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THE SPUTTERING OF SURFACES BY POSITIVE ION BEAMS OF LOW ENERGY

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Silver, germanium, and germanium-silicon alloy surfaces have been bombarded with the inert gas ions Ne^+, A^+, Kr^+, and Xe^+, at energies between 30 and 400 ev. Primary beam intensities between one and ten $\mu a/cm^2$ were obtained in an oscillating electron source of the Heil type. The secondary particles sputtered off, neutrals as well as positive and negative ions, were identified and recorded in a 180 degree mass spectrometer of 5.5-inch radius. They are partly background gases adsorbed on the surface, partly atoms and molecules characteristic of the sample. Among the latter particles, neutrals were about 100 times more abundant than those emitted as positive ions. Rather low yields (about one sample atom per 100 incident ions with 400-ev energy) and relatively high threshold energies (40-50 ev for an angle of 30 degrees between beam and surface) are believed to be caused by surface contamination. Retarding potential measurements showed that over 80 percent of the particles sputtered have initial energies of less than 5 ev. After bombardment, the *Ge* and *Ge-Si* surfaces showed oval-shaped hillocks, possibly caused by appreciable carbon concentrations in the samples studied. If the effects of surface contamination can be reduced, this method promises to be useful in the analysis of solid surfaces.

Introduction

Sputtering is defined as the removal of surface particles by positive ion bombardment. Although this phenomenon has been the subject of many scientific investigations during the past 100 years, the different theories proposed to explain the mechanism of sputtering were largely based on inadequate experimental data. Recent literature surveys of this field have been made by Massey and Burhop[1] and by Wehner[2]. Using a fresh approach and improved experimental conditions, Wehner[2,3] obtained sputtering yields and threshold energies for various metals bombarded by Hg^+ ions. His work led to the interpretation, now generally accepted[4,5], that sputtering is a momentum transfer process.

In the past, most sputtering studies have employed macroscopic means, such as weighing the target, to determine sputtering rates and thresnold energies. Assumptions had to be made concerning the nature of the sputtered particles since no experimental information was available. While this author had proposed[6], in 1951, to study the sputtering process in a mass spectrometer, actual work along these lines was begun in 1954 and continued through the first half of 1955. The preliminary results obtained, already reported[7] in brief, form the subject of this paper.

It is of interest to consider in detail the parameters and quantities involved in an *ideal* sputtering experiment. In Fig. 1 is shown an idealized lattice which is under

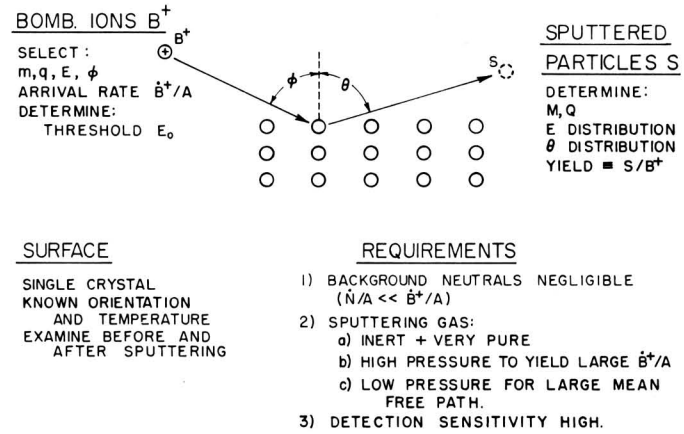

Fig. 1 - An idealized sputtering experiment.

bombardment by positive ions. The following requirements should be met:

a. The surface should be a single crystal of known orientation. Provisions should be made to heat the sample, either by direct electrical heating, R.F. heating, or electron bombardment, and its temperature should be known. It should be examined by optical and other means, before and after sputtering.

b. The bombarding ions B^+ should not react chemically with the sample atoms and should be removable from the lattice after bombardment. This limits the choice to rare gases. The ions should be selected according to their

mass m, their charge q, their kinetic energy E, and their angle of incidence ϕ.

c. For the sputtered particles S, the following quantities should be determined: their mass M and charge Q (if any); their kinetic energy distribution; their distribution in angle θ; their yield $Y = S/B^+$, i.e. the number of sputtered particles per incident ion, as a function of primary energy E. From these yield curves are obtained threshold energies E_o, which are characteristic of any given gas-surface combination, of the surface condition, and of the angle of incidence.

d. The vacuum system should be designed so that the background gas pressure is negligible. Expressed differently, the arrival rate of background gas neutrals N at the surface A should be much smaller than that of the bombarding ions ($\dot{N}/A \ll \dot{B}^+/A$).

e. The ion source should be designed so that ion current densities of several ma/cm² can be obtained at energies between 5 and several hundred ev, at a gas pressure low enough so that the mean free path is larger than interelectrode distances. The impurity content of the sputtering gas must be so low that the arrival rate of impurity neutrals is negligible compared to $\dot{B}^+/A$.

Some of the conditions enumerated above are mutually exclusive, others are hard to realize experimentally. The work to be described is admittedly preliminary since several of the requirements could not be met. Nevertheless, it constitutes a considerable experimental improvement over many of the earlier studies and has yielded some interesting new information.

Experimental

Design Considerations

While selection of the bombarding ions according to mass had been planned originally[6], this feature had to be sacrificed so that bombarding currents approaching sufficient density could be realized. Without mass selection, the surface is sputtered not only by singly-charged, but also by multiply-charged rare gas ions, as well as by impurity ions. It is well to keep in mind the potential effects of multiply-charged and impurity ions on yields, threshold energies, and lattice purity.

To obtain a clean surface, the rate of particles sputtered from the surface by primary ions should obviously exceed the combined arrival rate of background gases and impurities contained in the sputtering gas. In these experiments, spectroscopically pure gases are used with a total impurity content of less than 2×10^{-4} mole fraction[8]. The sputtering gas pressure in the source to be described lies between 10^{-4} and 10^{-3} mm Hg. Thus, during sputtering, the background pressure of adsorbable impurities will be less than 10^{-7} mm Hg. It can be shown[9] that the arrival rate of neutrals per unit area is given by $\dot{N}/A = 3.51_3 \times 10^{22} p_{mm}(MT)^{-1/2}$, where p_{mm} = pressure in mm Hg: M = molecular mass in atomic mass units, and T = absolute temperature in degrees K. For oxygen at room temperature and at a pressure of 10^{-7} mm Hg, $\dot{N}/A = 3.5 \times 10^{13}$ particles/sec-cm². To compute the minimum positive ion current density required to keep the surface clean, assume with Wehner[3] a yield $Y = S/B^+ = 0.1$ for ions of 100 ev energy and a condensation coefficient of unity. This yields $I^+_{min}/A = \dot{N}/AY = 3.5 \times 10^{14}$ particles/sec-cm², or about 5×10^{-5} amp/cm².

An adaptation of the oscillating electron source, first described by Heil[10] and used at the RCA Laboratories for some time[11] will produce ion current densities of several ma/cm² at gas pressures near 10^{-4} mm Hg. If these ions are to reach a target some distance away, the beam intensity will be limited by space charge. It can be shown[12] that for ions of mass 100, moving between plane-parallel electrodes 5 mm apart, currents at the target are limited to about 20 μa/cm² at 100 ev, and about 3 μa/cm² at 25 ev energy. To exceed these limits and, at the same time, achieve some focusing, the acceleration-deceleration scheme described below was tried and found to be suitable. In this fashion, densities of 30 μa/cm² at 100 ev, 10 μa/cm² at 25 ev, and 2 μa/cm² at 5 ev were obtainable. These densities still fall short of the desired value, especially at the lower energies, but they constitute the maximum obtainable at the time the experiments were made.

Sputtering Source

A scale drawing of the ion source is shown in Fig. 2. Electrons emitted by hot filament F_1 are accelerated by an electric field towards the center of box B_0, moving parallel to the lines of magnetic field B. They are slowed down to a stop near F_2, and are then accelerated in the reverse direction. Constrained to move along the magnetic field

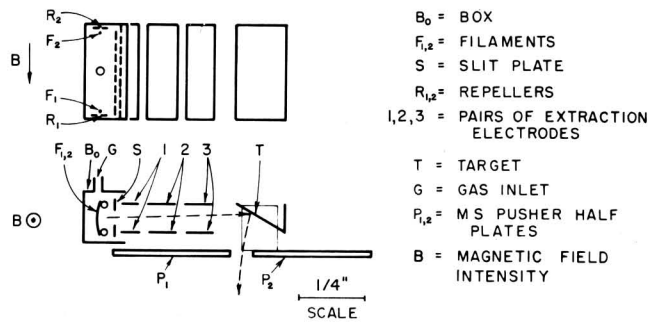

Fig. 2 - Scale drawing of sputtering source.

lines ($B \approx 2000$ gauss), the electrons perform several hundred oscillations and collide many times with the sputtering gas before they are collected on box B_0. Even though some of the ions impinge on filaments F_1 and F_2 and repellers R_1 and R_2, a considerable fraction can be drawn out transversely through slit plate S. These ions are accelerated through electrodes 1 and 2 to several hundred ev, then decelerated to the desired energy by a retarding field between electrodes 2 and 3. The electric fields are adjusted to provide optimum focusing and maximum current at target T. To compensate for the magnetic deflection of the ions, electrodes 1 and 2 are split into pairs, allowing electrostatic cross-fields to be applied. Except for the W filaments, all electrodes were made of tantalum sheet, 0.005 inches thick.

Mass Analyzer

The 180 degree mass analyzer had been designed to utilize fully an electromagnet of 15 inch pole face diameter and 2 inch pole gap. Details of the stainless steel tube and of the demountable source and collector ends are shown in Fig. 3. The mass spectrometer ion source has been described before [13]. As indicated in Fig. 2, the sputtering source was mounted on one of the pusher half-plates which form part of the slit plate assembly. An electron beam of about 100 μa, shown dashed in Fig. 3, served to ionize the particles emitted as neutrals by the target surface during ion bombardment. This electron beam was turned off when particles emitted as ions were to be studied. For negative ions both the electric and magnetic fields were reversed. The resolving power $M/\Delta M$ of this analyzer was about 250 for gas ions, but dropped to about 100 for sputtered particles with initial kinetic energies of several ev.

For degassing, the curved portion of the analyzer tube was wrapped with lengths of electrical heating tape. A power input of 650 watts raised the tube temperature to about 160 degrees C, a level considered safe in view of the Teflon gaskets employed. The sputtering gas was introduced into the source from a conventional gas handling system consisting of a metering volume, a reservoir, a cold trap, and a diaphragm leak assuring molecular flow.

The many circuit components associated with the analyzer are shown in Fig. 4 in the form of a block diagram. Details concerning this equipment have been published previously [14].

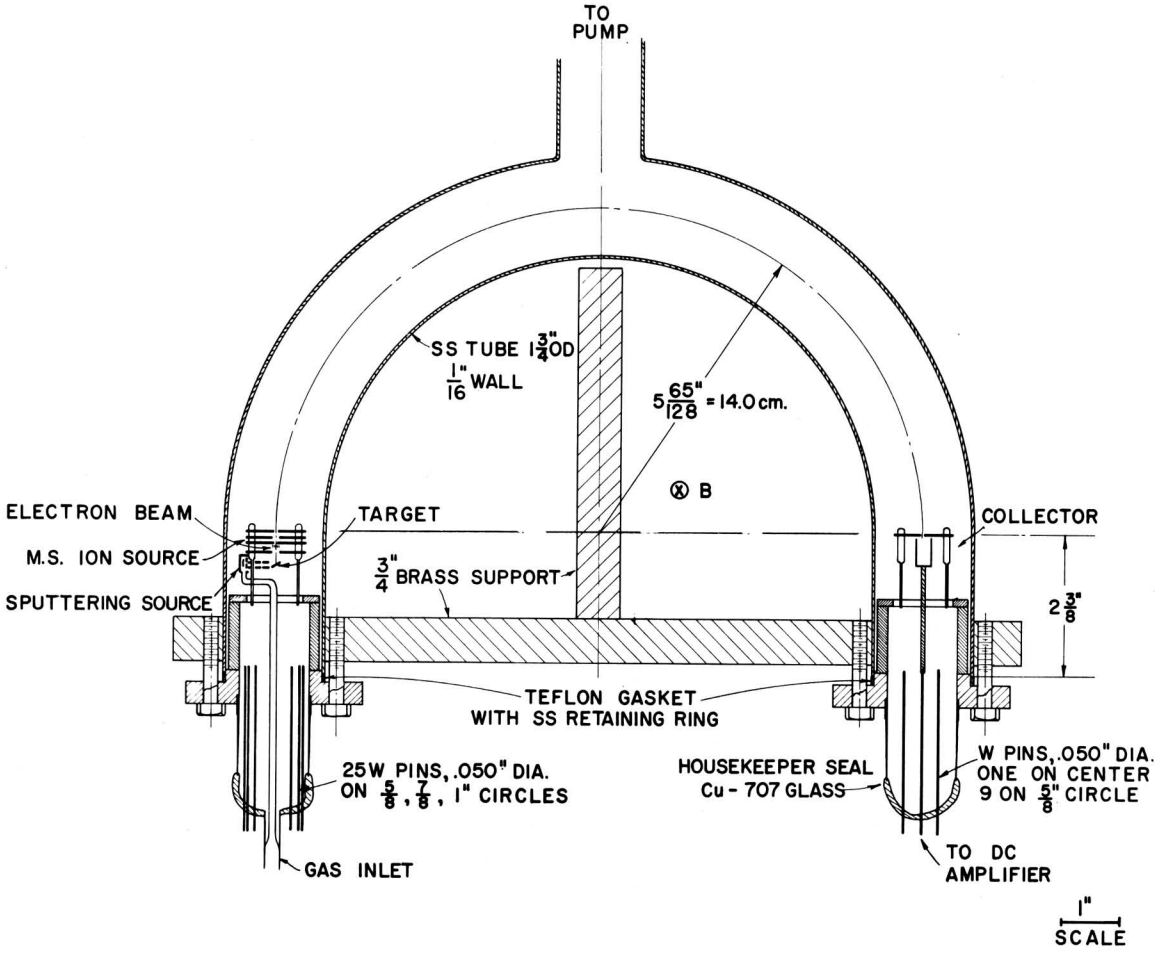

Fig. 3 - Complete scale drawing of mass analyzer.

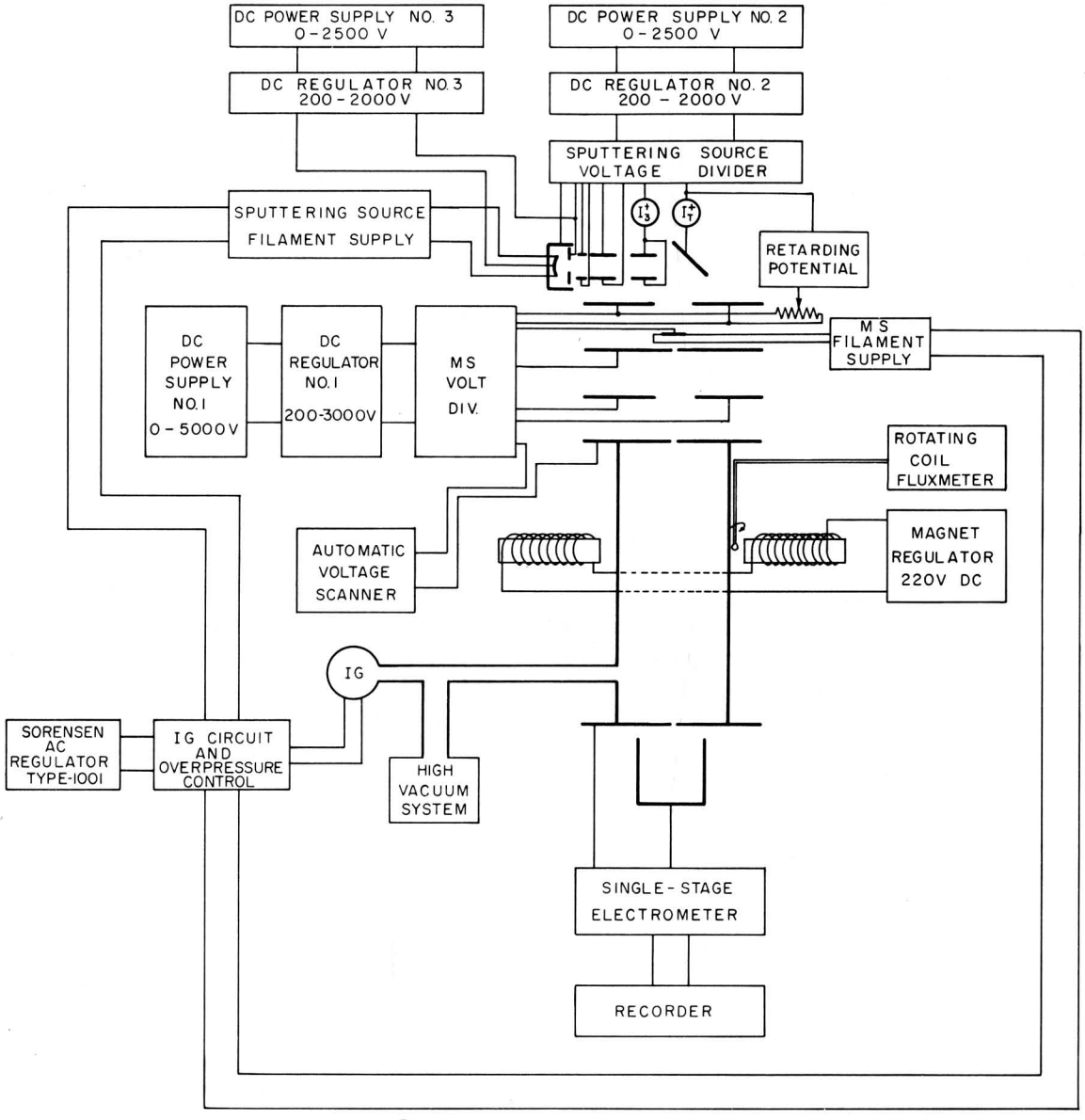

Fig. 4 - Block diagram of sputtering source, analyzer, and associated circuits.

Procedure

Preliminary surface treatments differed for the various samples studied. The silver samples used came from polycrystalline cold-worked stock and were degreased and mounted without additional surface treatment. The single crystal germanium sample was cut and ground parallel to the (111) plane, degreased, etched to a thickness of about 0.013 inches, and placed in the target holder. Two different germanium-silicon alloy samples were used. The first one was cut, ground, degreased, and etched in a solution containing hydrofluoric acid, nitric acid, and water. The second one received the identical treatment, but was subsequently polished with fine aluminum oxide powder until all etch pits had been removed.

With the sample in place, the vacuum system was pumped down overnight until the pressure, with the filaments on, was about 10^{-6} mm Hg. Next, the analyzer tube was baked for several hours at about 160 degrees C and then allowed to cool down to room temperature before any runs were made. After this treatment, the background pressure was always well below 10^{-7} mm Hg. To check for possible air leaks and to adjust for optimum resolving power and intensity, the instrument was first used as a conventional gas analyzer. For the sputtering runs, sufficient sputtering gas was introduced to raise the pressure to about 10^{-4} mm Hg. Next, the sputtering electrode potentials were adjusted until the positive ion beam hitting the target was at a maximum. Adjustments of the mass spectrometer source potentials were made for maximum intensity and optimum peak shape. It was found that the

TABLE I

PARTICLES SPUTTERED FROM Ag SURFACE BY Xe^+ IONS

($I^+/A = 4\mu a/cm^2$; $E^+ = 300 - 400$ ev)

MASS	NEUTRALS		POSITIVE IONS		NEGATIVE IONS	
	Species	Intensity	Species	Intensity	Species	Intensity
1					H^-	W
15			CH_3^+	W		
16					O^-	S
17					OH^-	S
18	H_2O	S	H_2O^+	W		
19					F^-	M
23			Na^+	VS		
24			Mg^+	S	C_2^-	M
25			Mg^+, C_2H^+	S	C_2H^-	M
26	C_2H_2	M	$Mg^+, C_2H_2^+$	S	$C_2H_2^-$	S
27			$Al^+, C_2H_3^+$	M	$C_2H_3^-$	W
28	CO	S	$C_2H_4^+$	W		
29			$C_2H_5^+$	M		
32			S^+	W	S^-	M
33					SH^-	M
34					SH_2^-	M
35					Cl^-	S
37					Cl^-	S
39			K^+	VS		
40			Ca^+	M		
41			K^+	S		
42			$C_3H_6^+$	M		
43			$C_3H_7^+$	M		
44	CO_2	M	CO_2^+ (?)	M		
45					(?)	W
48					C_4^-	W
49					C_4H^-	W
50	C_4H_2	W				
51	C_4H_3	W				

MASS	NEUTRALS		POSITIVE IONS		NEGATIVE IONS	
	Species	Intensity	Species	Intensity	Species	Intensity
52	C_4H_4	W	$C_4H_4^+$	W		
54			Fe^+	W		
56			Fe^+	M	(?)	W
57			$C_4H_9^+$	W	(?)	M
58			$C_4H_{10}^+$	W	(?)	W
59					(?)	M
60					(?)	W
62-68			Xe^{++}	S		
70			(?)	W		
75			As^+	W	(?)	M
76					(?)	M
77					(?)	W
78			$C_6H_6^+$	W	(?)	W
80			(?)	W		
82			(?)	W		
92			$C_5H_5CH_3^+$	W	(?)	W
98					(?)	VW
107			Ag^+	VS		
108					AgH^-(?)	
109			Ag^+	VS		
110					AgH^-(?)	M
124-136			Xe^+	VS		
160			Se_2^+(?)	W		
185			W^+ or Ta^+(?)	M		
198-204			Hg^+	S		
214-218			Ag_2^+	S	Ag_2^-	M
230-234			Ag_2O^+	W	Ag_2O^-	S
246-250					$Ag_2O_2^-$	W
321-327			Ag_3^+	VW		

optimum focusing conditions for sputtered particles emitted as ions differed significantly from those for the neutrals which had to be ionized by electron impact. When it was desired to record neutrals without interference from the particles emitted as positive ions, a retarding potential of 20 volts was placed between the target and the mass spectrometer ion source, to suppress most of the ions.

Results

Nature of the Sputtered Particles

The particles emitted from the surfaces under ion bombardment included atoms and molecules representing the solid, the solid and gaseous impurities in the lattice, and the gases adsorbed on the surface. These particles were in part neutral, in part positively or negatively charged. There were also found singly- and multiply-charged positive ions of the bombarding gas, apparently reflected at the target surface or formed by charge exchange. To detect neutral particles typical of the solid surface, special efforts had to be made. The electron beam, necessary to convert these neutrals into positive ions, produced at the same time large peaks of bombarding gas ions which would interfere with the detection of small peaks. Thus it was necessary in each case to choose an appropriate bombarding gas so that there was no interference in the mass region of interest.

In several experiments, silver targets were bombarded with Kr^+ and Xe^+ ions. The bombarding energies ranged between 200 and 400 ev, the current densities between 2 and 20 $\mu a/cm^2$. A thorough search was made for sputtered particles coming off as neutrals, as positive ions, and as negative ions. Because of the experimental conditions existing at that time, no neutral silver atoms or molecules could be detected. The following silver species emitted as ions were found (arranged in order of decreasing intensities): Ag_1^+, Ag_2^+, Ag_3^+, Ag_2O^-, Ag_2^-, and $Ag_2O_2^-$. In addition, there were found large currents of Na^+ and K^+, of the secondary bombarding gas ions (Kr^+ and Kr^{++}, or Xe^+ and Xe^{++}), and of Cl^-. A complete listing of all the peaks found is given in Table I which shows the species observed when Xe^+ ions of 300 to 400 ev energy bombard a silver target at room temperature. Intensities are semi-quantitatively given as very strong (VS), strong (S), medium (M), weak (W), and very weak (VW), and the peaks are identified where ever possible. Apart from the major peaks already mentioned, there were found a number of impurity ions (Mg^+, S^+, and Fe^+) whose intensities decreased with time, and also many neutrals, especially H_2O, CO, and CO_2, hydrocarbons, and Hg. The tungsten peak is believed to be caused by the erosion of the sputtering source filament.

A single crystal of germanium (n-type, resistivity about 0.5 ohm-cm), cut along the (111) plane, was sputtered in several experiments by the rare gas ions Xe^+, Kr^+, A^+, and Ne^+, at energies ranging from 30 to 400 ev. Under suitable experimental conditions, it was possible to detect very small concentrations of Ge_1^{n+}, the neutral species, subsequently ionized by the electron beam, when argon was used as the sputtering gas, and still smaller concentrations of Ge_2^{n+} when the surface was bombarded by Kr^+ ions. These gases had been chosen to avoid interference from the extremely large bombarding gas peaks. The relative numbers of positive ions, Ge_1^+, and neutrals, Ge_1^n, resulting from the bombardment of a Ge surface by 400 ev A^+ ions may be estimated as follows:

$$Ge_1^+/Ge_1{}^{n+} = 100 \text{ (measured)}$$
$$Ge_1^{n+}/Ge_1^n = 10^{-4} \text{ (estimated)}$$
$$Ge_1^+/Ge_1^n = Ge^+/Ge^n = 10^{-2}$$

The major peaks observed in this experiment are listed in Table II. The intensity ratio Ge_2^+/Ge_1^+ was about 1/50.

TABLE II

PARTICLES SPUTTERED FROM GERMANIUM SURFACE BY RARE GAS IONS

(Xe^+ Kr^+ A^+ Ne^+; ENERGIES: 30 – 400 ev)

NEUTRALS	Ge_1 H_2O	Ge_2 26	27	CO	N_2	O_2	CO_2	Hg
POS. IONS	Ge_1^+ Na^+	Ge_2^+ Al^+		GeH^+ K^+	$GeOH^+$ Rb^+		Ge_2O^+ Hg^+	
NEG. IONS	F^-	24^-		25^-	26^-		Cl^-	

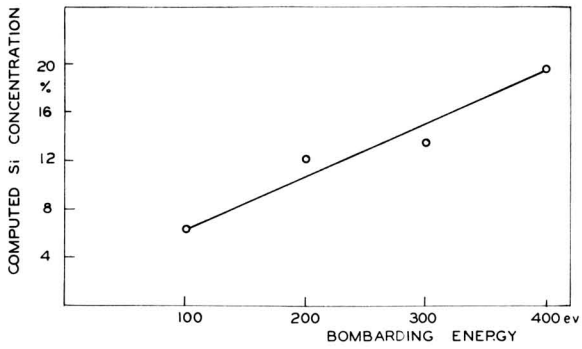

Fig. 5 - Apparent variation with bombarding energy of Si concentration in Ge-Si sample.

To test the potentialities of sputtering as an analytical tool, samples of a twinned germanium-silicon crystal (11 percent silicon by density), cut along the (221) plane, were sputtered with various rare gas ions at energies ranging between 100 and 400 ev. The neutral particles observed in these runs represented background gases, adsorbed on the surface and subsequently released by the ion bombardment. No special search was made to detect neutrals typical of the surface. The major species found are summarized in Table III. To estimate the silicon concentration in this sample, special attention was paid to the relative intensities of the Ge_1^+ and the Si_1^+ peaks. Several runs made with Xe^+, Kr^+, and A^+ ions of 400 ev energy yielded an intensity ratio Si_1^+/Ge_1^+ of about 1/4. Assuming that these ion intensities are representative of the neutral concentrations on the surface and that there is no instrumental discrimination, the silicon concentration in the alloy would amount to 20 percent, or almost twice the value measured by density. However, when these runs were repeated to include bombarding energies between 100 and 400 ev, the computed silicon percentage was found to depend markedly on energy, as shown in Fig. 5. The significance of this apparent variation is not clear at this time.

Initial Kinetic Energies of Sputtered Particles

To study the kinetic energy distribution of ions emitted by a germanium surface under bombardment, retarding potential measurements were made. In these runs, Kr^+ ions with energies between 100 and 400 ev bombarded the (111) germanium surface mentioned above. In Figs. 6 and 7 are shown the intensities of the Ge_1^+ and Na^+ peaks as a function of retarding potential. Differentiation of these curves yields the energy distributions shown, with widths of about 2.5 ev at half intensity. It is seen that the Ge_1^+ and Na^+ particles are emitted with most probable energies of about 2 ev.

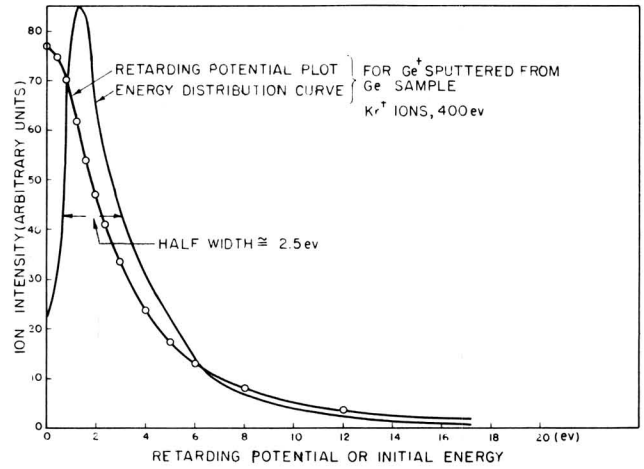

Fig. 6 - Retarding potential plot and energy distribution curve for Ge^+ sputtered from Ge sample by 400 ev Kr^+ ions.

Yields and Threshold Energies

A number of runs were made to measure relative yields as a function of primary energy and to obtain threshold values. Fig. 8 shows data obtained for the (111) germanium

TABLE III

PARTICLES SPUTTERED FROM GERMANIUM-SILICON (89 - 11) ALLOY SURFACE BY RARE GAS IONS

(Xe^+, Kr^+, A^+; ENERGIES: 100 - 400 ev)

NEUTRALS	H_2O	26	27	CO	N_2	O_2	CO_2	Hg
POS. IONS	Si_1^+ Ge_1^+ Na^+	SiH^+ GeH^+ Al^+		$SiOH^+$ $GeOH^+$	Ge_2^+ $GeSi^+$		Ge_2O^+ $GeSiO^+$	

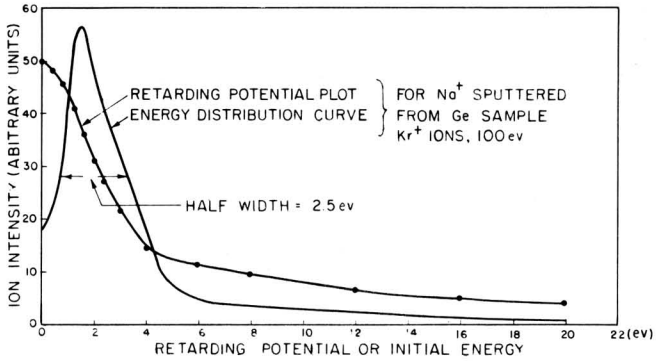

Fig. 7 - Retarding potential plot and energy distribution curve for Na^+ sputtered from Ge sample by 100 ev Kr^+ ions.

surface under Kr^+ bombardment. The curve obtained for increasing energies lies about 10 percent above that for decreasing energies. Such hysteresis could be caused by changes in surface conditions, such as gas adsorption or temperature changes, but at this time there is no clear-cut explanation. The yield curves level off to a small, constant background value below about 50 ev, which makes it difficult to obtain a well-defined threshold value. For the combination Kr^+ on germanium, a threshold of 50 ev was estimated, while for Kr^+ on silver a value of about 40 ev was found. Fig. 8 also shows the intensity of *secondary* Kr^+ ions as a function of bombarding energy. Such ions could be primary bombarding ions, reflected from the target without loss of charge, or they could be neutrals, ionized near the target by positive ion impact. If the dependence of ion current on bombarding gas pressure were known, a decision between these two alternatives could readily be made.

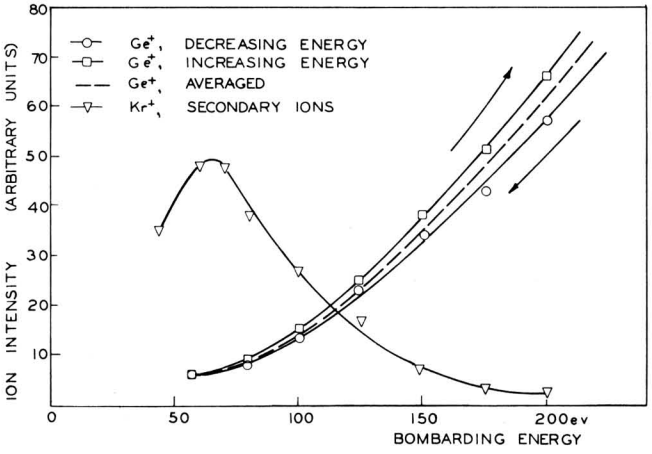

Fig. 8 - Yield curves obtained for Ge target bombarded by Kr^+ ions.

A rough estimate of absolute yields may be obtained from the total current of positive ions typical of the surfaces, the analyzer efficiency, the ratio Ge^+/Ge^n computed above, and the known primary bombarding current. These yields range from about 10^{-3} at 100 ev to about 10^{-2} at 400 ev bombarding energy. They are about 100 times smaller than the values found by Wehner, as will be discussed below.

Appearance of Bombarded Surfaces

The cold-rolled polycrystalline silver surfaces changed during bombardment from shiny to matte. Visual inspection indicated that the erosion was distributed uniformly over the entire surface.

After bombardment, the (111) germanium surface was inspected under a light microscope at magnifications up to 1000x. Oval-shaped irregularities were found which at that time were interpreted as small pits whose long axes were aligned with the plane of incidence of the bombarding particles. In the light of more recent information, it is possible that these pits were oblong hillocks.

The appearance of the (221) germanium-silicon surfaces was first studied under a light microscope. Again, oval-shaped irregularities were found whose long axes were aligned with the plane of incidence of the bombarding particles. Subsequently, a replica was made of the surface with the help of a shadow-casting technique, and electron micrographs made. It was deduced from the pictures that the irregularities were oval-shaped hillocks several hundred angstroms in height.

Discussion

Nature of Sputtered Particles

In the past, there had been considerable speculation[1] but very little experimental evidence[15] concerning the charge and state of aggregation of sputtered particles. The present study provides unambiguous answers to these questions. Sputtering at moderate energies, between 30 and 400 ev, produces not only atoms, but also molecular clusters typical of the surface. It remains to be shown in future studies if the ratio of atomic to molecular particles depends on such parameters as the energy and mass of the bombarding ions. While the sputtered particles are largely neutral, about one in a hundred is positively charged. In spite of the preponderance of neutrals, most of the results reported above are based on the positive ions for the following reasons. A considerable fraction of the positive ions emitted by the surface can be collected after mass analysis. On the other hand, the efficiency of conversion of neutrals into positive ions by electron impact is very low ($< 10^{-4}$), and interference from the extremely large bombarding gas peaks formed at the same time is severe.

The energy spread of the sputtered particles is quite small: 80 percent of the particles have energies below 5 ev. Therefore, analysis with a simple momentum filter is readily achieved.

Recently, Stanton[16] has observed Be^+ ions from a beryllium surface, and Bradley and collaborators[17] have reported Mo^+ ions from a molybdenum surface, emitted during bombardment by rare gas ions. Molecular ions were not discovered in either study, nor could estimates be made concerning the ratio of neutrals to charged particles. A Russian team[18] studied sputtering at elevated temperatures by Cs^+ ions. They found that their estimated ratio of sputtered ions to neutrals could not be made to fit the Saha-Langmuir formula, a result that is not surprising.

Yields and Thresholds of Sputtered Particles

Sputtering yields have been measured by many investigators[1,2], usually in high pressure gas discharge, sources. Wehner[2,3] has recently obtained results, under more suitable pressure conditions, for Hg^+ energies ranging up to 400 ev, the yields usually lying between 0.1 and 1. In the present experiments, the yields were found to lie between 10^{-2} and 10^{-3}, about 100 times smaller than anticipated. The main reason for this low figure is that the largest portion of the bombarding energy is expended to desorb background gases present on the surface. To obtain efficient sputtering in future experiments, it is clear that ion current densities of several ma/cm^2 should be attained.

In the present experiments it was difficult to determine threshold energies to an accuracy better than ± 10 ev. The values obtained for $\phi = 60$ degrees (50 ev for $Kr^+ - Ge$, 40 ev for $Kr^+ - Ag$) agree quite closely with Wehner's[3] results for $Hg^+ - Ge$ and $Hg^+ - Ag$ at $\phi = 0$ degrees. This agreement may be fortuitous because the angles of incidence employed were different and because background gases covered most of the surface in the present experiments.

Surface Properties and Analysis

The uniform sputtering of the polycrystalline silver surface on one hand, and the appearance of oval-shaped, lined-up hillocks on the oriented surfaces of germanium and germanium-silicon on the other, was initially interpreted to mean that crystallinity and orientation of a surface determine the erosion pattern, in agreement with Wehner's[3] results. However, there appears to be an alternative, or at least complementary, explanation based on the recent finding[19] that when germanium processed in graphite boats is heated in vacuo to 460 degrees C, more than 10^{18} molecules/cm^3 of carbon monoxide are liberated. From this it is concluded that considerable concentrations of carbon may dissolve in liquid germanium and remain in the solid lattice unless the sample is well preheated. During sputtering, aggregates of carbon atoms, because of their low sputtering yields, may serve to mask off parts of the surface which are left standing as hillocks. This interpretation would fit the observations made by Dillon and Farnsworth[20] and Wolsky[21] that the ion bombardment of germanium samples carefully degassed by prolonged heating did not produce any visible erosion patterns.

The surface analytical results obtained to date are preliminary in nature, yet encouraging. It has been shown that the sputtering of solids can be employed to detect surface impurities and to analyze alloys semi-quantitatively. It is interesting to note that hydride and hydroxyl groups, such as *SiH, GeH, SiOH,* and *GeOH* could be detected on chemically etched surfaces. The presence of such groups had been postulated for some time, but so far never proved.

Future Work

It is clear that future work should satisfy more fully the requirements for the ideal sputtering experiment, as outlined previously. Experiments are to be repeated in an ultra high vacuum system, capable of a base pressure of about 10^{-10} mm Hg to produce and maintain surfaces free of adsorbed gases. The sputtering source will be modified to produce bombarding current densities of several ma/cm^2. Provisions will be made to bake the target (by electron bombardment or direct heating) to allow thorough degassing before, and annealing after, each bombardment. Runs are to be made as a function of target temperature. Efforts will be made to increase the sensitivity of measuring techniques to permit the detection of surface impurities, and to make the analyses quantitative.

Richard E. Honig

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