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Surface Acoustic Waves/Silicon Monolithic Sensor/Processor

Report #4

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by

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**ORIGINAL CONTAINS  
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(NASA-CR-164476) SURFACE ACOUSTIC  
WAVES/SILICON MONOLITHIC SENSOR PROCESSOR  
(Syracuse Univ., N. Y.) 27 P HC A03/EF A01  
CSCL 11F

## I. Introduction

During the last six month period our efforts have been aimed at sputtering zinc oxide films using our Veeco Micro Etch System. We have also made a substantial effort to evaluate the possibility of a spray-on technique based on zinc chloride dissolved in an alcohol solution. The results on both of these techniques will be reviewed in this report. We have also continued to refine our techniques of making platinum silicide Schottky barrier junctions essential for constructing the ultimate convolver structure.

Our experiments to date on sputtering zinc oxide have not been conclusive. Our initial films were found to be rich in chromium and iron, the result of a substantial amount of sputtering of the stainless steel fixtures inside the vacuum system. After adjusting the geometry to the extent possible, additional sputtering experiments were performed. These zinc oxide films continued to be opaque. Analysis revealed that they were zinc rich. Obviously, the off-sputter from the zinc oxide target is not occurring stoichiometrically. Our current efforts are to attempt reactive sputtering through the introduction of a small partial pressure of oxygen inside the vacuum system. The hardware for these experiments has now been assembled and such experiments are now being conducted. This work is described in Section V.

Concerning the spray-on technique, a number of experiments have been performed. Apparently, zinc oxide does form on the heated substrate, but as the film grows it

deteriorates. Apparently, the growth of the film serves as an insulator preventing high enough temperatures from being maintained at the growth interface. Strong illumination from the top side of the experimental apparatus has now been put in place in order to maintain the temperature. The status of this work is reviewed in Section IV.

The use of argon ion beam sputtering or organo-metallic spray-on to form high resistivity, piezoelectric zinc oxide are new technologies and, undoubtedly, it will take some time to obtain definitive results. Sections of this report deal with the details of the experiments and their results up to this point. Progress on both technologies has been strong during this six month period. We expect to obtain conclusive evidence on the applicability of these techniques to our goal of fabricating a two-dimensional convolver structure during the next sixth month period.

Sections II and III of the report describe results on PtSi Schottky barrier diode arrays which we have fabricated. While some improvements are necessary, we have routinely produced useful diodes capable of serving as the nonlinear multipliers for the ultimate signal and optical image processors envisioned at the start of the effort.

## II. Fabrication of Silicides and PtSi Diodes

Metal semiconductor junctions having rectifying electrical properties have found many applications in present day semiconductor device technology. Among the three practical choices available for rectifying contacts (namely, Schottky or surface barriers, ion implanted and diffused junctions), diffused junctions offer relatively low cost. Silicide diodes have a number of unique features, such as, intimate metal-semiconductor contact and contamination-free interfacial contacts, high barrier height, low saturation current and chemical compatibility to IC fabrication processing. Some of the transition metal silicides meet all of the electrode material requirements. Single crystal (n-type) silicon wafers of 5 - 10  $\Omega\text{cm}$  resistivity were chosen as substrates and platinum selected for the formation of the silicides for our experiment. The unfinished side (back) was doped  $n^+$ .

The steps taken in the fabrication of platinum silicide diodes are as follows:

- (1) Silicon wafers are washed and cleaned in an ultrasonic cleaner with TCE, acetone, methanol, and DI water for the surface preparation for dielectric film deposition on the active side.
- (2) Oxide growth is carried out in a quartz diffusion tube at a controlled temperature range between  $900^{\circ}$  -  $1200^{\circ}\text{C}$  and in continuous flow of dry  $\text{O}_2$  for about 1 - 3 hours.

(3) From the silicon dioxide color-thickness relationship we estimate the oxide thickness to approximately  $1500 \text{ \AA}$  based on the blue color.<sup>(1)</sup>

(4) Windows of the required size and dimension were etched in the dielectric film using a suitable photoresist mask, U.V. light, and developer. A buffered HF solution capable of etching at a rate of  $15 \text{ \AA}/\text{sec.}$  is used to etch the  $\text{SiO}_2$  layer.

(5) The metallization process is carried out by using one of the Veeco vacuum deposition systems. Platinum is evaporated in a vacuum chamber pressure of  $10^{-6}$  torr. The Pt on top of the photoresist surface is stripped in acetone.

(6) Silicides are formed in contact windows by sintering at an elevated temperatures of  $450 - 600^\circ\text{C}$  in an argon atmosphere for a few minutes but not longer than 15 minutes. Unreacted platinum can be stripped with hot dilute aqua regia.

(7) Two classes of silicides form at different temperatures. At about  $200^\circ - 400^\circ\text{C}$ , metal-rich ( $\text{Pt}_2\text{Si}$ ) forms and between  $300^\circ - 600^\circ\text{C}$ , monosilicides ( $\text{PtSi}$ ) form. The resistivity of the platinum silicides is about  $28 - 35 \mu\Omega\text{-cm}$  and its melting point is  $1230^\circ\text{C}$ . (for  $\text{PtSi}$ )

(8) To get a good ohmic contact on the n+ side of the Si wafer, the specimen is annealed at  $400 - 500^\circ\text{C}$  for a few minutes after Al metallization of the back surface.

As the performance stability of a device depends on the stability of the silicide phase, the formation of platinum silicide has received special attention.

(9) Metal masks are aligned with the line of diodes and transparent Cr and then Au are evaporated through the mask at a vacuum chamber pressure of  $10^{-6}$  torr. The Cr is used for adhesion of the contact to the diode.

### III. Evaluation of the Diode Arrays

Figure 1 shows the complete PtSi diodes with a circular contact which admits testing of approximately ten diodes in parallel. In a finished device, all diodes would be connected by overlay contact lines.

Figure 2 shows a close-up of a single diode. The picture reveals the very accurate photolithography and the uniformity of the diffusion.

Figure 3 presents the current versus voltage characteristics for an isolated diode photographed on a curve tracer. The diodes exhibit considerable photosensitivity. Under some fabrication conditions, the diodes seem to operate in a photovoltaic mode with an induced voltage of several hundred millivolts. Under other conditions, there appears to be a photoconductive behavior with a change of slope in the conducting regions. Additional work is needed to correlate the behavior with fabrication details.



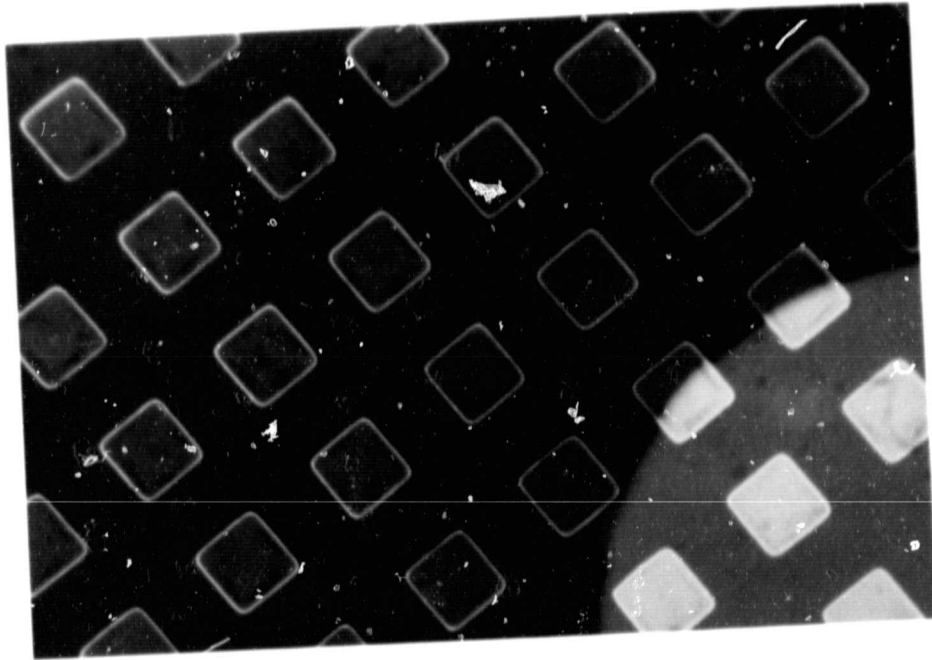


Figure 1 Platinum silicide diodes with Au as metal contact (lower right corner). The blue region is SiO<sub>2</sub>. The diodes are 60  $\mu\text{m}$  on a side.

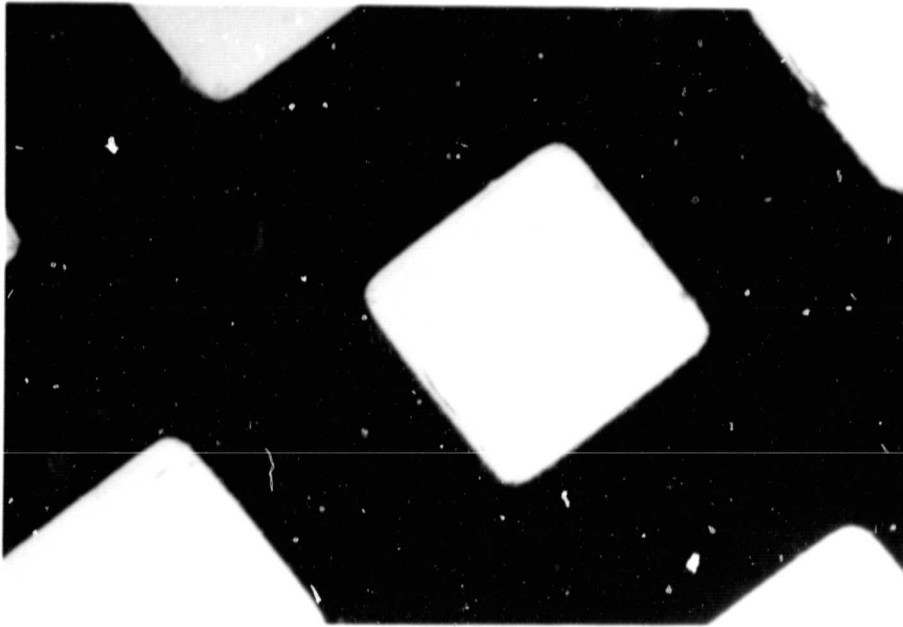


Figure 2 Platinum silicide diodes of 60  $\mu\text{m}$  dimension  
isolated by  $\text{SiO}_2$  layer.

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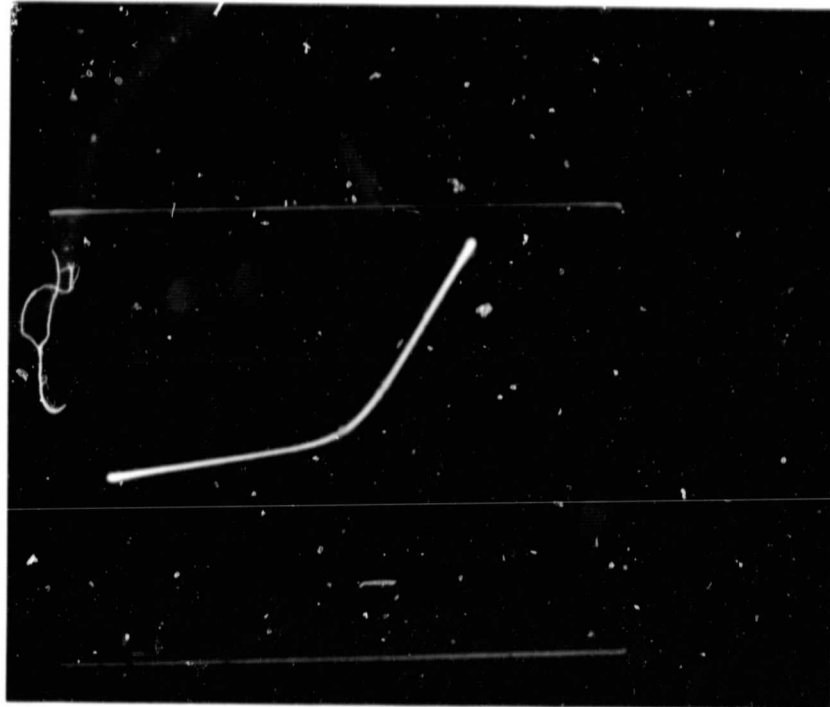


Figure 3 I-V characteristics of a single platinum silicide diode. The vertical scale is 5  $\mu$ A per division, the horizontal scale is 300 mV per division. The break point is at the origin.

#### IV. Deposition of Zinc Oxide Films by Spraying

The electrochemical properties of ZnO lend themselves to a variety of thin film deposition techniques: sputtering, vapor transport, and spray pyrolysis. In previous reports we have made reference to the technique most widely used at present, RF magnetron sputtering. The comparatively low cost for growing zinc oxide films by spray pyrolysis makes the method an attractive alternative for study.

The spray pyrolysis technique consist of spraying a solution onto a heated substrate. Our current experimental effort is to grow zinc oxide films by spraying the solution onto heated microscope slides. A solution of  $\text{ZnCl}_2$  in ethyl acetate was used with  $\text{N}_2$  as the carrier gas. In order to produce a useful film deposition rate, we must attain effective control over the substrate temperature, the chemistry of reaction on the surface, and the nitrogen flow rate.

The spraying is done while the substrate is maintained at a temperature between  $400^\circ\text{C}$  and  $500^\circ\text{C}$ . After 10 to 20 seconds of spraying a very thin transparent film, presumably of zinc oxide, forms on the substrate. Unfortunately, continuous spraying of the solution onto the substrate results in the reduction of the surface temperature due to the lower temperature of the spray and due to the liberation of heat by evaporation. The lowering of the temperature prevents further deposition of zinc oxide. The temperature of the substrate also affects the thermal and dynamic stabilization of the film, as well as the evaporation rate and the

bouncing and splitting of vapor droplets. The behavior of the droplets as they impinge on the substrate depends on the substrate temperature, nitrogen flow rate, and solution flow rate. Growing films at lower substrate temperatures and air flow rates, but in the presence of high solution flow rates, results in wetting of the surface and a slowdown of the reaction. The film is predominately zinc chloride. When spraying at increased substrate temperatures, wetting was decreased but splitting and bouncing of the droplets and the lateral mobility of the liquid increased.

In order to increase the substrate temperature we have added high-output incandescent lamps to the experimental apparatus. Recent thermocouple measurements indicate that we are now maintaining a temperature close to 500°C.

Figure 4 shows the spraying apparatus. Visible in the picture are a glass slide, a thermocouple base, the lamps, and a spray nozzle. Figure 5 shows the spraying operation underway. Careful inspection of the photograph shows the spray impinging on the substrate from the overhead nozzle.

We intend to pursue these experiments by the introduction of hydrogen peroxide,  $H_2O_2$ , in order to reduce the chloride content in the film and by using a gas mixture, 90% nitrogen and 10% oxygen, as the carrier gas in

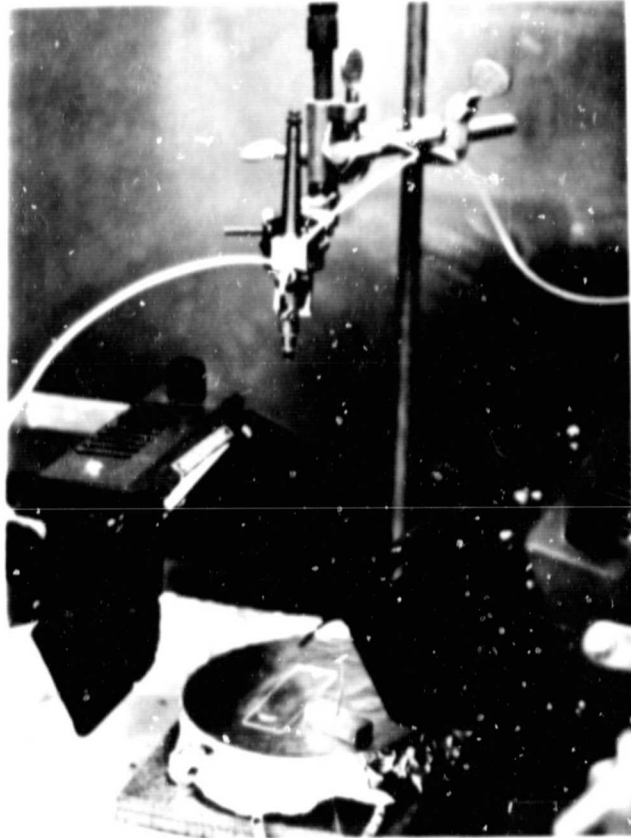


Figure 4 The spraying set up. The glass substrate rests on the hot plate and the thermocouple is attached to a metal block to monitor the temperature of the surface. The nozzle and lamps are shown.

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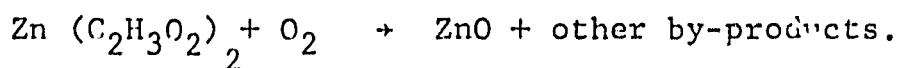
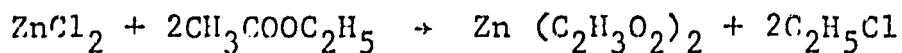


Figure 5 Operating under spray. While spraying, the lamps help in maintaining the temperature of the substrate surface. The solution impinging on the substrate reduces the temperature.

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place of pure nitrogen. Of course, the lamps would be used to maintain a high substrate temperature. By maintaining a higher concentration of oxygen and a higher temperature, we hope to begin to produce useful films. The reaction with which we are working

ethyl acetate    zinc acetate



is helpful in relating the impact of the constituents.



## V. Sputtering

Since the fabrication of the sputtering fixtures for the Veeco Micro Etch System was completed, experiments were carried out for the calibration of the system. The vacuum system was pumped down to check the chamber pressure, which was too high at first because of some leaks in the inner installation assembly. After some effort, the leaks were corrected and the system was functioning well enough to bring the vacuum pressure to as low as  $10^{-7}$  torr in a few minutes. The substrate holder could be heated to a temperature of  $200^{\circ}\text{C}$ .

Silicon dioxide was sputtered on glass to test the system, since we did not wish to risk the destruction of the ZnO target. When the operation seemed to be running smoothly, we replaced the target material with a 99.9% pure sintered ZnO disc of 5 inch diameter.

By adjusting the cathode, arc, magnet, coil, suppressor power supply and accelerating voltage controls to the desired stabilized position, we could see the glow discharge forming on the shutter. A tungsten filament is attached above the shutter to emit electrons to neutralize the argon ion beam which is focused on the target. The temperature of the substrate ( $100^{\circ}$  -  $200^{\circ}\text{C}$ ), sputtering time, gas inlet pressure, and the energy of the impinging particles were varied and their impact on the quality of deposited film was studied by scanning electron microscope and x-ray energy spectroscopy (XES). The x-ray analysis showed

that some impurities (Fe, Cu, Ni, Cr) were included in the deposited film. These inclusion were due to the sputtering of the stainless steel target holder and the copper pipes for the water coolant by the collimated ion beam. The resistivity measurements showed  $10^2 \Omega \text{ cm}$ , quite low for our requirements, due to the metal inclusions. The XES photographs shown here, Figures 6 and 7, display the energy peaks for those impurity metals.

Due to these unfavorable results, some modifications of the inner assembly design had to be made. The target holder assembly has been rearranged to minimize the sputtering of the stainless steel body and was installed and checked to make sure that the target is directly underneath the aperture of the ion gun source. The ZnO target being used is of 5 inch diameter and the extracted ion beam is supposed to be a collimated beam of 3 inch diameter. Even so, the stainless steel holder was sputtered off which means that the ion beam diverges with distance. To solve this problem we are undertaking to cover all parts that can possibly be bombarded by the diverging ion beam with ultra pure Zn foils.

The copper tubes and the mechanism for supplying the water coolant for the tested target holder were redesigned to have maximum clearance from the ion beam. Some changes also had to be made in the substrate holder tower. The distance between the target and the substrate was reduced from 8" to 3" and new gears have been installed to provide a smooth, constant speed, rotation of the substrate holder

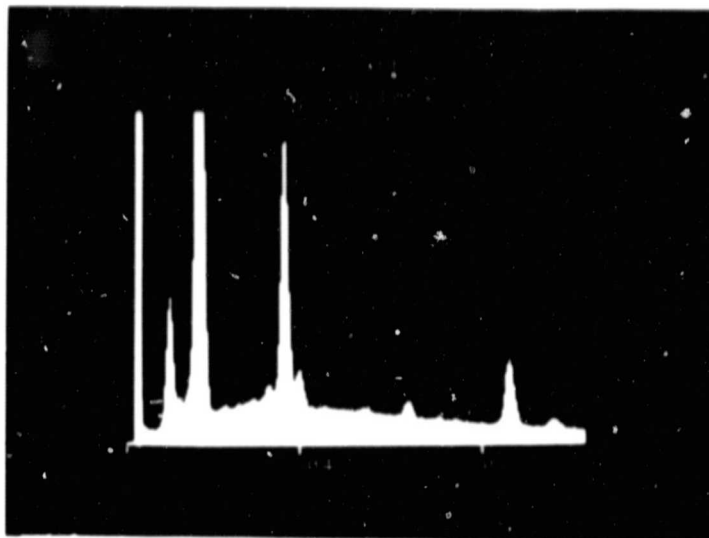


Figure 6a XES photograph of a sputtered ZnO thin film on a glass substrate. The spectrum consists of Zn peaks, the impurity elements in the sputtered film and the constituent elements of the glass substrate. The peaks with markers above them are peaks of Zn and the large peaks are the glass constituents and the few small peaks are the impurities in the film.

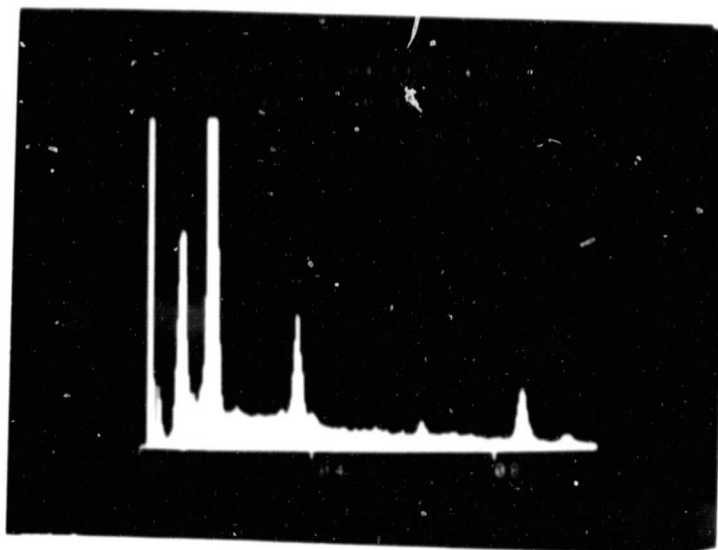


Figure 6b The sputtered film shows some decrease in the concentration of impurities after some changes were made in the target holder assembly.

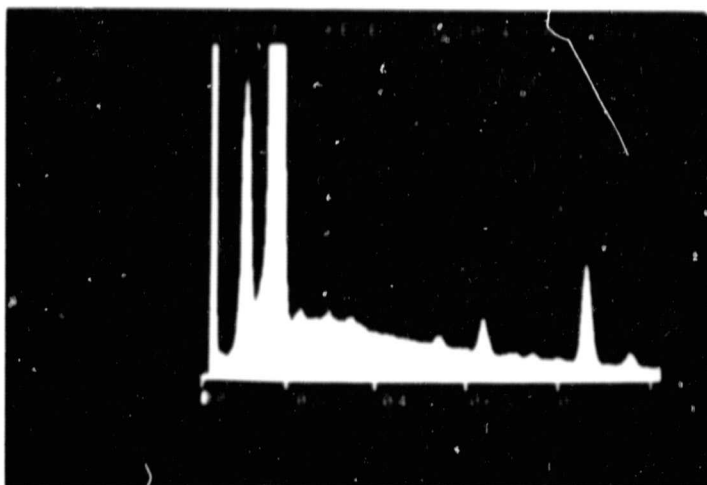


Figure 7a XES photograph showing the spectrum of the sputtered ZnO thin film on a silicon substrate. The three major peaks noted by the markers are Zn peaks and the small peaks are due to the constituent elements of the stainless steel target holder.

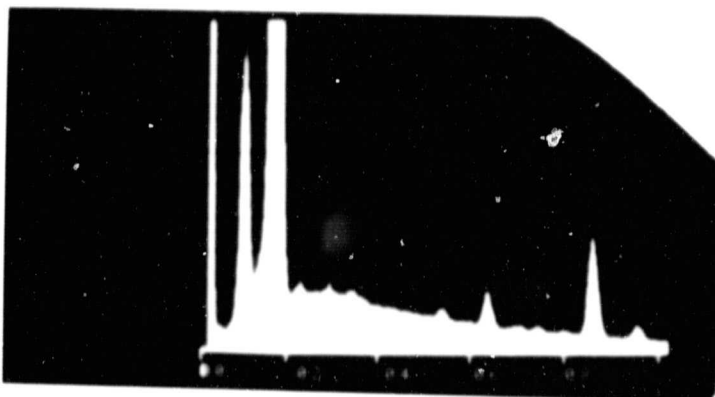


Figure 7b The improvement due to realignment of the system. After the alignment of the target holder and the re-arranging of the inner assembly there were some improvements in the spectrum. The peaks of Zn show some increase and the peaks of the impurity materials have become smaller.

by using a motor. This should improve the uniformity of the ZnO film. After these new changes the temperature was calibrated for the substrate holder surface and the back plate of the heating coil. Figures 8 - 11 show the modifications to the internal structures.

Silicon wafers and microscope glasses were ultrasonically cleaned in TCE, acetone, methanol, and D.I. water before placing them on the substrate holder. By tilting the target holder at different angles and by varying the sputtering gas pressure, the energy of the bombarding particles and the substrate temperature, we have deposited ZnO films with various qualities. SEM and XES analysis showed the difference in the deposited film and the considerable decrease of the impurities in the ZnO film. The photographs show that the peaks of the impurity elements have decreased.

Four point probe measurements of the film showed approximately  $10^4 \Omega \text{ cm}$  resistivity which is a confirmation of the reduction of the metal impurity content in the film. The murky color of the film reflects lack of oxygen in the film growth and so arrangements have been made to reactively sputter ZnO by using a gas mixture of 75% argon and 25% oxygen in place of pure argon. Due to these modifications we hope to achieve an improved film quality for our applications with  $10^6 \Omega \text{ cm}$  resistivity. Our effort now is to produce better quality ZnO films, to have an Auger analysis of the deposited material and then to characterize the surface acoustic wave properties of our film.



Figure 8 The target holder assembly has been realigned with the ion beam column. The ZnO target is seen at a  $45^{\circ}$  angle to the direction of the striking ion beam. The shutter covers the effective diameter of the target.

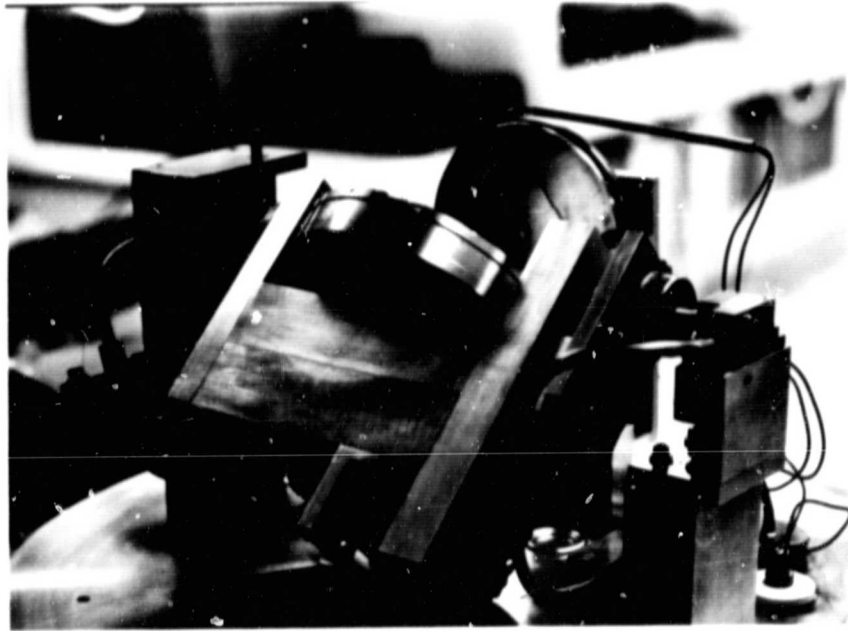


FIGURE 9  
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Figure 9 The target holder assembly rearranged to minimize the sputtering of the stainless steel body. The copper tubes and mechanism for the water coolant transport were redesigned to leave a clearance from the diverging ion beam.

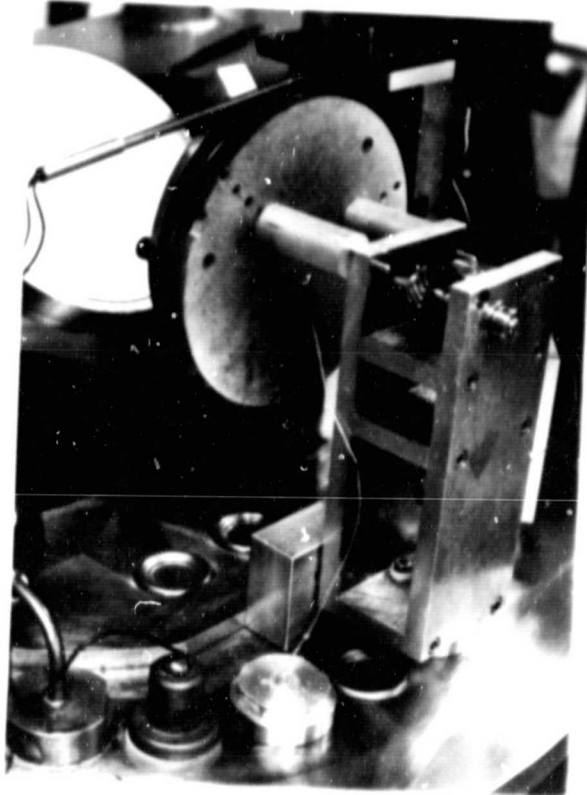


Figure 10 The substrate holder tower with thermocouples to calibrate the temperatures of the substrate holder surface and the back plate. The substrate holder itself is extended towards the target reducing the distance by approximately 5 inches. Once calibrated, monitoring of the back plate will permit inference of the substrate temperature.



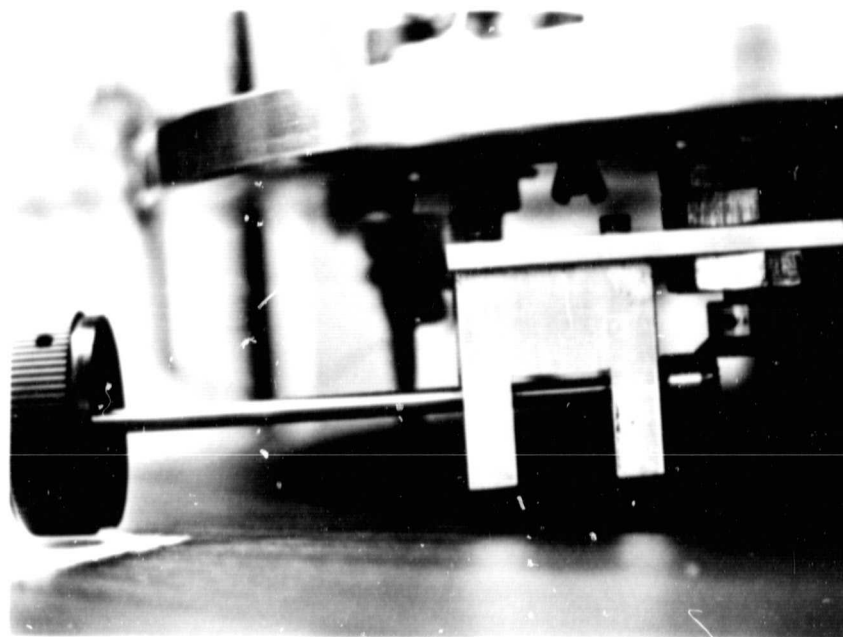


Figure 11 A new fixture with gears to provide a constant speed of rotation of the substrate holder. It can be rotated either manually or by motor.

## VI. Conclusion

We have made considerable progress in recent months towards the creation of a two-dimensional Fourier transformer for optical images based on the zinc oxide on silicon technology. Once we master the method of creating high resistivity, piezoelectric zinc oxide films on silicon all of the components of this project should be in place. The techniques which we are evaluating have yet to be investigated for ultrasonics applications. Thus the work has great significance in terms of the possibility of significantly enlarging the techniques available for making this important material, zinc oxide.

The sputtering system will have several components rebuilt to further reduce the amount of steel being sputtered. Other actions will include the covering of much of the internal hardware with zinc foil. Experiments will be done at different partial pressures of oxygen to determine the best mix of argon and oxygen for the reactive sputtering to yield piezoelectric zinc oxide films.

We will continue to study the spray-on technique. We will evaluate different organic carriers, concentrations, and temperatures.

Of course, the zinc oxide created by either of these techniques may not be sufficiently crystalline after deposition. If the crystallinity is not sufficiently high we will attempt to anneal the films in the diffusion furnace in the presence of powdered zinc oxide. This technique has been very successful in the past in creating polycrystalline cadmium sulfide films.

We continue to expect that we will be able to produce some significant results in the next few months. In that event, we will characterize the zinc oxide films created by both techniques. This in itself will be an important contribution to our understanding of the deposition and characterization of these materials.

Additional study of our Schottky barrier diodes will be performed in order to obtain the most useful photoreponse since we are now able to produce useful arrays. Of course, we hope to fabricate higher density arrays to obtain higher spatial resolution.

## VII. References

1. Sorab K. Gandhi; "The Theory and Practice of Microelectronics", John Wiley and Sons, Inc., 1968.