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INTERIM ENGINEERING REPORT NO. 2

for

NON-VACUUM DEPOSITION TECHNIQUES FOR USE

IN FABRICATING THIN FILM CIRCUITS

This report covers the period 1 October to 31 December 1964

456793

MOTOROLA INC.
Semiconductor Products Division
5005 East McDowell Road
Phoenix, Arizona

NAVY DEPARTMENT BUREAU OF SHIPS ELECTRONICS DIVISIONS

NObsr-91336   Project No. SR0080303; Task 9631

15 January 1965

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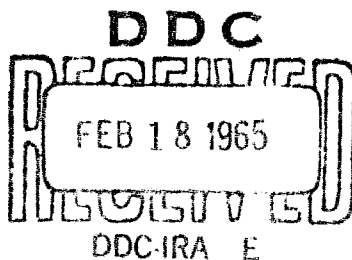This report covers the period 1 October to 31 December 1964

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ABSTRACT

The causes of instability of gas plated tin oxide resistors ha. been investigated. It has been found that the nature of the ambient tin oxide interface is the controlling factor which determines the electrical properties of thin (less than 1000 $\overset{o}{A}$) resistor films.

High temperature stress test has shown that protection of the tin oxide interface by an encapsulating dielectric film is successful in stabilizing the electrical properties of the thin film resistors.

A method for the delineation of tin oxide resistors and other hard-to-etch materials is described.

Investigation of deposited thin film resistors of In_2O_3, ZnO and NiO has been initiated. In_2O_3 and ZnO have been found to have some properties which indicates they may be sup..rior to tin oxide as resistor elements, and have been selected for further investigation.

Vapor deposited dielectric films of tantalum oxide and tantalum oxide-aluminum oxide have been prepared and their electrical properties investigated. Tantalum oxide-aluminum oxide films have dielectric constants in the range 20 to 25.

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Capacitors using this dielectric film have been prepared
with a Q in excess of 200 at 1 kc and a capacitance of
1 pf/mil^2.

A vapor plating machine suitable for pilot produc-
tion as well as experimental use is described.

Nickel and tungsten metal films have been prepared
by vapor plating techniques. Nickel has been shown to be suit-
able material for electrical interconnections and capacitor
plates.

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LIST OF ILLUSTRATIONS

1.0   PART I

1.1   PURPOSE

The purpose of this program is to develop vapor-phase techniques for the deposition of thin film passive circuit elements. Techniques developed will be evaluated for suitability for the fabrication of thin film components for microelectronic circuitry. Specifically, processes will be investigated for the deposition of gold, copper, aluminum, nickel, tin oxide, nickel-chromium, rhenium and tungsten for use as resistors and conductors and tantalum oxide, silicon dioxide and aluminum oxide for use as capacitor dielectrics and circuit passivation. The films deposited will be evaluated for use as microelectronic circuit elements.

The evaluation of the materials deposited will include compatibility of the material with the substrate, compatibility of the processing conditions and the determination that component parameters and tolerances are achievable as well as any parasitic effects. This evaluation will be accomplished by determination of the following film characteristics:

(1) Film resistivity

(2) Uniformity of film deposition

(3) Dielectric constants

(4) Structure of the deposited film

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(5) Chemical composition of the deposit

(6) Temperature coefficient of resistance and capacitance

(7) Dielectric strength

(8) The density of defects in the deposited film (No. of pinholes/sq. cm)

After initial evaluation of the various gas plated deposits a selection will be made of those systems providing the best characteristics for the fabrication of thin film circuit elements. Using the selected vapor deposition techniques, a pilot production line will be developed with a production capacity of at least 60 thin film circuits per day.

Based on the pilot production line operation, a determination will be made of product reproducibility and production costs. This will include a determination of the area required for the production of a given circuit function, the process limitations, the details of the processing and production controls necessary and the advantages of gas plating techniques over vacuum methods for the production of thin film circuit functions.

At the conclusion of this program three different functioning circuits will be produced for evaluation.

1.2   GENERAL FACTUAL DATA

1.2.1   Identification of Personnel

		Man Hours Performed this Period	Total to Date
Principle Engineer	James Black	56	88
Sr. Engr.	David Peterson	204	396
Engr.	Warren Brand	388.5	754.5
Engr.	David Dulaney	78	182
Tech.	Tom Elsby	419	723
Tech.	Bob Mattox	444.5	444.5
Tech.	Cecile Malkiewicz	332	448
Assembler	Darleen Ellis	285	367

1.2.2   Tabulation of Test Equipment Used for Film Evaluation

1.2.2.1   Test Equipment Used for Evaluation of Dielectrics

Capacitance Bridge - General Radio (G.R.)Type 716-C S/N 3012

Vacuum Tube Voltmeter - Hewlett Packard Model 400D

Oscilloscope - Hewlett Packard Model 122A

Audio Oscillator - Hewlett Packard Model 200C

Capacitance Bridge - General Radio Type 1615A S/N 165

Audio Oscillator - General Radio Type 1311A S/N 195

D-C Amplifier & Electrometer - General Radio Type 1230A S/N 905

Model 240 Regulated High Voltage Supply, Keithley Instruments

Model 414C Micro Microammeter, Keithley Instruments.

1.2.2.2   Test Equipment for Evaluation of Resistors and Conductors

4-Point Probe S/N 13

Audio Oscillator - Hewlett Packard Model 200AB

ESI Impedance Bridge Model 250 DA

Cenco Oven Cat. No. 95051

1.2.3   Measurement Procedures

To meet the goal of producing materials suitable for
practical circuit application, it is necessary to establish a
means of quickly obtaining basic electrical evaluations of the
deposited films, to provide information required for further
process development.

To perform this preliminary evaluation efficiently,
test procedures have been established which permit quick deter-
minations to be made of the more important electrical properties
for each type of circuit element to be produced under this
program.

1.2.3.1   Evaluation of Dielectric Films

The basic properties to be determined for the evalua-
tion of the dielectric films are dielectric constant, dielectric
resistance, dissipation factor and breakdown strength.

The evaluation procedure employed is to deposit the
dielectric under study onto a lapped and polished low resistivity
silicon wafer. By observation of the interference colors ex-
hibited by the deposited film, it is possible to estimate the

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film thickness with an accuracy of $\pm$200A and to obtain the uniformity of the deposit. Electrodes consisting of vacuum evaporated gold or aluminum spots, are vacuum deposited on top of the gas plated dielectric sample. Ohmic contact to the back of the silicon wafer is made with another gold evaporation. The wafer is then placed on a gold plated substrate holder to establish contact to the silicon wafer which serves as the common lower capacitor plate. The individual spots, evaporated on top of the dielectric, are contacted with a gold wire probe to complete the capacitor circuit. Capacitor measurements are then made on a General Radio Capacitance Bridge Model 716-C. This instrument provides an accuracy of $\pm$0.2 micromicrofarad for capacitance in the range of 100 cps to 300 kc and an accuracy of .0002 for dissipation factors below .001. Capacitor measurements are made at 100 cps, 1 kc and 10 kc, since measurement at only a single frequency does not permit estimation of the contribution of the various series and parallel losses which are present in any real capacitor. Since losses due to series resistance of the electrodes, contacts, etc. increase with frequency, while those caused by the leakage through the capacitor decrease with increased frequency, when combined with information obtained by dc measurements of film resistance, an improved means is provided for the evaluation of losses within the dielectric itself.

To obtain dielectric resistance and dielectric strength measurements, the samples prepared for the capacitance measurements are used. A dc voltage is applied to the capacitor structure by a Model 240 regulated high voltage supply manufactured by Keithley Instruments, and the current through the dielectric is read with a General Radio Model 1230A electrometer. Ultimate current sensitivity obtainable with this technique is 10^{-14} amps. After leakage measurements have been obtained, the electrometer is disconnected and the voltage increased until current exceeds 100 ma causing an opening of a fast acting circuit breaker within the power supply. This point is taken as dielectric breakdown.

1.2.3.2   Resistor Evaluations

The parameters of interest in the evaluation of resistor elements are ohms-per-quare, the temperature coefficient of resistance, stability and noise.

The resistor film to be evaluated is deposited on a 0.5-inch square substrate of Corning 7059 glass and the sheet resistance determined with a four-point probe. After the initial sheet resistance measurement is obtained, gold contacts are vacuum evaporated along opposite edges of the resistor film. Electrical contact is made to the metallized edge of the test structure and resistance of the film is then measured at room temperature with an EMI Impedance Bridge Model 200AB.

The test unit is then placed in a 125°C oven and allowed to come to thermal equilibrium before the resistance is again determined. From these measurements the temperature coefficient of resistance (TCR) is calculated. After the TCR measurements are completed, the thin film resistors are placed in a 500°C air oven for 2 hours, and the resistance is again measured. This high temperature stress testing allows an immediate comparison of the stability of the various resistor films under investigation. As the films are perfected, current noise measurements will be made.

1.2.3.3   Conductor Evaluation

Deposited conductors are evaluated with respect to sheet resistance, surface finish, and adhesion. The four-point probe used in the resistor measurements is used to obtain the sheet resistance of the conductor samples. Surface finish is evaluated visually for reflectance and microscopically for imperfections and defects. Adhesion is estimated by abrading the surface with cotton swabs and by noting the amount of metal pulled from the glass substrate by a piece of scotch type tape pressed against the deposited film and then stripped off.

1.3   Detailed Factual Data

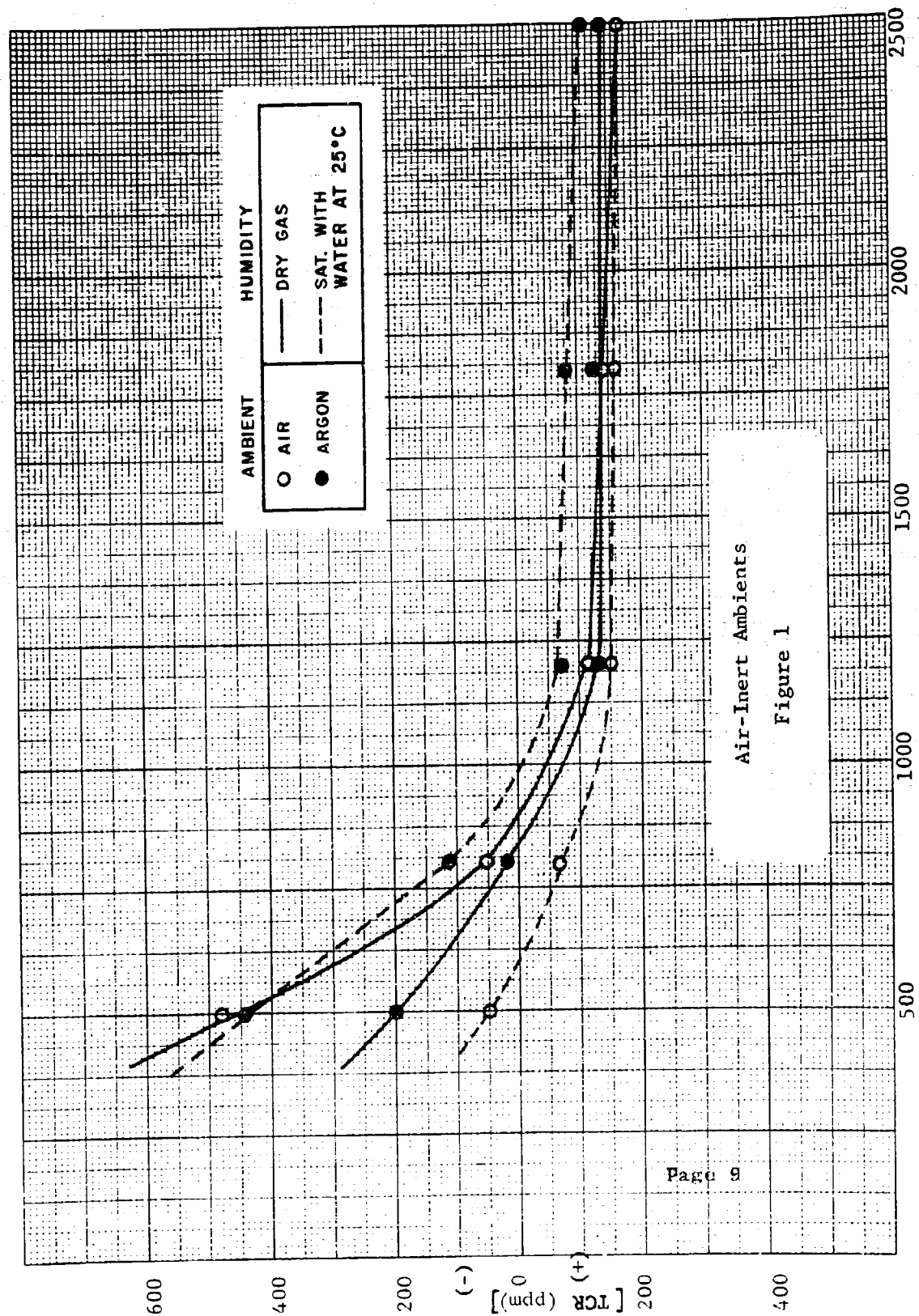1.3.1   Gas Plated Tin Oxide Resistor Films

As reported in Section 1.3.2 of the First Interim

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Engineering Report, gas plated tin oxide resistors show a
dependency of the temperature coefficient of resistance, TCR, upon
the thickness of the resistor film.

It was postulated that this effect is due to the
formation of surface states which produce a higher conductivity
channel in the underlining tin oxide. The induced channel
apparently is several hundred angstroms in depth, and at film
thicknesses below 1000 $\overset{o}{A}$ profoundly influences the overall
characteristics of the deposited resistor.

To determine the cause of such channeling, a series
of antimony aluminum doped tin oxide resistors were prepared
with film thickness of from 500 to 2000 $\overset{o}{A}$. The deposition
technique and apparatus used is described in Section 1.3.1
and 1.3.2 of the First Interim Engineering Report.

After deposition of the tin oxide, gold stripes
were vacuum evaporated to provide ohmic contact to the
resistor film. The resistors were cycled from $25^{o}C$ to $125^{o}C$
in air to determine the nominal TCR of the various thicknesses.
TCR measurements were then taken in atmospheres of dry oxygen,
argon, and forming gas, a mixture of nitrogen and hydrogen.
Measurement of the TCR was also performed in atmospheres
of the same gases which were humidified by bubbling through
water at $25^{o}C$. The results of this test are given in
Figure 1 and 2 . This data indicates that in each case the

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Air-Inert Ambients

Figure 1

2824-1-5

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Oxidation-Reduction Ambients

Figure 2

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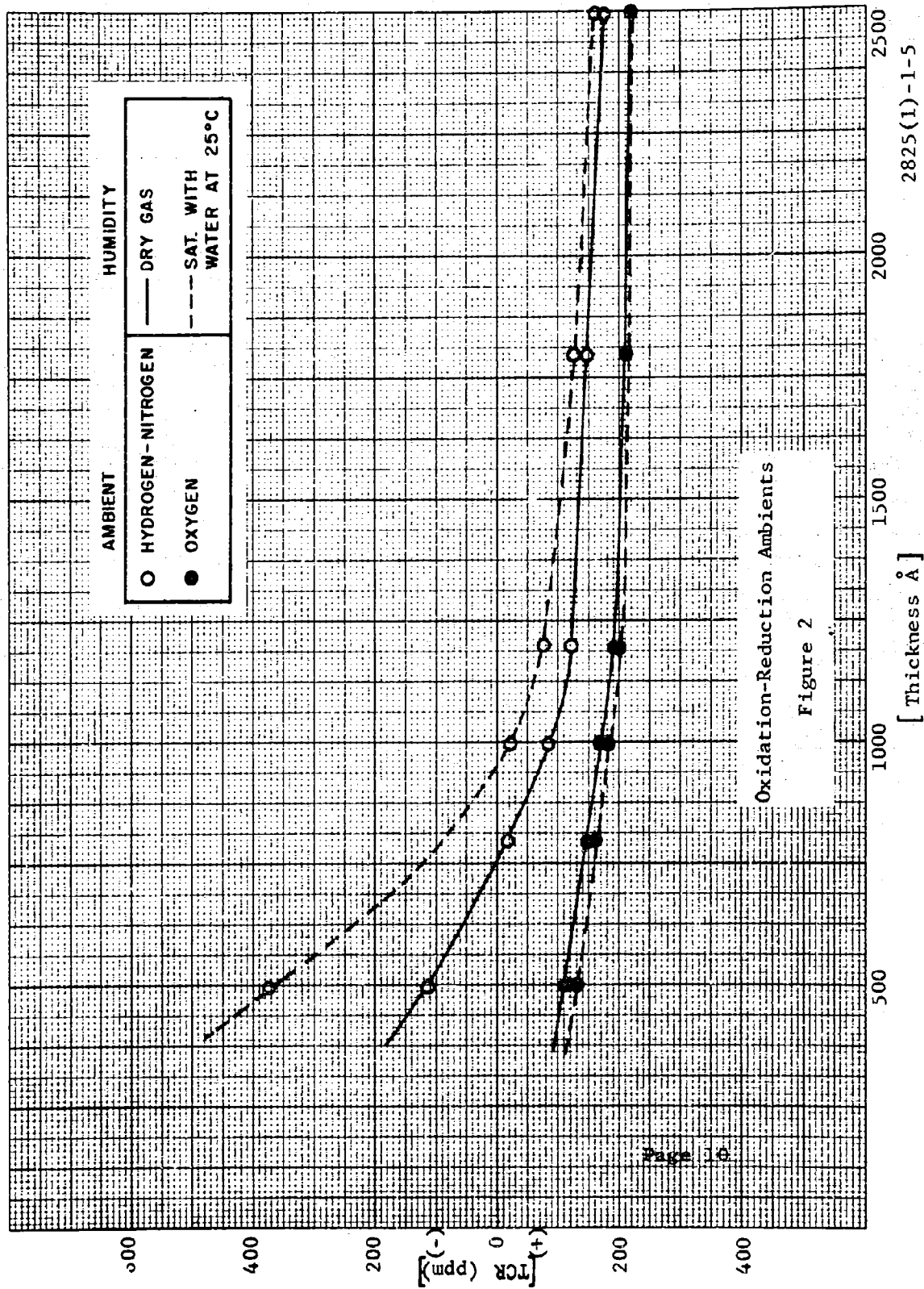
dry ambients resulted in the resistors having a much lower thickness dependence of TCR than that obtained when measurements were performed in room air, at 30% relative humidity. The oxygen ambient was particularly active in reducing the film thickness dependency of the TCR.

Measurements performed in humidified ambients showed an increasingly negative TCR for the thinner films measured in all cases except that of oxygen. The thickness dependency of the TCR was nearly identical with that measured in room air for all the humidified atmospheres except in the case of oxygen. With either "wet" or dry oxygen, the TCR was relatively independent of film thicknes; however, with continued temperature cycling in the oxygen ambient, a slight trend was noted for the thinner films to have a more positive TCR than the thicker films. This completely reverses the thickness dependency of TCR obtained in all other ambients. In no case did exposure to a particular ambient at room temperature, $25^{\circ}C$, result in resistance changes of more than $\pm 1\%$.

In summary, it has been found that ambient conditions have a great effect upon tin oxide resistor of less than a 1000 $\overset{o}{A}$ thickness and that the magnitude of the effect is greater at higher temperature. Oxygen, which tends to cause an increase in high temperature resistance, inhibits the effect of water vapor, which causes a decrease in the high temperature resistance.

It can be concluded that packaging of the tin oxide resistors
in dry ambients and/or oxygen will allow the use of thinner
films to obtain high ohms per square without changing the
TCR characteristic of the bulk material.

1.3.2   Encapsulation of Tin Oxide Resistors

An experiment was performed to evaluate the effective-
ness of the vapor plated boro alumina silicate dielectric on en-
capsulant for stabilizing tin oxide resistor films. Antimony-
aluminum doped tin oxide resistors were deposited according to
the method described in the First Interim Engineering Report,
Section 1.3.2, with the exception that half of the films were de-
posited without the addition of oxygen to the reactant gases.
After deposition, the two groups were divided in half. One half
of each group was etched to produce a pattern of resistor strips
using the method described in Section 1.3.3 of this report. Each
group was again divided with half of each group being encapsulated.

The final structure of the test series is shown below:
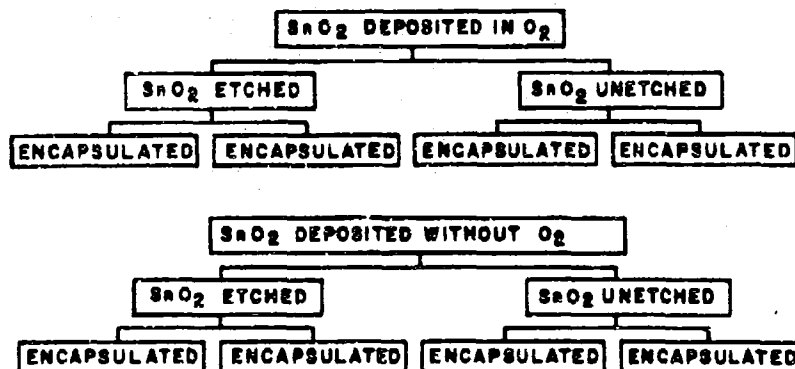
The test samples were held at 500°C in an air ambient and the resistance was measured at intervals. Figures 3 and 4 show the results of this experiment. It is seen from these figures that the etched films show a higher degree of instability than comparable films which were not etched. This is probably due to contamination of the tin oxide by the KOH etch solution used and indicates that more attention to post-etch cleaning procedures is necessary and/or the use of an acid etch. The tin oxide films deposited without the introduction of oxygen in the plating zone were more stable than those deposited in an oxygen-rich environment. This is probably due to the films prepared under low oxygen conditions being close to equilibrium conditions.

The effect of the encapsulation is a marked improvement in the high temperature stability of the resistor. Encapsulated tin oxide resistors may show a drop of approximately 40% during the first hours of exposure to 500°C and are stable thereafter maintaining a value ± 5% of a central value.

The high temperature stress conditions used in this experiment are far in excess of expected operating service but are useful in allowing a comparison between various resistor processing methods to be made quickly.

Long-term stability tests of resistor films will be conducted after determining the optimum processing parameters.

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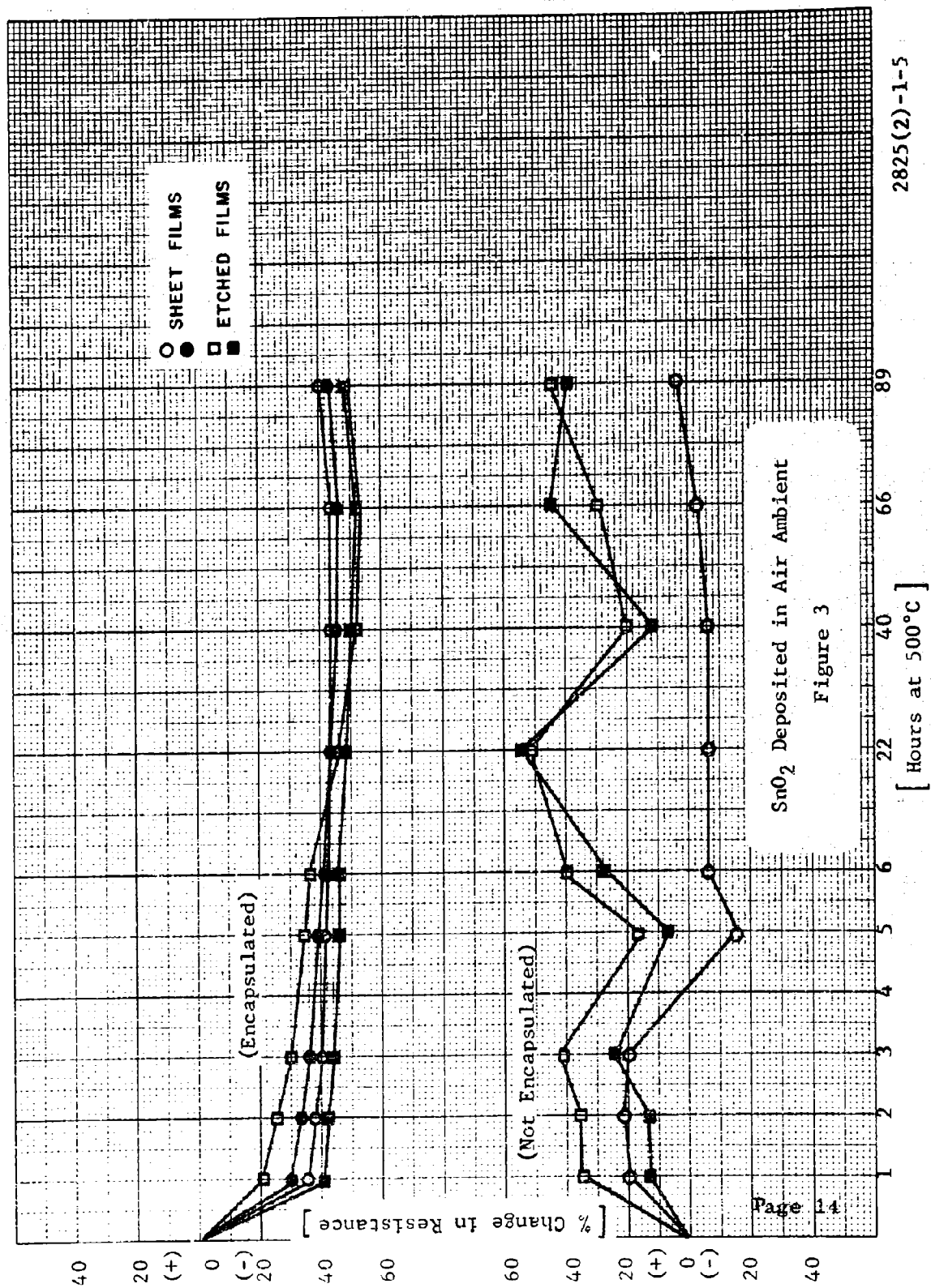
SnO$_2$ Deposited in Air Ambient

Figure 3

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SnO$_2$ Deposited in Oxygen Ambient

Figure 4

2223-1-5
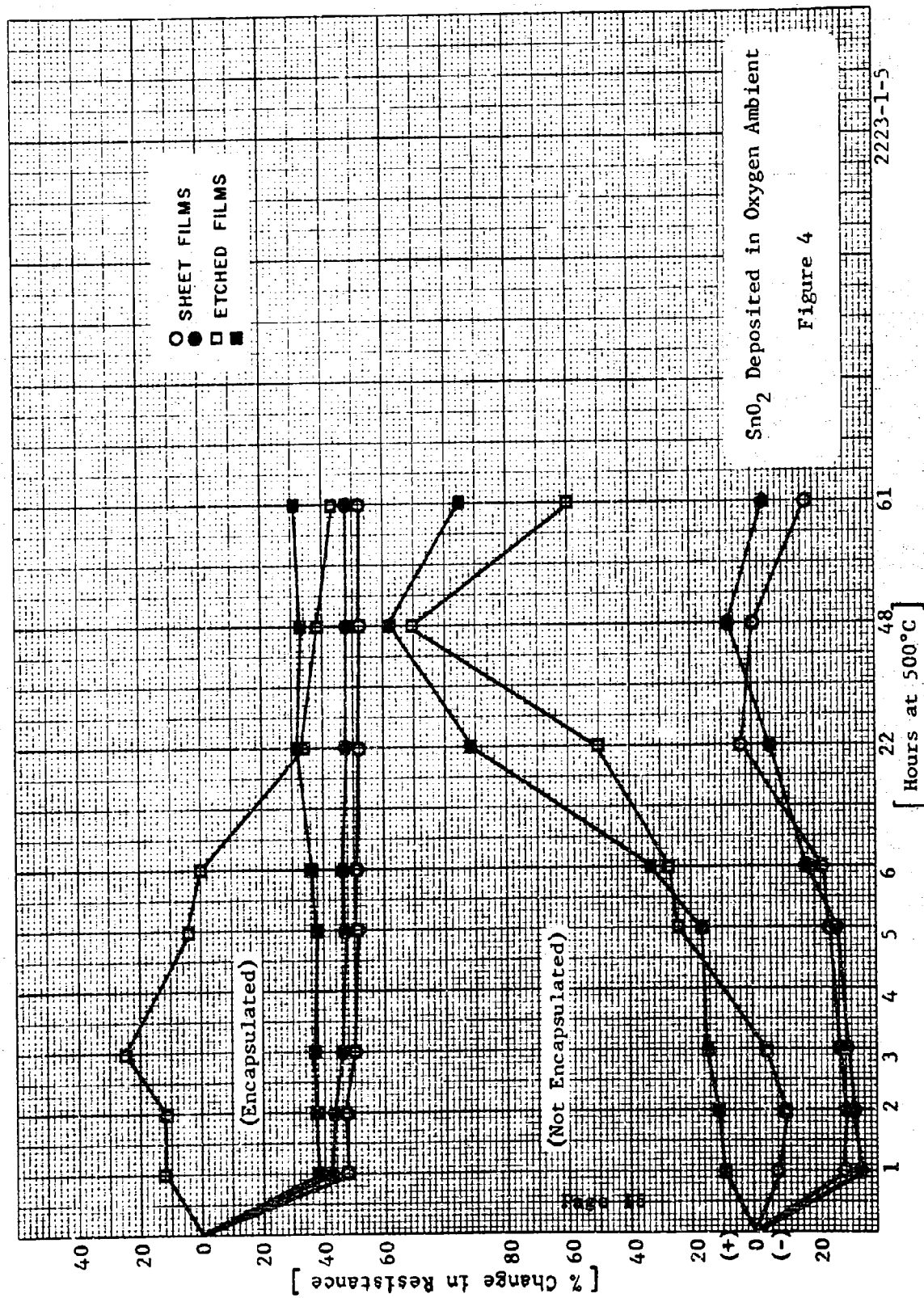
1.3.3   Delineation of Tin Oxide Resistors

A method for the delineation of tin oxide and other hard-to-etch materials has been developed. In this process, the entire substrate surface is covered with a metal such as aluminum and etched by KMER techniques to provide the negative of the desired pattern. A resistor test pattern is shown in Figure 5A, after the negative pattern of aluminum has been made. Figure 5B shows the substrate after the tin oxide resistor film has been deposited. Figure 5C shows the patterned tin oxide resistor after removal of the aluminum masking film with a KOH etch. The smaller lines in the pattern are 0.5 mil in width.

This technique is also applicable to the masking of dielectric films.

1.3.4   Resistor Films other than Tin Oxide

During this period a number of metal oxides were examined as to their suitability for use as thin film resistor elements.

1.3.4.1   Indium Oxide

Indium oxide was prepared by the pyrolysis in an oxygen ambient of indium acetylacetonate vapors at temperatures in excess of $300^{o}C$. Films prepared in this manner were quite hard and very adherent to the substrate. Sheet resistances as

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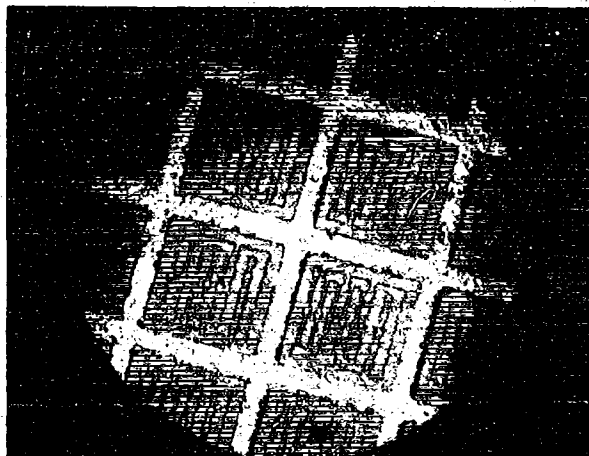
(A) Substrate with
    Negative Pattern
    of Aluminum
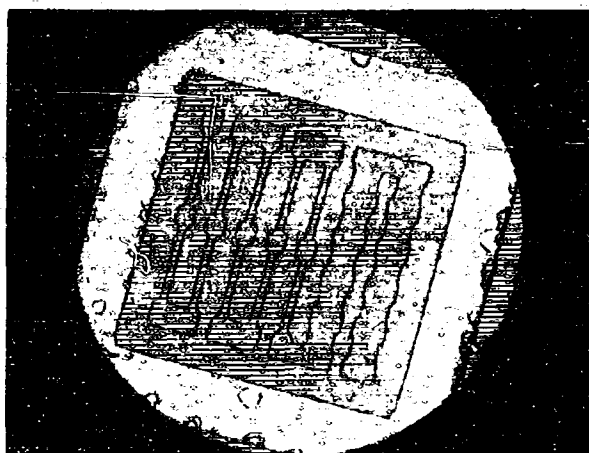
(B) Substrate After
    Deposition of Tin
    Oxide Resistor Film
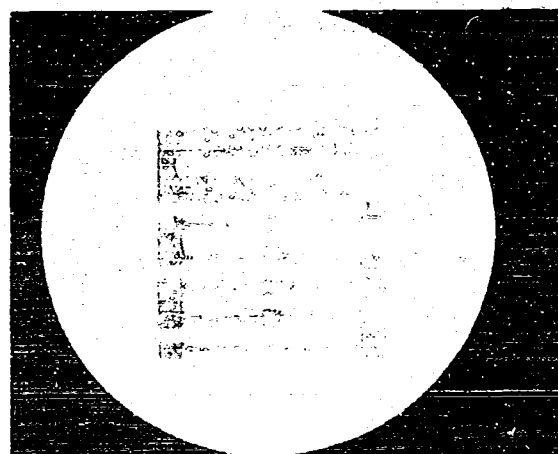
(C) Finished Resistor
    Pattern After Removal
    of Masking Aluminum
    Film

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Figure 5

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high as 10,000 ohms per square were obtainable for films approximately 1000 $\overset{o}{A}$ thick. The TCR of the indium oxide films was initially in the range of +200 to +500 ppm/^{o}C; however, stress at elevated temperatures caused the TCR to become strongly negative with average values lying in the range of -200 to -600 ppm/^{o}C.

Deposition of this material from indium acetylacetonate was difficult to control and later films were prepared from the reaction of triethyl indium and oxygen using an apparatus similar to that described in Section 3.1 of the First Interim Engineering Report.

Evaluation of doped indium oxide systems is now underway.

1.3.4.2   Nickel Oxide

Films of nickel oxide were prepared by the pyrolysis of nickel actylacetonate vapors at temperatures in excess of 350°C in an oxygen ambient.

Resistivities were extremely high and erratic. The few resistors on which it was possible to obtain TCR measurements showed a high degree of instability and a TCR in excess of -1000 ppm/^{o}C.

It was concluded that nickel oxide was not suitable as a material for thin film resistors.

1.3.4.3 Zinc Oxide

Zinc oxide films were prepared at substrate temperatures in excess of 300°C by the pyrolysis of zinc actylacetonate in an oxygen ambient. The deposited films were hard, transparent, and adherent to glass substrate. Resistivity ranged from 2000 to 10,000 ohms per square for films approximately 1000 Å in thickness. The temperature coefficient of resistance was -400 for a film having a sheet resistance of 1200 ohms per square. Zinc acetylacetonate sublimes rather than melts at atmospheric pressures, making it difficult to accurately control the deposition process.

The liquid diethyl zinc has a vapor pressure suitable for the control requirements of the vapor plating technique and is extremely oxygen active. The reactivity of diethyl zinc may allow film deposition at lower substrate temperatures and will provide a more pure product than that obtainable from the acetylacetonate. The investigation of zinc oxide reaction will be continued during the next period using diethyl zinc as the source material.

1.3.5 High Dielectric Constant Materials for Thin Film Capacitors

1.3.5.1 Tantalum Oxide

Tantalum oxide films were deposited by the vapor phase reaction of pentaethoxy tantalum and oxygen at substrate temperatures in the range of 350°C to 500°C.

The tantalum ethoxide is prepared by the method developed by Bradley et. al.[1] which reacts ethanol and tantalum pentachloride with anhydrous ammonia in dry benzene.

The tantalum pentaethoxide is a colorless liquid having a vapor pressure of 10 mm at 202°C and is fairly stable thermally but is readily decomposed by water. The equipment used for the vapor deposition of tantalum oxide films is similar to that previously described in Section 1.3 of the First Interim Engineering Report.

Capacitors using tantalum oxide dielectrics were formed on Corning 7059 fire-polished glass 0.5 x 0.5 inch substrates or silicon wafers for electrical evaluation. On the 7059 glass substrates, the electrode material was vacuum deposited aluminum. Vacuum evaporated gold was used on the silicon wafers as the top electrode in most cases, although some were prepared with aluminum electrodes.

Ohmic contact to capacitors formed on 7059 glass was provided by the evaporation of chrome-gold contact pads on top of the aluminum electrodes. Contact to the silicon, which forms the bottom capacitor plate for the capacitors formed on silicon substrates, was made by evaporated gold.

Electrical evaluation of the completed capacitors revealed that films deposited at 425° C provided the most desirable

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[1] D.C. Bradley, B.N. Chakravarti, W.Wardlow, J.Chem.Soc. 1956,2381

dielectric properties. Typical electrical values for capacitors using tantalum oxide dielectrics are given in Table I.

As reported in Section 1.3.7.5 of the First Interim Engineering Report, dielectric films formed by the codeposition of aluminum oxide and tantalum oxide have a somewhat lower dissipation factor than does tantalum itself. Further development of this mixed dielectric was undertaken this period.

Tantalum pentaethoxide was used as the source of tantalum oxide and triethyl aluminum was used as the aluminum source. Typical deposition parameters for this dielectric system are shown below.

Substrate Temperature	$475^{\circ}C$
Ta $(OC_2H_5)_5$ vaporizor temperature	$150^{\circ}C$
Argon flow through vaporizor	6 units
Argon flow through $Al(C_2H_5)_3$ source	15 units
Oxygen flow rate	15 units
Deposition rate	$200Å$/min.

Electrical parameters of typical films deposited by this technique as well as for typical films of tantalum oxide alone are presented in Table I.

Table 1   Electrical Parameters of Typical Films

f	C (pf)	DF (%)	V_{BD} (V)	(a) I_{DC} 10V	d ($\overset{o}{A}$)	Area (MM^2)	Type Dielectric
1kc	1973	.72	90	3×10^{-9}	4500	3	Ta_2O_5
1kc	1127	.71	90	1.5×10^{-9}	4500	2	"
1kc	3889	.77	30	1.5×10^{-5}	1500	2	"
1kc	764	.36	140$^+$	7×10^{-10}	6300	3	$Ta_2O_5.Al_2O_3$
1kc	1083	.47	60	2×10^{-8}	4500	2	"
1kc	1261	.57	30	10^{-6}	1900	1	"

Dielectric constants (k) calculated for the Ta_2O_5 and $Ta_2O_5.Al_2O_3$
films are 33 and 27 respectively. Estimated thicknesses are
based on the interference color pattern for Ta_2O_5 and are
accurate to $\pm$ 200 $\overset{o}{A}$. The calculated K values are based on
these estimates. Interferometric measurements of film thicknesses
will be made during the next period.

Twelve units with Al electrodes, Ta_2O_5 or $Ta_2O_5.Al_2O_3$
dielectrics, and Cr-Au contact pads were placed on electrical
and thermal stress. Test conditions were 25 vdc and 125^C.
After 750 hours under stress, 28% of the units failed. Of
these 10% failed within the first 24 hours on test. The average
change in capacitance for the units remaining on test was
-1.5%. The average change in dissipation factor was .15%.
The units are at present still under stress at the previously
stated conditions.

Three silicon wafers vapor plated with Ta_2O_5 and three vapor plated with $Ta_2O_5.Al_2O_3$ have been prepared for spectrographic analysis. One wafer from each series was baked out at $125^{\circ}C$ for 24 hours; another from each group baked out at $600^{\circ}C$ for 24 hours; and the remaining wafers left at room temperature. The amount of water present in the absorption band and the effect of bakeout on it should be determined from this analysis. Results of this analysis are not available at the time of this writing.

Another sample of $Ta_2O_5.Al_2O_3$ deposited on a fire-polished glass microslide has been prepared to obtain electron-micrographs of the film surface characteristics. Work on this has not yet been completed.

1.3.6   Pilot Production Gas Plating Apparatus

The pilot production machine which was previously designed has been completed and installed during this period. This equipment embodies several unique features which make it suitable both as a research apparatus and as a pilot production machine.
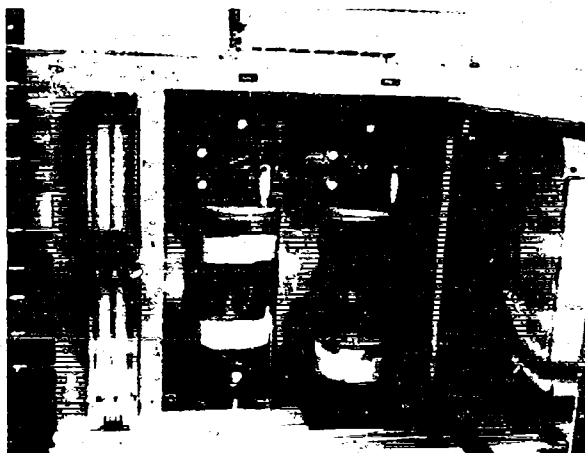
Three separate vaporizors have been provided for use with liquid vapor plating sources. Each vaporizor has a separately controlled constant temperature bath and the gas flow through the vaporizor is controlled by calibrated rotometers.

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Two of the vaporizors are shown in Figure 6. One of the constant temperature baths has been lowered to show the vaporizor chamber more clearly. Source materials may be easily changed to permit the vapor deposition of any oxide based system which uses a liquid source material. Separate provision has also been made for the use of sources which are normally in the gaseous state, such as silane. The substrate heater is controlled to $\pm$ 1°C by means of a proportional controller, and is moved under the plating head by a variable speed motor which is monitored by a tachometer. The time for one deposition pass may be varied from less than 2 minutes to more than 30 minutes with a reproducibility of $\pm$ 1%.

The plating head is shown schematically in Figure 7. The vapor plating head is located within a sheet metal hood enclosure which exhausts the spent gases and the by-products formed during deposition.

Figure 8 is a photograph of the complete apparatus. Initial runs with this apparatus were made with the deposition of boro alumina silicate glass dielectric films. It was found that deposition of 1000 $\overset{o}{A}$ of glass dielectric over an area of 4 inches x 11 inches required 8 minutes. The thickness variation of the deposit was less than 1% throughout the deposition zone.

Deposition of antimony aluminum doped tin oxide was also accomplished with this equipment with similar results.

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Vaporizors of Pilot Production Vapor Plater

Figure 6

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CERAMIC SADDLES
FOR GAS DISPERSION

BAFFLE PLATE
FOR CHAMBER II

INPUT TO
CHAMBER I

INPUT TO
CHAMBER II

OUTLET CHAMBER II

OUTLET CHAMBER I

SHEETMETAL
HOOD

TO VENT
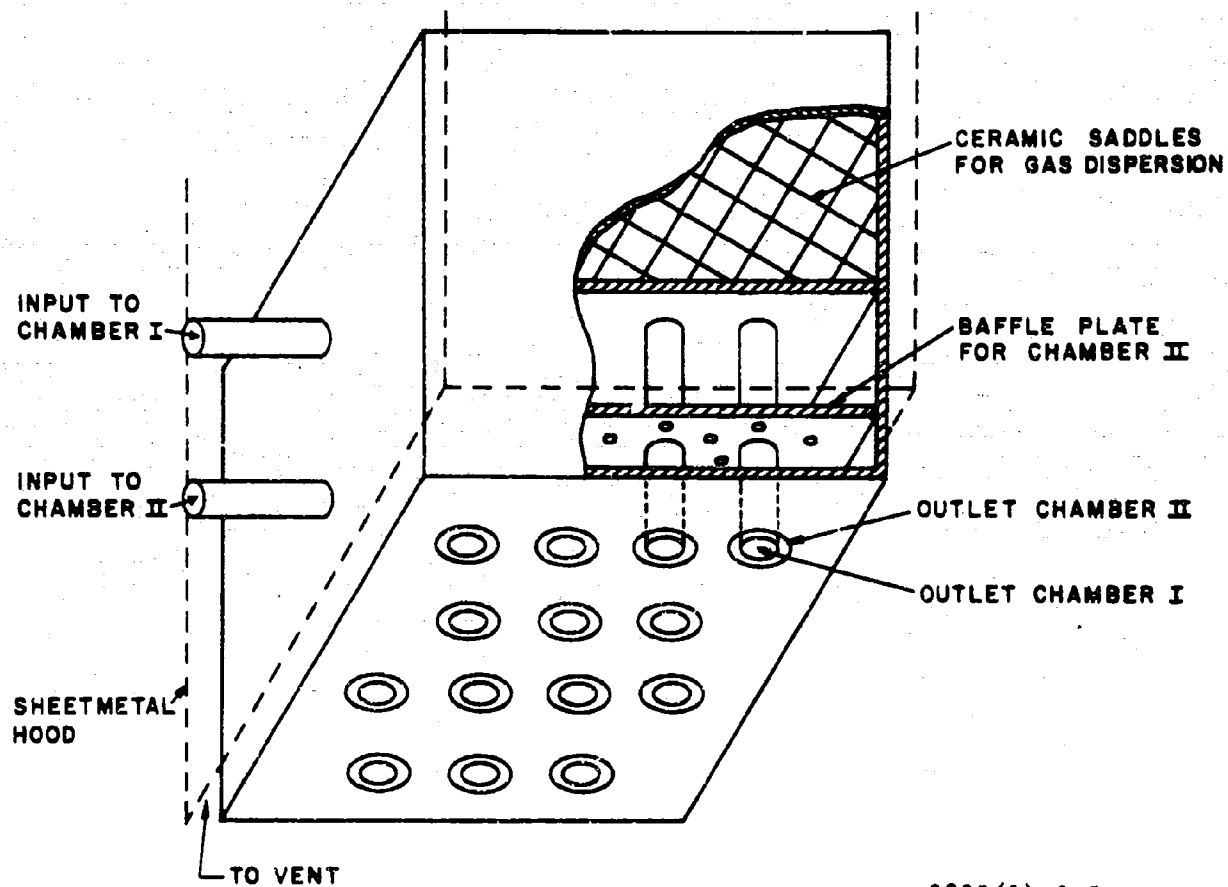
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Vapor Plating Head

Figure 7

2861-1-5

Pilot Production Vapor Plating Machine

Figure 8

The evenness of deposit, high production, rate
and reproducibility of deposition conditions achievable with
this equipment will materially aid in the evaluation of the
materials under development.

1.3.7   Vapor Deposition of Nickel Films

The application of nickel films as conductor paths,
bonding pads, and capacitor electrodes in thin film circuitry,
as well as the use of nickel in conjunction with chromium
to fabricate resistors, indicates the desirability of being
able to vapor plate this important material. The reaction
by which nickel films are deposited from vapor phase reactants
should produce films with high electrical conductivity, reason-
able surface smoothness (freedom from spicules and sharp dis-
continuities), and good adherence to glass and ceramic substrates.
In addition the chemical reaction should proceed at reasonably
low temperatures and produce no side products which would con-
taminate the desired nickel film, especially if these contaminants
could lower the conductivity. The reaction employed to vapor
deposit nickel was the pyrolysis of nickel carbonyl. Nickel
carbonyl, $Ni (CO)_4$, is a compound in which the nickel atom
is surrounded by four carbon monoxide groups spatially arranged
to form a tetrahedral structure[1] and weakly attached to the
nickel by coordinate bonds. In this type of chemical bond,
the carbon-oxygen bond in the CO group is affected very little[2],

[1]Brockway and Bross, J. Chem. Phys., 3, 828 (1935)

[2]Bailes, Chemistry of Coordination Compounds, 1956, p. 518.

the group being bound to the central nickel atom through the carbon atom. With sufficient thermal energy available, this molecule will decompose according to the reaction $Ni(CO)_4 \longrightarrow Ni + 4CO$. Using the known heat of formation of nickel carbonyl plus the heat of vaporization of nickel, the energy necessary to break the nickel-carbon bond in nickel carbonyl can be computed to be 42 Kcal/mole*. This energy is much smaller than that needed to break the C-O bond, a fact which suggests that there would be little carbide formation as a direct side-product of the pyrolysis reaction. Some carbon contamination of the nickel film can occur, however, through the catalytic disproportionation of the carbon monoxide by-product. This reaction, which proceeds as $2CO \longrightarrow C + CO_2$ is catalyzed by the nickel surface itself, especially at high deposition temperatures where premature decomposition of the nickel carbonyl can produce finely divided nickel with a large active surface area.

Two types of apparatus were used to deposit nickel films – a laboratory system which generates, then pyrolizes nickel carbonyl, and a large, production-type machine using a liquid source of commercial nickel carbonyl. In the laboratory apparatus (see Figure 9), carbon monoxide is passed through

*This is computed from the reaction
$Ni(g) + 4 CO(g) \longrightarrow Ni(CO)_{4(g)}$. Proper allowance is also made for the fact that nickel must be in the excited $3d^{10}$ state to form nickel carbonyl.
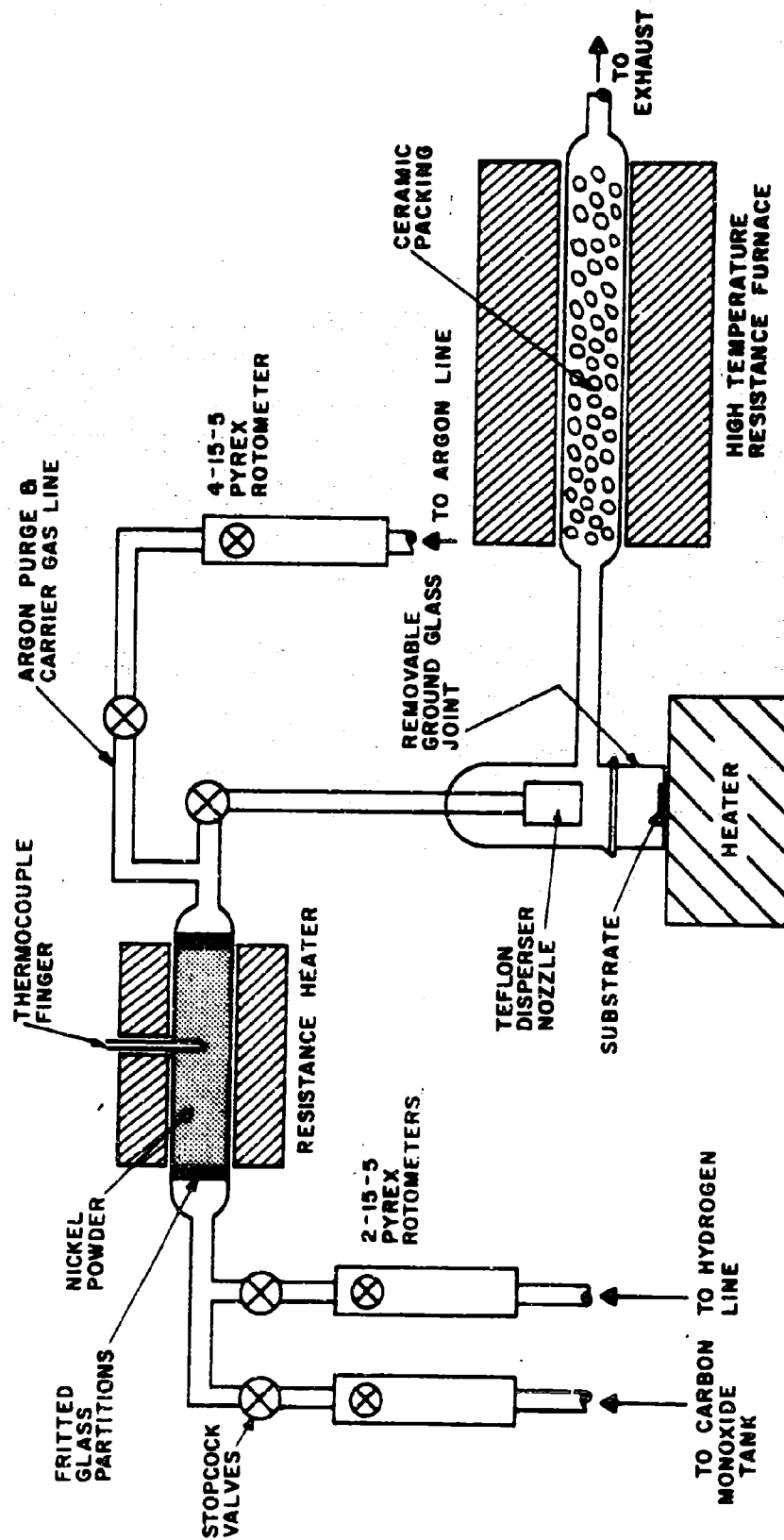
Laboratory Apparatus For Nickel Film Deposition

Figure 9

2822-1-5

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nickel powder which was freshly reduced at $300^{O}C$ in hydrogen and then cooled to a temperature under $100^{O}C$ where the absorption isotherm of the nickel allows it to rapidly absorb carbon monoxide with the subsequent generation of nickel carbonyl. This reaction, $Ni + 4CO \longrightarrow Ni(CO)_4$, is simply the reverse of the pyrolysis reaction. The $Ni(CO)_4$ vapor generated is then mixed with argon carrier gas and dispersed through a teflon nozzle onto the heated substrate. All remaining by-products are then swept into a heated furnace to decompose any remaining poisonous $Ni(CO)_4$.

Substrate temperatures ranged from $190^{O}C$ to $300^{O}C$ in the experimental series of nickel deposition runs, while film thicknesses varied from 1000-4000 angstroms. Throughout the above temperature range, the films were smooth and possessed resistivities ranging from .4 to .8 ohms per square. The thicker films (4000 $\overset{O}{A}$) grown at substrate temperatures in the 190° - 220° C range, however, displayed some surface roughness. Nickel films deposited at higher substrate temperatures (250° - 300° C) had better adherence and did not show any drop in conductivity, although this drop in conductivity might be expected from carbide formation. In general, the vapor deposited nickel films had better adherence, conductivity, and oxidation resistance than films of similar thicknesses prepared by vacuum evaporation in production line equipment.

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Motorola has in current use a production line facility for depositing nickel films from nickel carbonyl. The deposition machine essentially consists of an endless, woven metal belt isolated from the ambient and kept under an atmosphere of pure helium. Airlock and ultra-clean handling facilities are provided at both ends of the belt for sample introduction and removal. The prepared substrates, after being placed on the belt, are slowly moved through a tube furnace which brings them to a temperature of 190°C before they enter the plating chamber in which specially designed nozzles spray the substrates with a helium-nickel carbonyl gas mixture. The substrates are then slowly cooled and removed from the other end of the moving belt. As the machine is presently set up, one pass through the system takes approximately 30 minutes and 1000 angstroms of nickel are deposited in this time period, thicker films being deposited by repeated passes. The nickel films are very evenly deposited and possess resistivities of .3 ohms per square.

1.3.8   Vapor Plated Tungsten Films

Vapor plated tungsten films are generally prepared by the pyrolysis or hydrogen reduction of tungsten hexachloride. This method has the disadvantage in that the high substrate temperatures required (1000° - 2000°C) cause premature de-composition of the tungsten hexachloride with the result that powdery deposits are often obtained.[1] It was decided to use

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[1] Power, Campbell, and Gouser, "Vapor-Plating", Wiley and Sons, New York (1955), PP. 55-57

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the hydrogen reduction of tungsten hexafluoride as a method
of depositing tungsten films from vapor phase reactants.
This reaction, proceeding as $WF_6 + 3H_2 \longrightarrow W + 6HF$, has the
advantage of occurring at lower substrate temperatures ($350^{\circ}C$ -
$650^{\circ}C$) and being catalyzed by the surface of the substrate.
These factors would better insure the formation of an adherent,
continuous tungsten film without the need of using reduced
pressures in the deposition process (as is necessary in the
methods using WCl_6).

Tungsten hexafluoride, commercially available in
99.8% chemical purity, is a gas at room temperature and can
be directly metered into a carrier gas without any need for
a source vaporization process. In the apparatus used, the
tungsten hexafluoride was injected into a hydrogen carrier
gas at room temperature and then swept over the substrate
which was heated to the desired deposition temperature by a
cartridge resistance heater. Prior to the deposition, the
system was well flushed with argon, and then hydrogen.

It is often advantageous to purge the system with the
WF_6 before the substrate is placed in the system to remove
residual moisture adhering to the glass surfaces. Any moisture
or oxygen in the apparatus will result in tungsten oxide and
tungsten oxyfluoride contamination of the deposited film.
Although the stoichiometry of the reaction indicates three

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volumes of hydrogen are needed for every volume of WF_6, it
is desirable to use a large excess of hydrogen to obtain a
reasonably slow plating rate. Substrate temperatures ranged
from 450° - $520^\circ C$, and films were deposited with thicknesses
ranging from 2000 - 6000 $\overset{o}{A}$ units. The tungsten films obtain-
ed had the grey color of bulk tungsten, and electrical
resistivities in the .5 - .9 ohm/cm range. The films adhered
to smooth quartz substrates and unglazed ceramic substrates
but would not adhere to glass and glazed ceramic substrates.
It is probable that the HF by-product from the reduction
reaction is attacking the glass surfaces which have a greater
etch rate than the quartz or alumina substrates. Microscopic
examination of the glass substrates shows evidence of etch
damage.

Tungsten films deposited by a similar method were
shown to be quite pure by spectrographic analysis.[1] Excellent
adherence was obtained between the tungsten films and unglazed
ceramic substrates suggesting possible future use of the films
for bonding pad and conductor path applications in ceramic
circuitry. Future work will be done in attempting to secure
good adherence between tungsten films and glass substrates by
depositing tungsten from tungsten hexacarbonyl, a source which
will not produce by-products with deleterious effects on glass
surfaces.

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[1] Conabee, Cronin and Kinney, "Vapor Plating of Tungsten",
Semicon Final Report, 1961-2, p. 19

In a manner similar to nickel carbonyl, tungsten hexacarbonyl undergoes a pyrolytic decomposition which can be represented as $W(CO)_6 \longrightarrow W + 6CO$. The energy necessary to break the bond between the central tungsten atom and a carbonyl group is greater than that needed to separate a carbonyl group from the nickel carbonyl. This higher bond dissociation energy implies that higher substrate temperatures will be required to deposit tungsten from the hexacarbonyl than is required to produce nickel films.

Similar considerations also apply to the deposition of molybdenum and chrome from their respective carbonyl compounds, reactions which will also be explored. Calculation of the energy necessary to break the bond between the carbonyl group and chrome in chrome carbonyl, for example, shows that 57 Kcal* of energy is necessary to rupture the bond. (Compare this to the 42 Kcal necessary to break the nickel carbonyl bond.)

These necessary higher deposition temperatures pose two difficulties - predecomposition of the carbonyl before it reaches the substrate, and greater probability of carbon con- tamination from the disproportionation of the carbon monoxide by-product. A general purpose apparatus has been designed for laboratory scale deposition of chrome, molybdenum, and tungsten metal films from their respective carbonyl compounds. This

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*Calculations allowed for excitation energy needed to place chrome in the excited $3d^6$ state needed to form the $Cr(CO)_6$.

apparatus, which will be constructed primarily from quartz, will control the temperature of both the carrier gas and metal carbonyl source ($Cr(CO)_6$, $W(CO)_6$, and $Mo(CO)_6$ are solids at room temperatures), allowing for precise control of the carbonyl partial pressure in the system. The carrier gas-carbonyl mixture will be cooled during its passage through the dispersing nozzle to prevent pyrolysis before the gas reaches the heated substrate below. Fairly rapid flow rates with large carrier gas/metal carbonyl ratios will be employed to prevent a high concentration of carbon monoxide by-product from producing unwanted carbides.

Reduction of the total partial pressure of the entire system can also be employed to improve the quality of the metal films deposited. The resulting increase in the mean free path of the reactant molecules decreases their collisional frequency and thus the rate of thermal decomposition in the vapor phase, helping to prevent predeposition problems. The resulting longer mean free path of the carbon monoxide by-product will also decrease the probability of the disproportion-ation reaction occurring in the vicinity of the substrate with a subsequent reduction in carbide contamination of the film. A low partial pressure will in effect, favor reactions at the vapor-substrate interface at the expense of reactions in the vapor phase. This is often advantageous in producing smooth, adherent films.

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1.4   CONCLUSIONS

1.4.1   Vapor Plated Resistor Films

Water vapor and oxygen ambients strongly influence
the electrical characteristics of thin films <1000 $\overset{O}{A}$, tin oxide
resistors.

The encapsulation of tin oxide resistors with a
vapor plated dielectric film produces an improvement in high
temperature stability of the resistor films.

The delineation of tin oxide by means of aluminum
reverse mask techniques has been successful but there is some
indication that resistor stability may be degraded by residues
left by the etching process. Further work in this field is
required.

Zinc oxide and indium oxide will be investigated
for use as resistor materials having a high ohm per square
with low TCR.

1.4.2   Dielectric Films

Vapor deposited films of tantalum oxide can be
produced with values of capacitance up to 1 pf/mil^2. The
dielectric strength, resistivity and dissipation factor of
tantalum oxide dielectric can be improved by the addition of
aluminum oxide within the deposited film.

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Codeposition of tantalum-aluminum oxide films has produced capacitor dielectrics with values up to 1 pf/mil^2 and Q's in excess of 500 at 1 kc.

The tantalum-aluminum oxide dielectric system appears at this time to have great potential for thin film circuit applications and will be investigated further.

1.4.3   Metal Films for Resistors and Conductors

Vapor deposited nickel films may be prepared easily by pyrolysis of nickel carbonyl. The deposited nickel films have excellent adhesion, surface finish, and conductivity and are well suited to application as circuit interconnects and capacitor plates.

Tungsten metal films prepared from the hydrogen reduction of tungsten hexafluoride may have some application for the metallizing of thin film circuits, but are limited in application by the corrosive nature of the by-products formed during deposition.

Deposition of thin films of tungsten and chromium by the pyrolysis of their carbonyls will be attempted and the films evaluated as resistor elements.

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2.0   PROGRAM FOR THE NEXT INTERVAL

2.1   DIELECTRIC FILMS

Work will continue on the development of aluminum oxide tantalum oxide capacitor dielectrics. The parameters affecting deposition will be more fully determined and longer scale stress testing of these capacitors will be initiated.

2.2   RESISTORS

Developmental work on the antimony-aluminum doped tin oxide resistors will continue. Particular emphasis will be given to the investigation of cause of instability in etched resistors and to larger scale stress testing of encapsulated tin oxide resistors.

The investigation of resistor films based on vapor plated zinc oxide and indium oxide will be continued.

2.3   METAL CONDUCTOR AND CONTACT PADS

Deposition of tungsten and chromium from their carbonyls will be studied during the next period. Deposition of gold from the pyrolysis of gold compounds will also be studied.

APPENDIX A

Project Performance and Schedule

MOTOROLA, INC.
Semiconductor Products Division
PROJECT PERFORMANCE & SCHEDULE

CONTRACT NO. NObsr-91336

REPORT DATE 15 January 1965

PERIOD COVERED 1 July 1964 to

30 December 1964

		1964						1965									
	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D

1. DEPOSITION OF NON-OXIDE SYSTEMS CONDUCTORS AND RESISTORS

2. DEPOSITION OF OXIDE SYSTEMS, DIELECTRIC AND RESISTORS

3. COMPONENT DELINEATION

4. ELECTRICAL EVALUATION

5. PHYSICAL & CHEMICAL EVALUATION

6. CIRCUIT DESIGN

7. CIRCUIT PRODUCTION AND EVALUATION

8. CORRELATION OF DATA, TECH. DIRECTION AND PREPARATION OF REPORTS

PROJECT PERFORMANCE AND SCHEDULE CHART

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