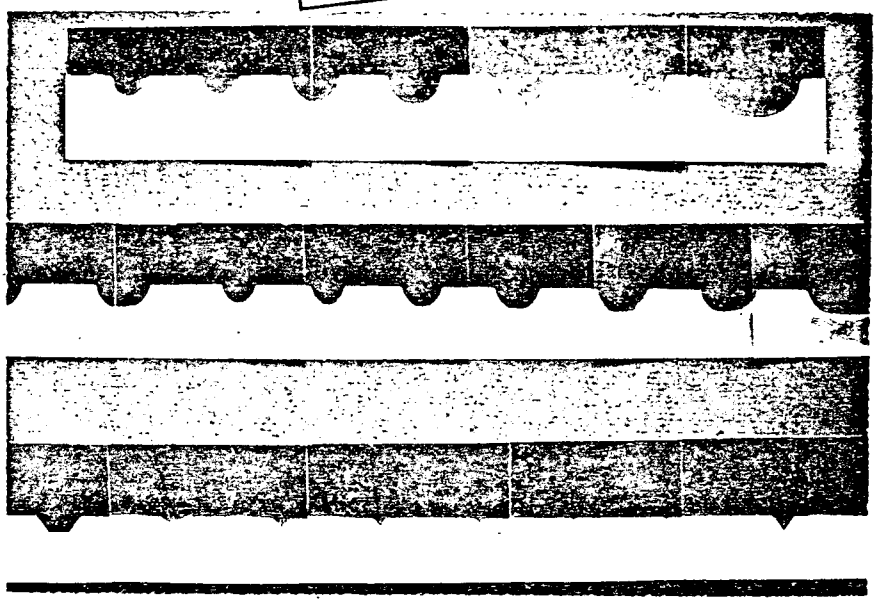

FIGURE 5

Etched spiral columns in 12 mil thich, 50 mm diameter silicon wafers. (Long and short spirals with oxide masks).

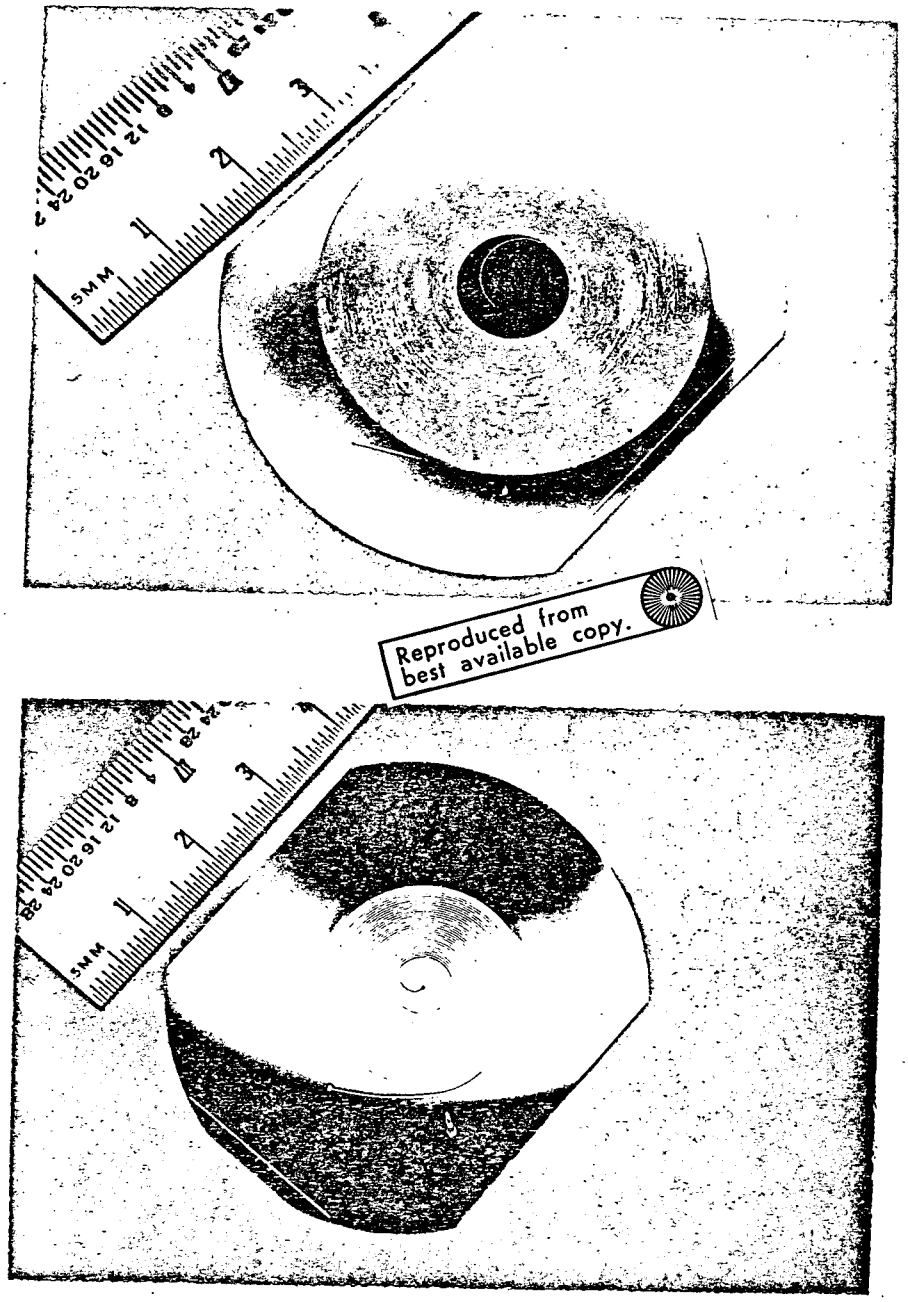

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FIGURE 6

Cross section of etched spirals with bonded cover plate. (Long spiral-semi circular & short spiral-"bath tub")

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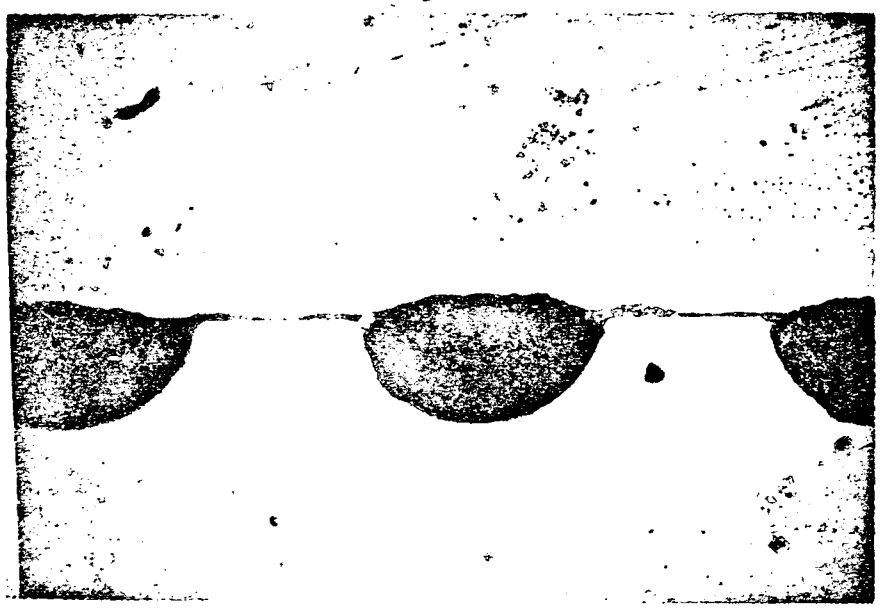


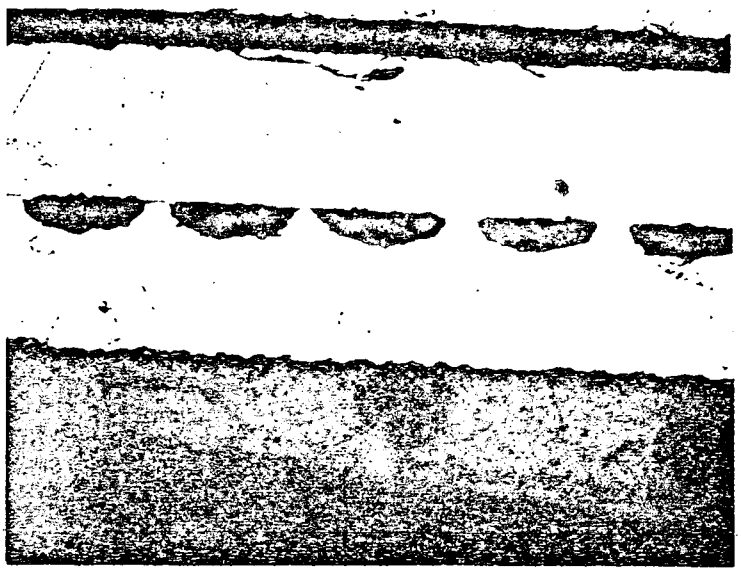
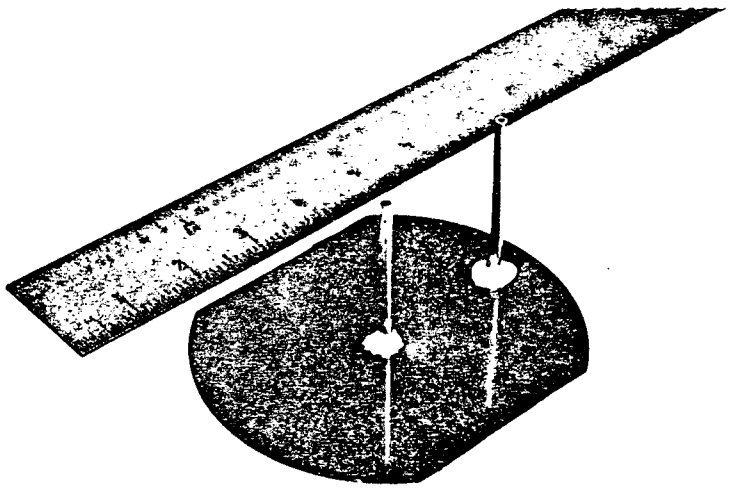


FIGURE 7

Complete gas chromatograph column assembly, including etched spiral wafer bonded to cover wafer with epoxied entrance and exit stainless steel tubes.