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Bismuth-Antimony Thermojunctions¹

by DAVID C. KANE²

Abstract. High purity bismuth and antimony were deposited by evaporation under high vacuum in separate processes onto glass substrates to form thermojunctions. Substrate cleaning methods, and means of attaching leads are mentioned. Measurements of the thermal emf produced are mentioned. Measurements of the thermal emf produced are discussed. Devices for regulating and measuring the temperature of the substrate in order to find the emf-temperature relationship of Bi-Sb thermojunctions are also discussed.

INTRODUCTION

This study was undertaken as a preliminary investigation of the relationship between thermoelectromotive force and temperature of a thermojunction, and also as an opportunity to develop procedures, methods, and techniques for further investigations in metallic films and vacuum techniques. This project is one of the several in progress at St. Ambrose College which are intended to develop techniques and experiments in vacuum work which can be duplicated on a secondary school level with a minimum of expense.

Theoretically (1), the thermal emf versus temperature relationship for a thermojunction is parabolic, while thermoelectric power versus temperature is a linear function.

To obtain the junctions, bismuth and antimony were evaporated in separate processes in electrically heated helical crucibles of molybdenum, and deposited as thin films on glass microscope slides within an evacuated pyrex bell jar. The degree of vacuum necessary for evaporation was such that the mean free path of the vapor molecules was greater than the diameter of the vacuum chamber (2). The degree of vacuum used was approximately 10^{-3} mm of mercury.

METHODS AND MATERIALS

Vacuum System

The main components of the vacuum system used were: (1) a pyrex bell jar 14 inches in height and 15 $\frac{3}{8}$ inches outside diameter, (2) a steel pump plate with eight holes for feed-throughs and accessories, (3) a "Cenco" megavac fore pump, (4) a "Con-

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³ A good explanation of the term "resistance per square" may be found in Reference 4 under Literature Cited.

⁴ A good introduction to thermoelectric units may be found in the first reference cited.

solidated Electro Dynamics Corporation VMF-20" oil diffusion pump, (5) a Pirani pressure gauge and a discharge gauge, and (6) an electrical circuit for varying the voltage across the heating element.

Substrate Cleaning

Both in the literature of metallic evaporation (3) and experimentally, it was found that the proper cleaning of substrates greatly improves the tenacity of metallic films to the glass microscope slides. Therefore, various methods of cleaning were tested. They included the use of commercial detergents, various acidic solutions, and alcohols. Methods of cleaning the slides were judged according to the adhering properties of the films that were later deposited. Best results were obtained when the slide was dipped into hot (50°C) chromic acid, thoroughly rinsed, first with distilled water and then with methanol, and finally, was dried in a stream of hot air.

Electrical Contacts

In order to make electrical measurements of the metallic films, electrical contacts had to be established and leads connected to the films. In the preliminary work with the first Bi-Sb junctions produced, copper strips were simply clamped to each end of the substrate for contacts in order to determine non-quantitatively whether or not a thermal emf was present. The least expensive method of providing leads which has proven to yield good electrical contact consisted of fastening squares of aluminum foil (2.5 cm x 2.5 cm) to each end of the substrate with a commercial adhesive, "E-POX-E" cement. Low resistance wire was then wrapped around each end over the foil ten or twelve times. Copper leads were soldered to the wire in such a way that the solder flowed over the leads and onto the aluminum foil. The metallic films were evaporated over the connections.

A more refined method is being tested now in which gold is first sputtered onto each end of the substrate. Then leads are placed over the gold and covered with a silver preparation purchased from the Electrochemical Division of E. I. du Pont de Nemours & Co., Inc. The substrate is fired in an oven at 1300°F to solidify the silver preparation. The bismuth and antimony are evaporated so as to overlap the sputtered gold films.

Several other methods were found in the literature but were rejected for various reasons. One, utilizing liquid gold or platinum and silver paste (4), was too expensive to attempt. Another elaborate method, which involved drilling conical holes in the substrate in which small spheres of platinum were to be placed (5), was rejected as impractical with the available equipment.

Film Thickness

Thermoelectricity literature reveals that the thermal emf varies with film thickness. The thermal emf decreases as the layer thickness increases.(6) Therefore, an attempt was made to control and determine the thickness of the films used. To control the film thickness, the substrate was monitored during evaporation of the metals in order to deposit each layer to a predetermined resistance per square value³. A formula (7) given in the literature was used to determine the desired resistance. However, satisfactory results were not obtained by this method due to an uneven coating of the metallic film.

A second method that was considered as a possible way of determining metal thickness involved weighing the slide before and after evaporation of each metal, and then dividing the weight increase by the surface area covered by the metal. Since the density of each metal is known, the thickness could then be calculated(8). This method was found to be unsatisfactory, because the metal layers deposited were not of uniform thickness. Therefore, thermal emf's were measured for several undetermined film thicknesses, and the results were evaluated separately.

Temperature Control and Measurement

Three techniques for controlling the temperature of the thermojunctions were used. The first consisted of mounting a simple heater, made by wrapping nichrome wire around a glass slide, immediately below the thermojunction. Since air currents in the room caused the temperature to fluctuate, the apparatus was enclosed with cardboard. The temperature readings then remained constant for a given heater current. However, when the position of the heater was changed with respect to the junction, the values for thermoelectric power of the thermojunction changed drastically, indicating false temperature readings with this method. Therefore an oven was constructed from a container, and the injunction and temperature indicator were mounted inside.

An iron-constantan thermocouple was calibrated to determine the temperature of the junction. At first it was attempted to calibrate the thermocouple with a microammeter. However, a temperature difference of 100 C° yielded only five microamperes. Therefore, this circuit was discarded as not sufficiently sensitive. Consequently, the thermocouple was calibrated with a reflecting galvanometer. This method has been satisfactory.

An iron-constantan thermocouple was chosen because it is characterized by a relatively high emf and is comparatively in-

expensive. Also, its emf-temperature curve is nearly a straight line within the temperature range used (25° - 150° C). Therefore, the calibration can be determined by emf measurements at only a few known temperatures. (9)

Emf Measurements

Thermal emf measurements were made at various temperatures in the range of 25° C to about 150° C by a Leeds & Northrup Student Potentiometer and its associated circuit. A potentiometer circuit is only as sensitive as the galvanometer used to indicate null points. When a Weston galvanometer was used, a sensitivity of only 15 to 20 microvolts could be achieved. Therefore, a General Electric reflecting galvanometer was used instead of the Weston. This increased the sensitivity to several microvolts.

RESULTS AND DISCUSSION

A typical thermojunction produced a thermal emf varying from zero to 725 microvolts for the small temperature range used. This junction had an average thermoelectric power of 20 microvolts/ $^{\circ}$ C.⁴ For another junction the thermoelectric power was found to average only 0.6 microvolts/ $^{\circ}$ C. The thermoelectric power varied from one junction to another due to a great difference in film thickness.

To test completely the theoretical prediction of parabolic shapes for the emf versus temperature curves, a greater range of temperature would be needed than that which was obtained with the equipment used. In individual graphs, the emf always increased when the temperature was raised—these curves could be thought of as the rising portions of parabolas.

The ideal method to determine this relationship is to take the thermal emf measurements and temperature measurements while the junction is still mounted in a vacuum chamber. This would eliminate possible aging effects which could result from oxidation when the junction is exposed to the atmosphere. This procedure could not be used in this project because some of the equipment used was not portable.

It is hoped that this preliminary groundwork will be of assistance to anyone interested in determining more precisely the thermoelectric characteristics of thin metal films.

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A Simple Transistor Characteristic Curve Tracer

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Abstract. A simple, inexpensive circuit for displaying the grounded emitter characteristic of transistors on a cathode ray oscilloscope is described. It is designed as a demonstration unit. With a calibrated oscilloscope, quantitative information can be obtained suitable for laboratory experiments.

The characteristic curve tracer to be described here was developed to permit the immediate examination of an entire family of transistor curves on an oscilloscope. Six characteristic curves are displayed. Each represents the range of collector current as a function of emitter-collector voltage for a particular base current. The simplicity of the circuit makes it a very instructive demonstration unit.

The curve tracer may be divided into three parts: (1) the collector-emitter sweep voltage, (2) the base drive generator, (3) the oscilloscope. The transistor is operated as a grounded emitter amplifier. The grounded emitter configuration is an important type of circuit: it is the most commonly used in amplifiers, and the parameters of transistors used in this circuit are published in transistor handbooks.

R_1 , the load resistor, has a voltage drop proportional to the collector current and this signal is applied to the vertical input of the oscilloscope. R_2 is the base limiting resistor. Since the maximum base and collector currents for a particular transistor can be found in a transistor handbook, and the voltage that will be applied is known, R_1 and R_2 may be determined by Ohm's law. For the TI492 NPN transistor, I_1 , 2.2K and 56K were used

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