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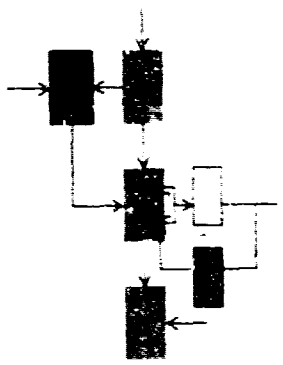

THIN-FILM ACTIVE DEVICE INVESTIGATIONS

W. S. Nicol

Final Status Report
December 1, 1967 - August 31, 1968

Electronic Systems Laboratory

MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS 02139

Department of Electrical Engineering

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ABSTRACT

This report describes the concluding nine-month phase of a three-year investigation into the feasibility of constructing active devices in thin-film form. During the reporting period, work was concentrated on evaporated gallium arsenide with the aim of determining electrical and structural transport properties necessary for a coplanar-electrode, space-charge-limited triode. Both amorphous and single-crystal substrates were used in this work. Differences in results from those obtained by other investigators led to two subsidiary investigations into methods for thermoelectric power measurements and for substrate temperature measurement. Although definitive film properties for active devices have not been determined, the results of these investigations should be of interest in any future work in this area.

CONTENTS

A. INTRODUCTION

The overall goal of these investigations during the period 1964 to the present has been to obtain a useful active device in thin-film form. The primary advantage of such a device would be the potential for economical batch fabrication, together with other passive elements, by evaporation techniques. There is also potential for reduced size of circuits, greater tolerance to severe environmental conditions such as temperature and radiation, and very high gain-bandwidth products.

During the period up to mid-1967, work concentrated on space-charge-limited triode structures consisting of either gold or aluminum grids imbedded between layers of evaporated CdS films. As previously reported, problems were encountered with both the formation of a Schottky barrier between the gold grid and the CdS films, and with breakdown of the oxide layer insulating the aluminum grid. These problems cast doubt on the feasibility of this approach, and no further investigations were made during this reporting period. A discussion of the thickness variation of breakdown field strength found for our plasma-oxidized aluminum films was published in the IEEE Proceedings Letters, January, 1968.

With the conclusion of the triode structure investigations, emphasis turned to an attempt to obtain evaporated gallium arsenide films with electrical properties useful in a thin-film, coplanar-electrode, space-charge-limited triode. A description of our method for evaporation of gallium arsenide films was given in the previous report, and was also published in the Review of Scientific Instruments Notes, August, 1968. During the present terminal reporting period, research has concentrated on a study of the structural and electrical transport properties of GaAs films evaporated on both amorphous and single-crystal substrates. Also, differences in results from those obtained by other investigators led to two subsidiary investigations into methods for thermoelectric power measurements and for substrate temperature measurement. Although definitive film properties for active devices have not been determined, the results of these investigations should be of interest in any future work in this area.

During the reporting period, the final report on our previous work on coincident-radio-frequency techniques for writing and non-destructive readout of thin magnetic-film memories was completed. This report is in publication and should be distributed in October, 1968.

B. GALLIUM ARSENIDE FILMS EVAPORATED ON AMORPHOUS SUBSTRATES

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1. Film Structure

Our modified Gunther method of co-evaporation of gallium and arsenic described in the previous reports has been used for film fabrication. Films have been evaporated on amorphous quartz, Corning 7059 glass and Fisher microscope slide glass. Substrate temperatures were in the range 250° C to 400° C. Reflection electron diffraction patterns were obtained with a Siemens Elmiskop I microscope, and X-ray diffraction measurements were made with a Norelco diffractometer. Above 400° C substrate temperature, [111] texturing was predominant as shown by both electron and X-ray diffraction in agreement with the extensive observations of Davey and Pankey.[1,2] For lower substrate temperatures texturing was generally [100] or [111]. At 300° C, distinct [211] texturing was observed in one film by reflection electron diffraction, as shown in Fig. 1(a). However, X-ray diffractometer measurements showed the bulk of the film to be predominantly textured [111], with additional reflections corresponding to the $(1\,0\,\bar{1}\,0)$ and $(1\,0\,\bar{1}\,2)$ reflections of wurtzite gallium arsenide. A second film was evaporated at the same substrate temperature, but exposed to a prolonged arsenic evaporation for 30 minutes after the gallium source had been switched off, during which time the substrate remained at 300° C. This film had predominantly [100] surface texturing by reflection electron diffraction as shown in Fig. 1(b); X-ray diffraction again indicated only [111] texturing. As far as is known, the prolongation of the arsenic evaporation was the major difference between these films. It was considered that [211] texturing, not previously reported for evaporated GaAs films at 300° C substrate temperature, was associated with excess gallium; however, the film showing [100] surface texturing also had excess surface gallium, as was detected by slow alloying over a period of several days, with an overlying evaporated gold electrode film. It is likely, however, that the amount of excess gallium was smaller for this film.

a) [211] texturing

b) [100] texturing

Fig. 1 Reflection Electron Diffraction Patterns of Evaporated GaAs Films on Quartz Substrates

2. Electrical Transport Properties

Films evaporated without intentional doping have all shown resistivity in the range 10^3 to 10^7 ohm-cm. Films doped by diffusion from an evaporated sandwich layer of copper or tin have resistivities of the order of 10^2 ohm-cm. These films are fabricated by evaporating a film of GaAs onto a quartz substrate at 330 to 360° C, cooling the substrate to approximately 150° C, and evaporating the dopant film; a second GaAs film is then evaporated with the substrate temperature again raised to 330 to 360° C and the layered structure baked inside the vacuum system at 400° C for 30 minutes. The undoped, high-resistivity films are usually n-type as verified by thermoelectric power measurements, but a change to p-type has been observed for one film. Doping with copper has produced p-type films. Doping with small concentrations of tin has produced both p- and n-type films. Although this effect for tin was anomalous, it was found that higher concentrations of dopant did in fact produce n-type films. No measurable Hall mobilities were obtained for either undoped or doped films.

Stainless steel evaporation masks were fabricated by standard photomasking techniques so that we have been able to evaporate simultaneously an array of nine gallium arsenide films on a single one-inch square substrate. These films have a geometry convenient for four-point probe measurements of resistivity and Hall mobility. A series of experiments to find the effect of subjecting individual films from a single evaporation to post-deposition annealing has been made. This was carried out by sealed-tube annealing in an arsenic atmosphere. It has been demonstrated by Barrie et al.[3] that above 400° C GaAs tends to dissociate with liberation of arsenic. The conditions necessary to suppress evaporation of arsenic have been given recently by Roberts.[4] Since no measurable Hall mobilities have been observed prior to annealing, film resistivities and activation energies alone have been measured. Activation energies found for undoped films are 0.10 eV and 0.60 eV, for temperatures above 300° K. Activation energies for copper-doped films are 0.20 eV and 0.42 eV. These are in agreement with the acceptor levels found by Blanc, Bube and Rosi[5] for copper-doped bulk GaAs. The activation energy being equal to the acceptor level to valence band energy suggests that there are fewer available holes for conduction than there

are donor impurities present. This agrees with our observation of the unintentionally doped films being n-type.

Annealing was made at temperatures of 400° C and 700° C. Films annealed at 700° C for 24 hours were observed to evaporate, either through dissociation or through reaction with residual impurity gases. Films annealed at 700° C for two hours and four hours did not evaporate. Films annealed at 400° C did not evaporate. Time did not permit Hall measurements to be made on these films. Their resistivities were observed to have increased. It is considered that this approach of post-deposition annealing in arsenic should be investigated much more fully in future research.

3. Optical Absorption Measurements

Optical absorption edge measurements for undoped films have shown that the edge occurs at values ranging from 1.5 to 2.0 eV. These measurements were made with a Cary 14 Recording Spectrophotometer. A reduction of the data is still being made.

C. GALLIUM ARSENIDE FILMS EVAPORATED ON SINGLE-CRYSTAL SPINEL SUBSTRATES

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1. Objective

Since spinel (Mg O. Al_2O_3) is a convenient insulating material and has the same structure as gallium arsenide (face-centered cubic), it provides a suitable substrate for investigating single-crystal, high-resistivity films, even though it has a much greater lattice constant, 7.99 Å compared with 5.65 Å for GaAs.

2. Film Structure

Mechanically polished substrates of both [100] and [111] oriented spinel were provided by the M.I.T. Insulating and Optical Crystal Growth Facility. After mechanical polishing, the substrates were either cleaned by conventional methods of rinsing in distilled water and isopropyl alcohol, or were chemically polished. Some experimentation was

necessary to find the best etchant and the conditions to obtain a good chemical polish. Heated potassium hydroxide gave complete corrosion. Orthophosphoric acid, H_3PO_4, heated to 200° C gave a good polish of [100] surfaces after 10 minutes immersion. The immersion time was reduced to 5 minutes for [111] surfaces since etch pits appeared after this time. At 280° C, [111] surfaces were strongly etched after several minutes in H_3PO_4.

Gallium arsenide films were evaporated onto the spinel through both square and clover-leaf shaped masks. For substrate temperatures between 400° C and 500° C, the films generally showed strong texturing over most areas but with some regions having only randomly oriented crystallites, when examined by reflection electron diffraction. At 500° C there was an increase in crystallite size, but numerous extra reflections, presumably from free gallium, were present.

Some [110] orientation at 450° C has been observed on a [100] spinel face which was mechanically polished and cleaned. Reflections from [111] and [333] planes were also present. [110] texturing has not been observed on a chemically polished surface. X-ray diffractometer measurements show the underlying films to have [111] texturing, with some reflections from the hcp modification. A more recent evaporation on [100] and [111] spinel substrates at 650° C has shown the formation of strongly textured films.

3. Electrical Transport Properties

The films are semi-insulating, being of the order of 10^6 ohm-cm, which is consistent with the high substrate temperatures used. They are also photoconductive. An interesting photovoltaic effect has been observed in that potentials of 2 to 3 volts are generated when the films are illuminated by white light from a tungsten source of approximately 50 mW/cm^2. The spectral response has not yet been measured. The effect is apparently due to barriers existing between different regions of the films. The film surfaces have generally two distinct regions: highly reflecting, having the same appearance as films on amorphous substrates at lower temperatures; and duller grey regions considered to be associated with wurtzite GaAs. The photovoltages measured with a Keithley 601 electrometer are generated between electrodes contacting the two regions, with the grey region being positive.

An attempt was made to establish an upper bound to the value of Hall mobility of these films by using a d-c method. A Van der Pauw method was employed with a square sample geometry. The sample current was obtained from a 22.5-volt battery and the positions of the Hall voltage contacts adjusted until the unbalance voltage was less than 150 millivolts. This voltage was measured with a Keithley 601 electrometer which, along with the sample, was allowed to stabilize over a period of several days. From the film resistivity and thickness it was calculated that a change in the unbalance voltage of 15 millivolts would represent a mobility of 1 cm^2/sec. On applying a magnetic field of 10K Gauss, a change of 5 millivolts was detected which was independent of field direction, indicating only magnetoresistance. It was concluded that the Hall voltage was less than one milivolt, so that the Hall mobility is certainly less than 0.07 cm^2/volt-sec.

D. THERMOELECTRIC POWER MEASUREMENTS ON GALLIUM ARSENIDE FILMS

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1. Objectives

Since we obtained differences between the type of majority carrier in our films from those of other investigators, it was decided to improve our thermoelectric power apparatus to provide more accurate measurements of the value of thermoelectric power, as well as its polarity.

2. Thermoelectric Power Measurements

Apparatus has been constructed for the measurement of thermoelectric power of thin films having resistances up to 10^{11} ohms over the temperature range 25°C to 200°C. The films have evaporated aluminum electrodes and contact is made to aluminum wire leads by means of aluminum blocks. One of these blocks has a small heater inserted, while the other makes good thermal contact with a much larger block forming the base of the apparatus. Heating the base raises the temperature of the whole assembly, and hence the film temperature. Then by applying a very small amount of power to the small heater, a differential

temperature of a few degrees centigrade can be applied between the ends of the film. The thermoelectric voltage is then read with an electrometer. When a steady voltage is obtained, the differential temperature is read by moving a thermocouple to make contact with the smaller heated block.

Copper-doped, p-type, films have thermoelectric powers which increase with temperature from 130 microvolts/^{o}K at 25^{o}C to 435 microvolts/^{o}K at 150^{o}C. Undoped, n-type, films have thermoelectric powers of approximately 15 microvolts/^{o}K which is constant over the temperature range 25^{o}C to 200^{o}C. However, one of the n-type films measured changed to p-type after cycling to 200^{o}C several times with a correspondingly higher thermoelectric power.

A paper discussing this research on thermoelectric power measurements and correlating the results with activation energy measurements on films having copper, tin and zinc doping, is being prepared for possible publication in the future.

E. INSULATING SUBSTRATE TEMPERATURE MEASUREMENTS

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Although substrate temperature is a critical parameter in thin-film deposition, the conditions of its measurement are sometimes overlooked. A brief subsidiary study has been undertaken to investigate the influence of thermocouple wire diameter and method of attachment to insulating substrates. Chromel-alumel wires of diameters from 0.0005 in. to 0.010 in. have been used. These were attached to 2 in. x 1 in. x 1 mm. quartz substrates by using fused quartz cement supplied by Thermal American Fused Quartz Co. The substrates were heated by being in contact with a stainless steel heater block. To ensure as much isolation of the substrate from thermal conduction as possible, the substrate was supported on small ceramic pillars placed at the corners. A comparison was made between measurements for the following cases: (1) thermocouple junctions imbedded in the substrates, close to the surface; (2) junctions

contacting the surface, but with the connecting wires free, and (3) junctions plus a length of the connecting wires in contact with the surface. The results of this study showed that both the method of attachment and wire size are important, but wire size is more critical. For temperature measurement on quartz substrates it was found that accurate and consistent results are only obtained for wire sizes below 0.005 in. For this case, method of attachment to the substrate was found to be relatively unimportant.

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G. PUBLICATIONS OF THE PROJECT

1. Current Publications

a. Reports

"Thin-Film Active Device Investigations," Part II, Status Report ESL-SR-337, January 1968.

"Investigation of Coincident Radio-Frequency Drive for NDRO in Thin-Film Memories," Final Report ESL-FR-361, September 1968.

b. Technical Papers

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Nicol, W. S., "Two-Source Evaporation of Uniform Thickness Gallium Arsenide Films." (To be published in August 1968 issue of Review of Scientific Instruments Notes.)

2. Past Publications

a. Reports

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