

Positive-Ion Bombardment of Germanium and Silicon*

SUMNER P. WOLSKY

Research Division, Raytheon Manufacturing Company, Waltham, Massachusetts

(Received July 1, 1957)

A very sensitive vacuum microbalance has been used to study the sputtering of germanium and silicon by argon ion bombardment. Current densities of 1 to 12 $\mu\text{a}/\text{cm}^2$ were used.

The rates of sputtering of these materials were observed as a function of ion energy. A sputtering threshold energy of 46 eV was determined for germanium. The bombardment data are discussed in terms of the nature of the target surface. Oxidation data at 3 mm oxygen pressure are offered as evidence of the cleanliness of the bombarded surface. Approximately 10^{15} argon atoms/cm² were trapped or adsorbed by the target during the bombardment process.

I. INTRODUCTION

FOR investigations of many of the basic properties of solid surfaces to be meaningful, it is necessary to study surfaces which are atomically clean and reproducible. Those interested in the surface properties of germanium and silicon have attempted to satisfy these requirements by bombardment of the surfaces with positive ions in very high vacuum. As a result, considerable interest has been aroused concerning the sputtering of these materials with positive ions and much discussion has been carried on concerning the nature of the surfaces produced.

While studying the oxidation kinetics of germanium and silicon, using a very sensitive vacuum microbalance, it became apparent that the experimental method in use at that time could readily be adapted to an investigation of the physical sputtering of solid surfaces. An investigation of the sputtering of silicon and germanium by positive-ion bombardment was then undertaken, since there was considerable interest in this application of the microbalance technique, as well as in the sputtering data. The experiments were carried out using the apparatus as it was originally set up for the kinetic studies and some of the data were actually obtained in the process of preparing for oxidation measurements. Consequently, it is probable that the system could be improved upon if it were to be used solely for bombardment investigations. The oxidation data, however, have provided additional information as to the cleanliness of the surfaces produced by the bombardment.

Direct weighing methods have been used by others to determine rates of sputtering. Guenther-schulze and Meyer¹ suspended a sample from a spring balance and followed the extension of the spring as an indication of weight losses caused by bombardment. Others² have made use of ordinary analytical balances to weigh samples immediately following ion bombardment. In general these workers have not had sufficiently sensitive weight-determining methods or the extremely pure discharge conditions necessary for work in the

low current-density region. With the apparatus used in this investigation, however, it has been possible to obtain efficient sputtering with current densities of 1 to 12 $\mu\text{a}/\text{cm}^2$.

The positive-ion bombardment of germanium and silicon, although used widely to prepare clean surfaces of these materials, has not been studied to any great extent. Measurements with inert gas ions³ showed yields of one atom of germanium sputtered per 100 incident ions at 400 eV, and a threshold for sputtering of about 40 eV for an incident angle of 30°. The rather low yields were attributed to probable surface contamination. Using an empirical law, Wehner⁴ has predicted threshold energies of 49 eV and 27 eV for germanium and silicon, respectively, for the normal incidence of argon ions on targets of these materials. He also found experimentally thresholds of 40-50 eV for germanium and 60-70 eV for silicon upon bombardment with the heavy mercury ion.

II. EXPERIMENTAL

All measurements were made with a quartz microbalance with which weight differences of 0.15 μg could be detected reproducibly. A schematic representation of the balance, similar to that used by Gulbransen and Rhodin,⁵ is shown in Fig. 1. The precision-made

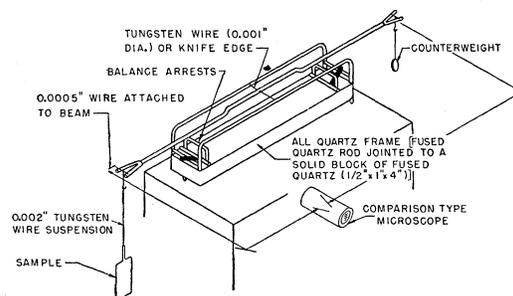


FIG. 1. Schematic diagram of quartz microbalance.

³ R. E. Honig, Bull. Am. Phys. Soc. Ser. II, 2, 34 (1957).

⁴ G. K. Wehner, Phys. Rev. 102, 690 (1956).

⁵ T. N. Rhodin, in *Advances in Catalysis* (Academic Press, Inc., New York, 1953), Vol. 5, pp. 40-114. See also E. A. Gulbransen, in *Advances in Catalysis* (Academic Press, Inc., New York, 1953), Vol. 5, pp. 120-174.

* This work has been partially supported by the Bureau of Ships.

¹ A. Guenther-schulze and K. Meyer, Z. Physik 62, 607 (1930).

² J. F. Strachan and N. L. Harris, Proc. Phys. Soc. (London) B69, 1148 (1956).

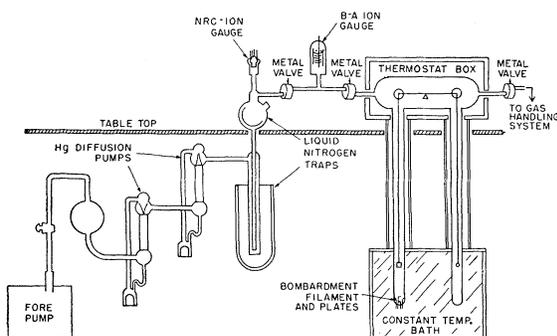


FIG. 2. Vacuum microbalance system.

quartz beam (0.075 in. diameter) is supported on a 0.001-in. tungsten wire. The end supports are 0.005-in. tungsten wire. The wires are joined to the beam and quartz frame with fused silver chloride. Iron cores sealed in small quartz sections allow external manipulation of the balance arrests by means of a small magnet. Static charge effects are eliminated by a ground connection to a conductive coating of platinum or gold evaporated onto the balance. Weight changes are followed from observation of the deflection of the beam ends. The images of the beam ends are projected with 90° prisms onto the fixed scale in the eyepiece of a comparison-type microscope. The balance is calibrated by measuring the deflection from an observed zero point caused by known weight differences. Buoyancy effects were less than the sensitivity at all pressures used.

The vacuum microbalance system is represented schematically in Fig. 2. The balance was enclosed in a Pyrex case which was connected through a double liquid-nitrogen trap with two mercury diffusion pumps (Nottingham type) working in series. After a bakeout of 12–24 hours, a vacuum of 5×10^{-10} mm was obtained, using the Westinghouse WL5966 Bayard Alpert

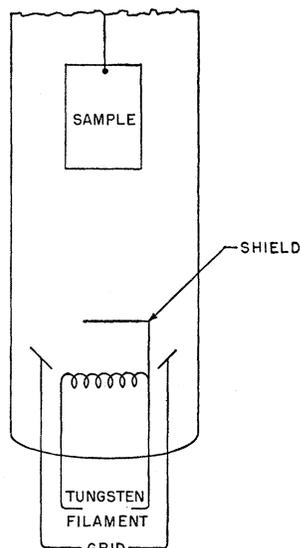


FIG. 3. Bombarding apparatus.

ionization gauge. The bakeout temperature was limited since fused silver chloride exhibits plastic flow at about 300°C. Molybdenum getters (not shown on the schematic diagram) were used to reduce further the partial pressure of impurity gases.

The sample was placed twenty-two inches below the balance beam by means of a 0.002-in. tungsten wire suspended from the beam-end cross wire. The specimen faces were parallel to the enclosing hang-down tube sides. The sample was heated with a small external heater which fitted around the hang-down tube. The use of quartz tubing in the sample region allowed temperatures of up to 1000°C to be maintained. The samples were given a post-bakeout outgassing at 700°C for at least one hour prior to any experiments.

Provisions were made for positive-ion bombardment. A tungsten filament and two molybdenum plates were mounted on a standard four-pin tube base and sealed into the bottom of the sample hangdown tube (Fig. 3). A

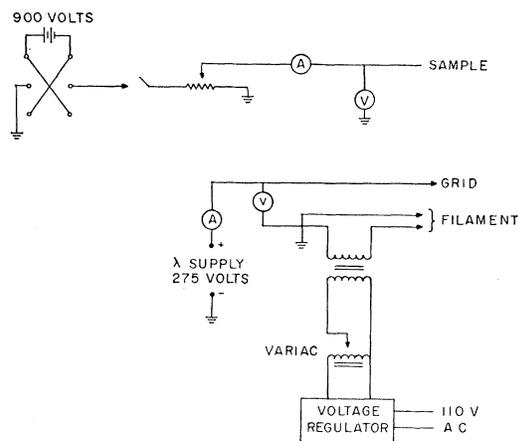


FIG. 4. Circuit diagram.

metallic shield was placed above the filament to prevent evaporated tungsten from depositing on the sample. The distance from the filament and grid plates to the sample was approximately 10 cm. All metal parts were thoroughly outgassed prior to use. Linde mass-spectrographically pure gases were allowed to remain in a liquid-nitrogen trap for at least one half hour before being passed over a freshly flashed molybdenum getter into the microbalance system. The pressure prior to admitting the inert gas was usually 10^{-9} mm. All bombardments were at a static pressure of 10^{-3} to 10^{-4} mm of the inert gas.

The schematic diagram of the circuit used with this apparatus is shown in Fig. 4. With the grid plates +275 volts, an electron current of 10–50 ma was drawn by varying the emission of the filament. Potentials of up to 850 volts with respect to ground, were placed on the sample through the balance ground connection. The balance beam was arrested during the experiments. The bombardments were at constant voltage and ion

TABLE I. Summary of bombardment data for germanium.

Sample voltage	Current density $\mu\text{a}/\text{cm}^2$	Bombard. time sec	Total bombarding charge (10^{-3} coulomb)	Prior to heating μg	Weight losses Due to heating μg	Total μg	Rate of sputtering ($10^3 \frac{\mu\text{g}}{\text{coulomb}}$)	Yield $\frac{S}{1+\gamma}$	Sample designation
500	8.3	600	78.2	58.1	0	58.1	0.743	0.988	A-1
700	9.6	1500	225.0	165.3	0	165.3	0.735	0.973	A-2
500	11.8	300	45.0	13.3	0	13.3	0.296	0.391	B-1*
500	11.8	360	54.0	42.1	0.5	42.6	0.789	1.05	B-2
500	11.8	360	54.0	42.8	0	42.8	0.793	1.05	B-3
500	11.8	180	27.0	22.7	0.842	1.11	B-4
100	2.0	1020	25.4	5.89	7.29	13.2	0.523	0.692	D-1
50	1.2	900	10.8	<0.15	0.0	...	D-2
700	5.13	720	48.0	38.8	0.808	1.07	D-6
450	7.17	360	33.6	25.9	0.02	25.9	0.771	1.03	D-7
250	2.39	600	18.6	11.0	0.589	0.786	D-8
80	0.89	780	9.0	1.74	0.51	2.25	0.250	0.331	D-9
62	0.85	1080	12.0	3.10	0.258	0.343	D-10
90	0.82	1200	13.8	5.7	0.413	0.549	D-11

* Sample B—white oxide visible on surface.

current conditions, with the ion current being adjusted by varying the filament emission. Ion currents and voltages were read with a Keithley electrometer. After bombardment, the sample was baked at 450°C for one half-hour in order to remove any gas which was adsorbed or trapped by the sample during the bombardment process. Weight changes were recorded at several stages of the bombardment process.

Single-crystal material was used in all experiments. The germanium samples were (100)-oriented. The orientation of the silicon sample was unknown. All specimens were chemically etched with CP-4⁶ to remove at least 0.005 in. from each face. The final sample plates were 0.002 to 0.004 in. thick and weighed approximately 0.3 gram. Geometric sample areas were 10 to 15 cm^2 . This was ten to one-hundred times the area of a spherical counterbalance made of the same material as the sample plate and matched to within 10–100 μg of the weight of the plate.

III. RESULTS

In order to obtain significant results in a low-pressure discharge such as ours, it is necessary to satisfy the following conditions. (1) The rate of ions striking the target surface must be greater than the rate of surface poisoning by adsorption of impurities from the environment. This condition concerning the cleanliness and purity of the system is discussed in a later section. (2) The mean free path of the bombarding ions (λ_i) must be greater than the thickness of the positive-ion sheath (d_i) so that energy is not lost by collisions in the sheath region. In our experiments, it was found that λ_i was greater than d_i (calculated from the Langmuir-Childs space-charge equation). In addition, in the low-energy region (<100 volts) the target dimensions (D) were greater than d_i , while in the higher energy region, $D \geq d_i$ in all but one instance (sample D-6).

⁶ A mixture of 15 cc glacial acetic acid, 25 cc concentrated nitric acid, 15 cc of 48% hydrofluoric acid and 0.3 cc bromine.

Therefore, it is possible to conclude that the ion energies were well defined and that the incidence of the ions was predominantly perpendicular to the target surface. The reliability of the sputtering data at ion energies of 500 ev is further evidenced by the observed independence of yield and current density (Fig. 8).

It should be added that in any refinement of this technique for even lower current-density measurements (as may be desirable for surface investigations), attention should be given to the relative magnitudes of λ_i , d_i , and D .

Summaries of the data obtained for germanium and silicon are presented in Tables I and II. Graphs of the rates of sputtering vs sample voltage are shown in Figs. 5–7. The germanium experiments were carried out over a wider range of voltages than the silicon. The silicon measurements were made on one sample and have not yet been extended to the threshold region. Most bombardments were of 10–20 minutes duration. Total observed weight changes ranged from 1.0 to 165 μg , with the average being 20–40 μg , or at least 120–240 times the sensitivity of the balance. There was an uncertainty of as much as 5% in some of the silicon sample voltages. Current densities varied from 0.8 to 12 $\mu\text{a}/\text{cm}^2$. Since the secondary electron contribution to the measured ion current was not determined, the yield is given as $S/(1+\gamma)$, where S is the number of atoms sputtered per impinging ion and γ is the number

TABLE II. Summary of bombardment data for silicon.

Sample voltage	Current density $\mu\text{a}/\text{cm}^2$	Bombard. time sec	Total bombarding charge (10^{-3} coulomb)	Prior to heating μg	Weight losses Due to heating μg	Total μg	Rate of sputtering ($10^3 \frac{\mu\text{g}}{\text{coulomb}}$)	Yield $\frac{S}{1+\gamma}$
350	4.02	270	16.2	5.7	0.355	1.22
850	6.67	300	30.0	15.4	0.515	1.78
525	3.41	390	51.0	19.3	0.379	1.30
775	5.93	840	89.0	40.7	0.0	40.7	0.458	1.57
825	4.00	600	60.0	28.1	0.468	1.61

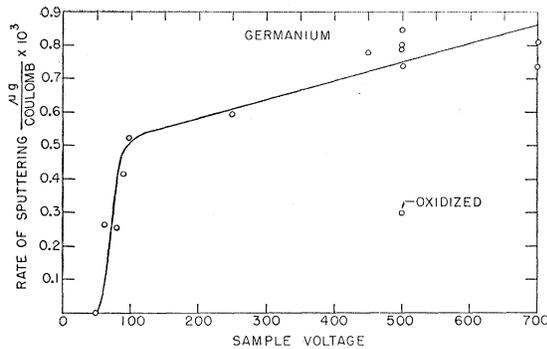


Fig. 5. Rate of sputtering vs sample voltage for germanium.

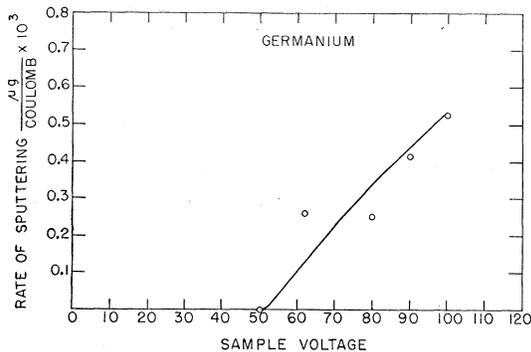


Fig. 6. Rate of sputtering vs sample voltage for germanium (low-energy region).

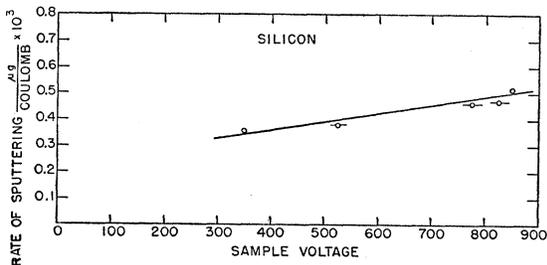


Fig. 7. Rate of sputtering vs sample voltage for silicon.

of electrons emitted per ion striking the sample. For clean target surfaces, γ usually is of the order of 0.2 and, as an approximation, may be considered to be independent of the ion energy in the range covered by these experiments.⁷ As calculated from the measured ion currents, 10^{16} – 10^{17} ions were generally involved in the bombardments.

The samples were generally of the same approximate shape and size, and their positions in the hang-down tube were also identical. The balance was arrested during the bombardment process. Owing to the relative position of the filament, grid, and sample and the existence of a low plasma density, the plasma potential could not be accurately predicted. Fortunately, experimental determination of the plasma potential is

⁷ H. D. Hagstrum, *Phys. Rev.* **96**, 325 (1954).

possible by means of a retarding potential plot. Such measurements, using the sample as a probe, indicated a space potential in these experiments of -4 volts (with respect to ground).

IV. DISCUSSION

The data for both germanium and silicon show the rates of sputtering of these materials to vary linearly with voltage in the range above 300 volts. This relationship is in agreement with the observations of others^{2,8} and appears to hold for the sputtering of almost all materials, up to ion energies of several thousand volts. The sputtering rate is also observed to be greater for the larger atomic-weight material, germanium, but is not proportional to the atomic weight of the target material at the ion energies used here. The germanium plot reveals a sharp drop in rate in the region of 100 volts with no measurable sputtering below the corrected critical value of 46 volts. The threshold of 46 volts as determined in this work may be compared with that of 49 volts predicted by Wehner for normal incidence of argon ions on germanium targets.

The very low current-density measurements provide some interesting observations of possible value in understanding sputtering mechanisms. Because of the low density of ions arriving at the surface, it is very unlikely that more than one ion is involved in the removal of one atom. For example, at a current density of $5 \mu\text{a}/\text{cm}^2$, each surface atom would receive an ion impact on the average of every 33 seconds. Consequently, for bombardment in a uniform plasma, one would expect the sputtering yield to be independent of current density. This is shown for germanium at an ion energy of 500 ev (Fig. 8). In addition, the yield value of one indicates that either almost every ion collision is successful in removing a surface atom, or that more than one atom is removed per ion impact.

A careful analysis of the data provides considerable information relative to the germanium and silicon surfaces used in these experiments. Studies with metals have shown the nature of the target surface

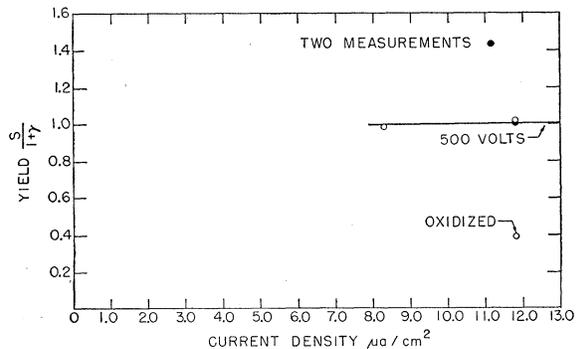


Fig. 8. Sputtering yield vs current density for germanium.

⁸ H. Massey and E. Burhop, *Electronic and Ionic Impact Phenomena* (Clarendon Press, Oxford, 1952).

to have a marked effect upon the rate of sputtering. Such materials as aluminum which form strongly bound oxide layers have been found to have very low sputtering rates prior to removal of the surface oxide.⁸ This effect has been illustrated quite strongly by experiments with a germanium sample (B-1) which gave visual evidence of considerable oxidation. In that instance, the rate of sputtering was at most one-third that of the nonoxidized surface; that is, assuming the surface to be GeO_2 , at least three argon ions were required per GeO_2 removed. That the oxide film was removed, even at these low current densities, was indicated by subsequent bombardments (B-2, B-3, B-4) having yield values comparable to those obtained in other experiments at the same ion energy, by the independence of yield and current density, and also by the proportionality between the weight of germanium sputtered and the number of coulombs involved in the sputtering process (Fig. 9).

It is significant that the proportionality illustrated in Fig. 9 existed for experiments of 3 to 10 minutes duration at current densities of 7 to 12 $\mu\text{a}/\text{cm}^2$, even though our procedure included no removal of initial surface layers prior to bombardment. From this fact and from the independence of sputtering yield and current density, it is possible to conclude that: (1) The rate of formation of impurity layers due to either reaction with impurities in the gaseous environment or impurities diffusing to the surface from the bulk of the sample was small, (2) The sample surfaces were essentially reproducible from experiment to experiment (usually a period of 6–24 hours in very high vacuum),

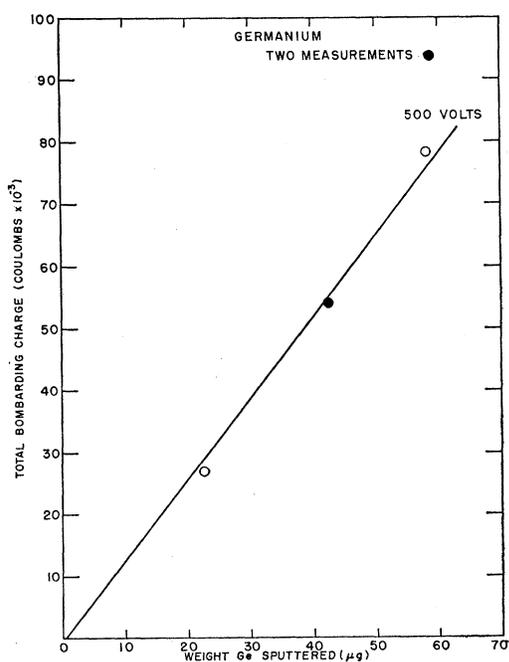


FIG. 9. Total bombarding charge vs weight Ge.

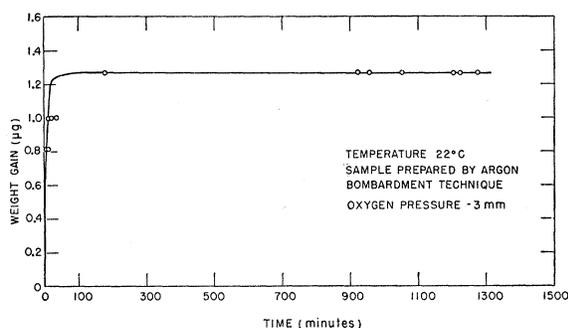


FIG. 10. Oxidation of germanium at 3 mm pressure.

and (3) The removal of adsorbed gas impurity layers by ion bombardment was relatively simple.

Further information concerning the nature of the surfaces produced in these experiments is provided by oxidation data⁹ obtained immediately following several of the bombardments. A plot of weight gain vs time is presented in Fig. 10 for a typical oxidation at 3 mm oxygen pressure. The oxidation kinetics are similar to those expected for monolayer adsorption. An average of three experiments at 3 mm oxygen pressure gave an equilibrium value of $(1.7 \pm 0.2) \times 10^{15}$ oxygen atoms/ cm^2 or 2.7 ± 0.3 monolayers of oxide. This is in general agreement with the oxidation data obtained by workers using powdered samples prepared by crushing in vacuum.¹⁰ On the basis of the oxidation and bombardment experiments, it is possible to assume that the surfaces prepared here by argon ion bombardment were clean to some fraction of a monolayer of oxygen.

Experimenters using the argon-ion bombardment technique with germanium have noted a sharp increase in the system pressure on post-bombardment heating of the sample.¹¹ This has been taken to indicate the presence of argon atoms either adsorbed or trapped on or below the sample surface. Such trapping has been found to occur for metals as a function of ion energy.¹² For example, for 10^{16} – 10^{17} argon ions striking a tungsten surface at 400 ev, about 8×10^{13} atoms were trapped; at 700 ev, 2×10^{14} ; and at 5000 ev, about 9×10^{14} atoms, or almost enough to form one surface layer. On the basis of such work one would expect 10^{14} – 10^{15} argon atoms to be trapped by the germanium at the ion energies used here. The limit of detection of our apparatus, based on the sensitivity of the balance, was 2.2×10^{15} atoms or about 0.1 liter-micron of argon.

⁹ A more complete discussion of the oxidation data is to be published elsewhere.

¹⁰ M. Green and J. Kafalas, in *Semiconductor Surface Physics* (University of Pennsylvania Press, Philadelphia, 1957), pp. 349–361.

¹¹ R. E. Schlier and H. E. Farnsworth, in *Semiconductor Surface Physics* (University of Pennsylvania Press, Philadelphia, 1957), pp. 3–22.

¹² J. H. Leck (private communication). Work is being published by Butterworths Press following conference at the University College of North Staffordshire.

The microbalance measurements on post-bombardment heating of germanium and silicon have generally shown at most about 5×10^{14} trapped argon atoms/cm², or less than one atom per surface atom. There are, however, occasional exceptions (*D-1*), when as many as 10^{16} argon atoms appear to have been trapped during the sputtering process. It is difficult to explain these exceptions. It is possible that something other than argon, either in the form of bulk or surface impurities, is being removed by the heating.

V. CONCLUSION

The vacuum microbalance has been shown to be a very useful tool for investigations of the phenomena of sputtering with positive ions. The extreme sensitivity of the apparatus is especially valuable for studies in

the threshold region. Bombardments at low current densities and short time intervals should provide considerable information concerning the nature of the target surface and also contribute to the understanding of the basic processes involved in sputtering.

In this work the microbalance studies have enabled us to establish criteria of the reproducibility and cleanliness of the ion-bombarded surfaces prior to subsequent adsorption or kinetic studies.

ACKNOWLEDGMENTS

The author is indebted to Dr. S. Aisenberg and Mr. A. Fowler for their helpful discussions and to Mr. L. Rubin for his assistance with instrumentation problems. The continued aid of Mrs. P. M. Rodriguez is also acknowledged.

Galvanomagnetic Effects in *n*-Type Indium Antimonide*

H. P. R. FREDERIKSE AND W. R. HOSLER
National Bureau of Standards, Washington, D. C.
(Received August 12, 1957)

The magnetic field dependence of the magnetoresistive effects and the Hall coefficient have been investigated at 78°K and at liquid helium temperatures. Results at very low magnetic field strength are in agreement with the assumption of an isotropic conduction band. Quantization of the electron orbits causes deviations from the conventional theory at large fields (of the order of a few thousand gauss and higher). Oscillations in the magnetoresistance observed at 4.2°K and lower are attributed to these quantum effects. The measured period of oscillation agrees reasonably well with theoretical predictions. An effective mass value of $0.01 m_0$ is obtained from the field and temperature dependence of the amplitude of the oscillations. The magnitude of the magnetoresistive effects appears to depend considerably on the geometry and inhomogeneity of the sample. Strong magnetic fields also influence the distribution of "free" and bound electrons, causing a freeze-out effect at temperatures of liquid helium.

INTRODUCTION

INDIUM antimonide is by far the most extensively studied member of the group of III-V compounds. There are two reasons why this semiconductor has received so much attention. First, it is rather easy to prepare indium antimonide in single crystals of a purity approaching that of the purest germanium and silicon, and second, it has striking physical properties: small energy gap, high mobility and small effective mass of conduction electrons. A number of experiments^{1,2} have now established a value of 0.23 eV for the width of the energy gap at $T=0^\circ\text{K}$. Fan and Gobeli³ reported an optical activation energy of 0.175 eV at room temperature involving direct transitions. The room temperature mobility of electrons is $65\,000\text{ cm}^2/\text{volt-sec}$,⁴ while

mobilities as high as $5 \times 10^5\text{ cm}^2/\text{volt-sec}$ have been measured in very pure samples⁵ just below 78°K. Cyclotron resonance experiments have shown that the conduction band of this material has only one minimum (at $\mathbf{k}=0,0,0$) and a very small density of states corresponding to an effective electron mass of $0.013 m_0$.⁶ The latter value is in close agreement with results from other experiments. Hall effect and conductivity data⁷ can be fitted with $m_e^*=0.015 m_0$, while thermoelectric power measurements⁸ give $m_e^*=0.014 m_0$. Burstein *et al.*⁹ have observed the cyclotron resonance at infrared frequencies in intrinsic InSb and found $m_e^*=0.015 m_0$. These values pertain only to the bottom of the conduction

* A. C. Beer (private communication). [See also Reports of the Battelle Memorial Institute (unpublished).]

⁵ Dresselhaus, Kip, Kittel, and Wagoner, *Phys. Rev.* **98**, 556 (1955).

⁷ Hrostowski, Morin, Geballe, and Wheatley, *Phys. Rev.* **100**, 1672 (1955).

⁸ H. P. R. Frederikse and Eugenie V. Mielczarek, *Phys. Rev.* **99**, 1889 (1955).

⁹ Burstein, Picus, and Gebbie, *Phys. Rev.* **103**, 825 (1956).

* Research sponsored by Office of Naval Research.

¹ R. G. Breckenridge *et al.*, *Phys. Rev.* **96**, 576 (1954).

² V. Roberts and J. E. Quarrington, *J. Elec.* **1**, 152 (1955).

³ H. Y. Fan and G. W. Gobeli, *Bull. Am. Phys. Soc. Ser. II*, **1**, 111 (1956).

⁴ H. Welker, *Physica* **20**, 893 (1954).