or

Whether the semi-conductor or the metal predominates in determining l, and thus the barrier height, depends on the relative magnitudes of the terms on the left and right sides of Eq. (28). The terms on the right side will be negligible if

 $l_1 \ll 2\kappa a \tag{29}$ 

$$l_0 \gg l_2^2 / 2 \kappa a.$$
 (30)

The first condition requires that

$$n \gg \epsilon_0 / 2\pi e^2 a,$$
 (31)

and the second that

and

$$n \gg (\epsilon_0/4\pi e^2 a)(\chi_1 - \varphi_s - \zeta)/(\epsilon_0 - \zeta).$$
 (31a)

These conditions are essentially equivalent to that given by Eq. (23), and lead to the conclusion that  $n \gg 10^{13}$  in order that the metal have little influence on the space charge region. In this case of high density of surface states, the equation for the layer thickness reduces to that for the free surface of the semi-conductor:

$$l^2/l_1 + l - l_0 = 0. \tag{32}$$

Equation (32) may, of course, be used to estimate the thickness of the space change region at the free surface of the semi-conductor, regardless of the density of surface states. The limiting

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## Contact Potential Difference in Silicon Crystal Rectifiers\* \*\*

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The rectifying portion of a crystal rectifier is the contact between a small point made of metal such as tungsten, and a semiconductor such as silicon or germanium containing suitable impurities. The potential energy of a conduction electron near the contact determines the rectifying action of the crystal rectifier. The most important feature of this potential energy, as far as the present paper is concerned, is the height of the potential barrier, which the electrons have to overcome when they pass from the metal to the semiconductor or vice versa. The height of the barrier is called here contact potential difference (c.p.d.), because theoretically it is equal to the difference in the work func-

tions of the substances in contact. The c.p.d. has been measured using both n- and p-type silicon and different metallic contacts. (The c.p.d. can be obtained from the variation of the contact resistance with temperature.) The work function differences (w.f.d.) between the same substances were obtained independently by a parallel plate condenser method (Kelvin method). The results showed no correlation between the c.p.d. and the w.f.d. The c.p.d. is practically independent of the kind of metal used and also of the structure of the silicon surface. These results are in contradiction to the present theoretical model of the silicon crystal rectifier.

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case of high density corresponds to

$$l_0 \gg l_1,$$
 (33a)

$$n^2 \gg N \kappa \epsilon_0^2 / 2 \pi e^2 (\epsilon_0 - \zeta).$$
 (33b)

This is essentially the requirement, stated above Eq. (15), that *n* be large compared with *Nl*. The approximate solution of Eq. (32) is then

$$l^2 \approx l_0 l_1$$
.

The product  $l_0l_1$  is independent of n, and is just the square of the thickness of the Schottky layer for a barrier height

$$\varphi_0 = \epsilon_0 - \zeta. \tag{34}$$

This is the condition that the Fermi level cross the surface near the energy corresponding to zero surface states charge.

In the limiting case of a vanishingly small density of surface states, the thickness of the barrier layer is determined by setting the righthand side of Eq. (28) to zero. This gives

$$\varphi_0 = \chi_1 - \varphi_s - \zeta. \tag{35}$$

The height of the barrier is equal to the difference in work functions.

Equation (28) may be used for intermediate cases.

<sup>\*</sup> Condensation of a dissertation in Physics presented to the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Dissertation published with limited distribution under "University of Pennsylvania, BuShips Contract NObs-34144, Technical Report No. 5, August 10, 1946." Copies available from University of Pennsylvania, Department of Physics, Philadelphia 4, Pennsylvania.

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FIG. 1. Energy level diagrams for metal and semiconductor in equilibrium.

## INTRODUCTION

HE essential constituents of a crystal rectifier are a metal and a semiconductor in contact. Under suitable conditions these contacts have rectifying properties.

In general one distinguishes large-area-contact rectifiers, such as copper oxide and selenium rectifiers, from point-contact rectifiers, such as silicon and germanium rectifiers, which will be described here. In both kinds of rectifier the semiconductor is in the form of a slab, making contact on both sides to a metal. Although each side will rectify in the opposite direction from the other, a net rectification is obtained in the case of the large-area-contact rectifiers by making the intrinsic rectification property of the two contacts different. In the case of point-contact rectifiers the same effect is obtained by making the area of one contact very much smaller than the area of the other.<sup>1</sup> Any voltage drop across the rectifier is then concentrated across the small area (high resistance) contact; in considering the theory of the point-contact rectifier one may justifiably neglect the large area contact.<sup>1</sup>

## THEORY OF THE SEMICONDUCTOR-METAL CONTACT

When a metal and a semiconductor are brought into contact, the electron distributions adjust themselves in such a way as to make the average thermodynamic potential<sup>2</sup> of the conduction electrons in the solids everywhere the same. This adjustment is always accompanied by a transfer of electrons from the solid with the lower work function<sup>3</sup> to that with the higher work function. The transferred electrons stay in the neighborhood of the contact surface and, together with the positive charges they leave behind, form a double layer which just compensates for the original difference in work functions.

The potential (resulting from a superposition of the original lattice potential and of the potential caused by the double layer) in which the conduction electrons move has been investigated carefully by Fan.<sup>4</sup> In the case of silicon and germanium, though, one may make certain approximations resulting from the fact that the activation energy of the electrons (or holes) from the impurity levels into the conduction band is only of the order of a few hundredths of an electron volt<sup>5</sup> so that practically all the impurities are ionized at room temperature. The exact shape of the potential near the contact then depends uniquely on the distribution of impurities in the semiconductor.<sup>6–8</sup> For example, a uniform impurity distribution produces a parabolic potential.<sup>6,7</sup>

In the present considerations, it is necessary only to note that the potential jump which a conduction electron experiences in traversing the

<sup>4</sup> H. Y. Fan, Phys. Rev. 62, 388 (1942).

<sup>6</sup> K. Lark-Horovitz, private communication; G. L. Pearson and W. Shockley Bull. Am. Phys. Soc. [6] 21, 9 (1946); B. Serin, University of Pennsylvania dissertation, Phys. Rev. (to be published).

<sup>6</sup> N. F. Mott and R. W. Gurney, Electronic Processes in Ionic Crystals (Clarendon Press, Oxford, 1940). <sup>7</sup> H. A. Bethe, NDRC Div. 14 report, MIT Rad. Lab.

43-12, Nov. 23, 1942 (Copies obtainable from Publications Board, Department of Commerce, Washington, D. C.). <sup>8</sup> B. Serin, Phys. Rev. 69, 357 (1946).

<sup>&</sup>lt;sup>1</sup>Actually the ratio of the large to the small area must be appreciably larger than the back to front resistance ratio of the rectifier.

<sup>&</sup>lt;sup>2</sup> See R. H. Fowler, *Statistical Mechanics* (University Press, Cambridge, 1936), Chap. XI. <sup>8</sup> Work function is defined here as the difference in po-

tential of an electron just outside the surface of a solid and of an electron with an average thermodynamic potential energy

contact surface between a metal and a semiconductor is, to a first approximation, equal to the difference in work functions of the two solids. If  $\phi_M$  is the work function of the metal and  $\phi_S$ the work function of the semiconductor, the work function difference,  $\varphi$ , is defined here by

$$\varphi = \phi_S - \phi_M, \qquad (1)$$

when the solids are in contact. When they are separated the same symbols with the subscript zero will be used. Figure 1 shows the various possible potential diagrams for these two situations.9 Since the activation energies of the impurity states are only a few hundredths of an electron volt, as was mentioned above, the position of the average thermodynamic potential energy level may be taken with sufficient accuracy at the top and bottom of the forbidden zone for n- and p-type semiconductors respectively.<sup>2,9</sup>

The theory of the silicon or germanium pointcontact rectifier was given by Bethe,7 who pointed out that in the case of these substances the number of conduction electrons colliding with the potential barrier is appreciably larger than the number of electrons scattered by the lattice and the impurities in the barrier region. Therefore the diffusion theory, developed by Schottky,<sup>10</sup> Mott,<sup>6</sup> and others and generally applied to largearea-contact rectifiers, is not valid, but a simple diode theory will be more satisfactory for calculating the current flow across the contact. If n is the density of impurities in the semiconductor, v is the thermal velocity of the electrons perpendicular to the contact surface, e is the absolute value of the electronic charge, A is the effective contact area, k is Boltzmann's constant, T is the absolute temperature and m is the effective mass of the electron, then the current i through the contact is

 $i = j_0 A \cdot \exp(-e |\varphi|/kT) \cdot [\exp(kT) - 1],$ 

where

$$j_0 = \frac{1}{2}nev = \frac{1}{2}ne(2kT/(\pi m))^{\frac{1}{2}}$$

(2)

for *n* small compared to the number of atoms per  $cm^3$ . V is the voltage drop across the contact barrier.<sup>11</sup> The quantity  $\varphi$  is called here the contact potential difference (abbreviated below by c.p.d.) and is defined by Eq. (1). It is the purpose of this paper to present some results of an experimental investigation of  $\varphi$ .

Actually it is necessary to take into account the effective lowering of the potential barrier at the contact because of the image force<sup>7</sup> and the tunneling of the electrons (or holes) through the barrier. Courant<sup>12</sup> has shown that under those conditions Eq. (2) must be written:

$$i = j_0 A \cdot \exp(-\theta e |\varphi|/kT) \cdot \left[ \exp(\theta e V/kT) - \exp(-(1-\theta) e V/kT) \right].$$
(3)

 $\theta$  is a numerical factor, depending on  $(|\varphi| - V)$ , which essentially lowers the barrier height, as shown in Fig. 2. Figure 3 is a plot of  $\theta | \varphi |$ calculated by Courant for a typical contact.<sup>13</sup>

It is now necessary to make several remarks about the rectifier characteristic, Eq. (3). First, considering Fig. 1 it is easily seen that an n-type contact will rectify only if  $\varphi < 0$  and a p-type contact only if  $\varphi > 0$ . If these conditions are not



FIG. 2. Effective potential barrier for electrons or holes in a rectifying contact.



FIG. 3. Potential and observed potential for image force and tunnel effect (Courant).

<sup>12</sup> E. Courant, NDRC Div. 14 report, Cornell University, May 17, 1943; Phys. Rev. 69, 684 (1946). <sup>13</sup>  $m = 9.1 \times 10^{-28}$  g,  $n = 5.93 \times 10^{18}$  cm<sup>-3</sup>,  $T = 290^{\circ}$ K, di-electric constant = 10.

<sup>&</sup>lt;sup>9</sup> See also F. Seitz and S. Pasternack, NDRC Div. 14 report, University of Pennsylvania. D1-102, June 10, 1942. <sup>10</sup> W. Schottky, Zeits. f. Physik 118, 539 (1942).

<sup>&</sup>lt;sup>11</sup> The voltage actually applied to the rectifier is  $V+iR_{s}$ , where  $R_{s}$  is the spreading resistance of the "point" contact.



FIG. 4a. Apparatus used to measure c.p.d.



FIG. 4b. Crystal rectifier assembly.

fulfilled, there will be no effective barrier for the electrons (or holes) traversing the contact. The barrier resistance is then independent of the voltage  $V^{11}$  and equal to zero. Second, in general the c.p.d. will not be uniform over the entire contact area. This so-called multi-contact effect has been examined by Sachs and others.14 The essen-



FIG. 5. Typical plot of low level resistance versus 1/T. B-Be doped Si, polished, treated 2 hrs. at 975° C; 0.007" W point, ground; ½ mil. spring deflection, crystal tapped.



FIG. 6. Variation of observed c.p.d. Si-W as a function of W point area.

tial result is easily seen by considering the contact as made up of two spots with different values of  $\varphi$  and A.<sup>15</sup> These spots will act like two resistances in parallel and most of the current will flow through the spot of low resistance, i.e., low  $|\varphi|$ , if the spot areas are not too different. This means of course that the lowest absolute value of the c.p.d. will determine the effective exponent  $\theta e |\varphi|/(kT)$  in Eq. (3).

## MEASUREMENT OF CONTACT POTENTIAL DIFFERENCE (c.p.d.)

In the present work it was proposed to compare the c.p.d. with the actual work function difference of a semiconductor and a metal not in contact. The c.p.d. was determined by a previously described method,16 which consists in measuring the zero voltage resistance of the contact<sup>17</sup> as a function of the temperature. Equation (3)yields for this resistance:

$$R = \left(\frac{dV}{di}\right)_{V=0} = \left(\frac{kT}{j_0 A e}\right) \exp(\theta e |\varphi| / kT). \quad (4)$$

In general the linear variation of R with T can be neglected, especially since theoretically  $j_0$  is proportional to  $T^{\frac{1}{2}}$ .

Figure 4a gives a diagrammatic sketch of the apparatus. The semiconductor-metal contact was mounted in a conventional temperature stable cartridge18 shown in Fig. 4b. The oven was heated

<sup>&</sup>lt;sup>14</sup> R. G. Sachs, NDRC Div. 14 report No. 168, June 15. 1943; V. A. Johnson, R. N. Smith, and H. J. Yearian, NDRC Div. 14 report, Purdue University, August 14, 1943.

<sup>&</sup>lt;sup>15</sup> This was kindly pointed out to the author by B. Serin. <sup>16</sup> W. E. Stephens, B. Serin, and W. E. Meyerhof, Phys. Rev. 69, 42, 244 (1946).

<sup>&</sup>lt;sup>17</sup> The spreading resistance of the contact was subtracted from the measured resistance whenever it was not negligible compared to the barrier resistance R. <sup>18</sup> See W. E. Stephens, Electronics **19**, 112 (July 1946).



FIG. 7. Distribution curve of observed c.p.d. Si-W.

to a temperature of about 130°C in a few minutes and then allowed to cool.

About 5 millivolts were applied to the crystal in both directions, and the average current was used to calculate the resistance of the contact, thus eliminating the effect of any thermal e.m.f. The cooling of the oven was slow enough (approx.  $\frac{1}{2}$  hr. from 130°C to 50°C) to permit a practically simultaneous measurement of temperature and resistance. Figure 5 shows a typical semi-log plot of R versus 1/T. The high temperature end of the curve indicates that the semiconductor had not reached the temperature of the crystal base at the time of measurement.

### RESULTS OF CONTACT POTENTIAL DIFFERENCE MEASUREMENTS

In order to study the variation of the c.p.d. with the nature of the metallic component of the contact, a particular piece of p-type silicon<sup>19</sup> was mounted in a cartridge and different wires were pressed against it with various pressures. The wires were previously sharpened on Arkansas stone to a point of less than  $10^{-3}$  cm radius so that different contact pressures produced different contact areas. Figure 6 shows the variation of the c.p.d. silicon-tungsten with contact area, measured microscopically.

For most metals used, the c.p.d. was roughly independent of area, although there was a trend towards an increase in c.p.d. with decreasing area especially noticeable for areas less than  $0.5 \times 10^{-6}$ cm<sup>2</sup>. This might be caused by a multi-contact effect which raises the probability of finding a larger minimum (i.e., effective) c.p.d. with small contact areas than with large contact areas.

The unavoidable electrical non-uniformity of



Silicon ground with No. 600 carborandum.



Silicon polished on 0000 emery paper.





Tungsten point pressed on polished silicon.

Tungsten point pressed on ground silicon,

FIG. 8. Photomicrographs of silicon surfaces and tungsten

the silicon surface itself is brought out by Fig. 7 which shows the distribution curve of approximately 50 measurements of the c.p.d. silicontungsten using the same piece of silicon (2 mm<sup>2</sup> area). For comparison, Fig. 8 gives an idea of the geometrical non-uniformity of different silicon surfaces and the corresponding tungsten points.

points ( $1000 \times$  magnification).

Table I summarizes the c.p.d. using various metals. The first column gives the measured c.p.d.  $\theta \varphi$  and the second column the c.p.d.  $\varphi$  corrected by means of Courant's curve (Fig. 3). Each mean value of the c.p.d. (heavy type) is the average of at least 8 measurements. The extreme values of the c.p.d. measurements are also given.

Table II presents some comparison measurements on a piece of p-type and a piece of n-type

 $<sup>^{19}</sup>$  99.95 percent pure Dupont silicon, 0.002 percent boron, 0.02 percent beryllium; dry polished on 0000 emery paper; heat treated 2 hours at 975°C (see ref. 18).

c.p.d. p-type silicon—metal erved Corrected Observed  $\theta \varphi$  (volts) Metal φ (volts) Al 0.00, 0.01, 0.09 0.00, 0.07, 0.21 0.21, **0.23**, 0.28 0.15, **0.22**, 0.36 0.36, 0.39, 0.44 Au Cu 0.29, 0.38, 0.53 0.14, 0.17, 0.22 0.28, 0.32, 0.38 Fe 0.17, 0.26, 0.39 0.32, 0.42, 0.57 Mo Ni 0.16, 0.31, 0.33 0.30, 0.48, 0.50 Ni-alloy<sup>20</sup> 0.21, **0.26**, 0.41 0.36, 0.42, 0.59 0.10, 0.17, 0.20 0.22, 0.32, 0.35 Pt Pt-alloy<sup>21</sup> 0.17, 0.19, 0.37 0.32, 0.34, 0.55 Ta 0.10, 0.18, 0.26 0.22, 0.33, 0.42 W 0.15, 0.23, 0.32 0.29, 0.39, 0.49

TABLE I. Contact potential differences of various metals with respect to p-type silicon.

silicon treated as nearly alike as possible,<sup>22</sup> but differently from the piece of p-type silicon used in Table I. Only two or three measurements of the c.p.d. were made with each metal.

A comparison of the c.p.d. for the p-type silicon with that in Table I shows that the surface structure of the silicon does not seem to affect the c.p.d. (the silicon of Table II was ground and that of Table I polished-see Fig. 8 for difference in structure).

Both Table I and Table II indicate also that the c.p.d. is, within the electrical non-uniformity of the surfaces, independent of the nature of the metal for the p-type as well as for the n-type contacts. This is quite contrary to theoretical expectations considering the large variety of metals used, which have unoutgassed work functions between about 3 and 5 volts.23 In fact the c.p.d. values for p-type silicon all lie between 0.6 and 0.0 volts. Actually the only substance giving sometimes the value  $\varphi = 0$  is aluminum, which has one of the lowest work functions (even unoutgassed) and which therefore should be expected to give one of the highest values of the c.p.d. according to Eq. (1).

Before considering further experiments it is of interest to present Table III which gives the change in c.p.d. when a crystal rectifier is mechanically tapped and when it is overloaded with

TABLE	II.	Con	nparison	ιof	contac	t pote	ntial	difference	es o	f
	p-	and	n-type	silic	on wit	h vario	ous m	ietals.		

Metal	c.p.d. p-type Observed $\theta \varphi$ (volts)	e silicon—metal Corrected $\varphi$ (volts)
Pt	0.165. 0.20	0.305. 0.35
Ťa	0.15, 0.20	0.29, 0.35
W	0.16, 0.18, 0.20	0.30, 0.325, 0.35
	c.p.d. n-typ	e silicon—metal
Pt	-0.16, -0.16	-0.30, -0.30
Ta	-0.09, -0.095	-0.22, -0.225
Ŵ	-0.07, -0.09, -0.10	-0.19, -0.22, -0.2

microwave power (i.e., "burnt out"). Only two series of measurements were made. The last two columns in Table III show the barrier resistance at room temperature and the relative contact area compared to the initial value and calculated from Eq. (4) assuming  $j_0$  constant. It can be seen that tapping increases the c.p.d. and the resistance. Burnout decreases the c.p.d., the resistance<sup>24</sup> and the effective contact area.

#### MEASUREMENT OF WORK FUNCTION DIFFERENCE (w.f.d.)

Since the above mentioned experiments showed no correlation of the c.p.d. between silicon and various metals, and the work functions of the metals, it was thought advisable to measure the work function difference (abbreviated below by w.f.d.) directly, under various conditions. Although these measurements eventually did not suggest any new phenomena which would make the c.p.d. roughly independent of the silicon surface and the nature of the metal, they demonstrate very clearly the disagreement of the c.p.d. measurements with the presently assumed model of the contact.

TABLE III. Change of contact potential difference of a p-type silicon-tungsten rectifier with tapping and power overloading.

	c.p.d. p-typ	pe silicon— zsten		Relative contact area
Treatment crystal rectifier	Observed $\theta \varphi$ (volts)	Corrected $\varphi$ (volts)	Resistance $R$ (k-ohm)	A /A init (%)
Initial values After tapping After 7 watt RF peak power <sup>25</sup>	0.21, 0.17 0.28, 0.20 0.18, 0.14	0.36, 0.32 0.44, 0.35 0.33, 0.28	4.8, 2.4 37, 17 6.4, 3.8	100, 100 200, 47 23, 24
After 70 watt RF peak power	0.08, 0.10	0.20, 0.23	0.4, 0.9	6, 15

<sup>24</sup> For a more detailed study of resistance as a function of burnout see A. W. Lawson et al., NDRC Div. 14 report No. 113, November 1, 1942.

<sup>25</sup> 10 cm microwave microsecond pulses were used in this experiment; the power given is available peak power.

<sup>&</sup>lt;sup>20</sup> 96.75 percent Ni, 1.00 percent Al, 2.00 percent Mo, 0.25 percent C, work hardened wire. <sup>21</sup> 90 percent Pt, 10 percent Ru.

<sup>&</sup>lt;sup>22</sup> For impurities in the p-type silicon see ref. 19; the impurities in the n-type piece were not known. Both pieces were ground with No. 600 carborundum and water, etched together in hot sodium hydroxide, washed and dried.

See for example, A. L. Hughes and L. A. DuBridge, Photoelectric Phenomena (McGraw-Hill, New York, 1932).

Metal	φυ (τοπο)	$\varphi_0$ (volts)	air (volts)	oxygen (Dubois) (volts)	water vapor (Dubois) (volts)
Al	0.75	0.21			
A1*26	0.69	0.26			
Au	-0.31	-0.45	0.14	0.14	-0.14, -0.21
Cu	-0.37	-0.42	0.05	0.15, 0.16	-0.03, -0.06
Cu*	-0.34	-0.40	0.06	,	,
Fe	-0.18	-0.41	0.23	0.22, 0.34	-0.56, -0.56
Mo	-0.17	-0.42	0.25	0.18	-0.16, -0.18
	-0.21	-0.38	0.17		
Ni	-0.09	-0.18	0.11	0.15	-0.16
	-0.08	-0.12	0.04		
Ta	0.13	-0.04			
Pt	-0.60	-0.61	0.01	0.04	-0.02
W	-0.19	-0.33			

TABLE IV. Variation of work function difference between p-type silicon and various abraded metals.

The method of measurement of the w.f.d. was essentially a parallel plate condenser method (Kelvin method). The two substances under investigation form the two plates of a variable condenser. The field established by the w.f.d. (see Fig. 1) is brought to zero by an externally applied voltage (equal to the w.f.d.). The details of the method are described elsewhere.<sup>27</sup> In opposition to the c.p.d. measurement, this method gives practically the *average* w.f.d. between two surfaces.

The surfaces under study were usually abraded with 000 emery cloth in order to produce a surface treatment similar to grinding the metal points in the c.p.d. experiments. Also an appa-

TABLE V. Variation of work functions of tungsten and silicon after abrasion.

Gas	Initial impurities	Increase in 10 min in in Tungsten (volts)	work function in gas after abrasion vacuum Silicon (volts)
Air		0.33, 0.41	0.10, 0.12 p-type
			0.22, 0.26 n-type
Oxygen		0.42, 0.46	0.11, 0.15 p-type
Oxygen and Water vapor		0.46, 0.50	0.16, 0.18 "
Nitrogen	0.1% O <sub>2</sub> 0.4% A	0.14.0.16	0.10.0.12 "
Hydrogen	0.1% 0.	0.08 0.12	0.08.0.08 "
Helium	1.6% N <sub>2</sub> , 0.2% hydro-	0.06, 0.08	0.04, 0.06 "
Argon	0.5% N <sub>2</sub> , 0.001% O <sub>2</sub> , H <sub>2</sub> , H <sub>2</sub> O	0.04, 0.06	0.03, 0.05 "

<sup>&</sup>lt;sup>26</sup> All metals guaranteed pure except the starred metals which are commercial stock. The purity of the metal does not influence the work function to any appreciable extent in these experiments.

Metal	Oxide coating in air	Work function of oxide (Lammermann and Lange)	w.f.d. silicon metal (Table IV) $\varphi_0$ (volts)	Work function of silicon surface $\phi_0 S$ (volts)
Al	Al <sub>2</sub> O <sub>3</sub>	3.9 <sup>28</sup>	$\begin{array}{c} 0.21, & 0.26\\ -0.42, & -0.40\\ -0.41\\ 0.13\end{array}$	4.11, 4.16
Cu	Cu <sub>2</sub> O	4.47		4.05, 4.07
Fe	FeO or Fe <sub>3</sub> O <sub>4</sub>	4.54 or 4.58		4.13 or 4.17
Pb <sup>29</sup>	PbO	4.06		4.19

TABLE VI. Data for the determination of the absolute work function of a silicon surface.

ratus was construe	cted which	permitted	this abra-
sion in a vacuum	of about 5	5×10−5 mm	Hg.

## RESULTS OF WORK FUNCTION DIFFERENCE MEASUREMENTS

It is recalled that the w.f.d.,  $\varphi_0$ , is defined by an equation similar to Eq. (1):

 $\varphi_0 = \phi_{0S} - \phi_{0M},$ 

where  $\phi_{0S}$  is the work function of the silicon and  $\phi_{0M}$  is the work function of the metal, as measured in the present experiment.

Table IV summarizes the experiments in air (on the same metals as used in Table I). A piece of polished p-type silicon<sup>19</sup> was taken as standard surface. Each metal was abraded with 000 emery cloth and the w.f.d. measured approximately 1 min. and 50 hrs. after abrasion. The results on Mo and Ni in the above table give an idea of the reproducibility of the results. The fourth column in Table IV gives the change in the metal work function during 50 hours exposure in air. For comparison the last two columns show some results of Dubois<sup>30</sup> on the influence of oxygen and water vapor on outgassed work functions. It can be inferred from these results that the increase in work function of the metals after abrasion in air is mostly caused by (pure or activated) adsorption of oxygen and that the humidity in the air does not play any significant role.

This is also brought out by Table V which gives the change in work function of tungsten and silicon (each measured against a standard surface) abraded in a vacuum of about  $5 \times 10^{-5}$  mm Hg and then subjected to various gases at atmospheric pressure for 10 minutes. The numbers

<sup>&</sup>lt;sup>27</sup> W. E. Meyerhof and P. H. Miller, Jr., Rev. Sci. Inst. 17, 15 (1946).

<sup>&</sup>lt;sup>28</sup> Compare with 3.95 volts obtained by H. J. Spanner, Ann. d. Physik **75**, 608 (1925).
<sup>29</sup> Not shown in Table IV.

<sup>&</sup>lt;sup>30</sup> E. Dubois, Ann. de physique 14, 627 (1930).



FIG. 9. Work function of tungsten and tantalum after abrasion in partial vacuum.

given represent averages of two experiments. The gases in which oxygen was an impurity were passed over red hot copper, so that the percentage oxygen present was certainly less than shown. Table V would indicate then that nitrogen and hydrogen can also affect the work function of solids.<sup>31</sup>

It is known that most metals oxidize in air. Lämmermann and Lange<sup>32</sup> have measured the work functions of several oxides and their values allow a calibration of the standard silicon surface used in Table IV, if we assume that the metals in the present experiment were coated with the oxides shown below, 50 hrs. after abrasion in air. From Table VI a work function between 4.1 and 4.2 volts may be obtained for the standard silicon surface.

Figures 9 and 10 show the variation of work function of tungsten, tantalum, n- and p-type silicon after abrasion in a vacuum and then subjecting the surfaces to air at atmospheric pressure within  $\frac{1}{2}$  min. The measured w.f.d. was calibrated by using the standard silicon surface and calling its work function 4.2 volts. The in-



FIG. 10. Work function of p- and n-type silicon, after abrasion in partial vacuum.

accuracy of this value will evidently not affect the relative scales of Figs. 9 and 10. These figures show that for each solid the work function increases on exposure to air.

## DISCUSSION OF EXPERIMENTAL RESULTS

Several comments on these measurements are now in order. First, assuming the effect of abrasion to be the same on the surfaces of both nand p-type silicon, the difference in work functions of the two solids should be equal to the width of the forbidden region in silicon (1.12 volts<sup>33</sup>). Figure 10 shows that it is only about 0.3 volts. Second, since the work functions of the solids examined change very markedly on exposure to air, one might assume that on forming a contact between a metal and silicon, there occurs a change in the oxide layers in such a way as to make the results of Tables I and II consistent with those of Table IV and Figs. 9 and 10.

Holm<sup>34</sup> has found that in the case of metalmetal contacts the plastic deformation of the metal parts actually in contact causes a breaking of the oxidation layers. Let us assume a similar simple mechanism in the formation of crystal rectifier contacts. Since the silicon is too hard to

<sup>&</sup>lt;sup>31</sup> Since nitrogen is generally an impurity in argon this might invalidate some of the conclusions which O. Klein and E. Lange, Zeits. f. Elektrochemie 44, 542 (1938), drew from a change of the work function with time in an atmosphere of argon.

Values given by O. Klein and E. Lange (reference 31).

<sup>&</sup>lt;sup>33</sup> F. Seitz, NDRC Div. 14 report No. 113, November 1, 1942.

<sup>&</sup>lt;sup>34</sup> R. Holm, Die technische Physik der elektrischen Kon-takte (Julius Springer, Berlin, 1941; reproduced by J. W. Edwards, Ann Arbor, 1944), pp. 63-139.

be deformed, we may assume that its oxidation layer is conserved during contact formation, so that a crystal rectifier contact is perhaps roughly a silicon "oxide"-metal contact. Table VII compares the w.f.d. (assuming this kind of contact and assuming a silicon "oxide"-metal "oxide" contact) with the c.p.d. (Table II) for the same metals. (The work functions of the p- and n-type silicon were measured after treating the surfaces similarly to those of Table II22 and were found to be 4.13 and 3.95 volts respectively.) It is easily seen that the w.f.d. measurements cannot be made consistent with the c.p.d. measurements. In this connection it should be noted that the multi-contact theory requires for a p-type contact  $\varphi = 0$ , if  $\varphi_0 \leq 0$ , and for an n-type contact  $\varphi = 0$ , if  $\varphi_0 \ge 0$ .

The general nature of the results is in essential disagreement with some experiments on largearea contact rectifiers performed by Joffe.<sup>35</sup> Joffe finds that there is agreement between the sign of the w.f.d. and the finite or zero value of the corresponding c.p.d. It might not be justified, though, to compare those results (on semiconducting oxides mostly) with the present experiments (on silicon).

#### CONCLUSION

Assuming the correctness of the experimental results, it seems desirable to reinvestigate the physical picture of the silicon-metal contact. Essentially it is necessary to construct a model which makes the c.p.d. roughly independent of the surface structure of the silicon and roughly independent of the work function of the metal. It is possible to construct such a model by assuming the surface of the silicon to be practically

Nature of contact	c.p.d. (Table II) ¢ (volts)	w.f.d. for part of cc Silicon "oxide"- metal $\varphi_0$ (volts)	ticular model mtact Silicon "oxide"- metal "oxide" $\varphi_0$ (volts)
p-Si—Pt p-Si—Ta p-Si—W n-Si—Pt n-Si—Ta n-Si—W	$0.3 \\ 0.3 \\ 0.3 \\ -0.3 \\ -0.2 \\ -0.2$	$ \begin{array}{r}     \overline{0.4} \\     0.1 \\     \overline{0.2} \\     -0.1 \end{array} $	$ \begin{array}{r} -0.7 \\ -0.1 \\ -0.4 \\ -0.9 \\ -0.3 \\ -0.6 \\ \end{array} $
		0.1	0.0

TABLE	VII. Comparison of values for contact potential
	difference and work function life
	difference and work function difference.

"metallic" <sup>36</sup> so that the potential barrier would be located inside the silicon surface. Any metal making contact to such a surface would introduce no further discontinuities in the potential, just as in the case of metal-metal contacts, so that the c.p.d. would be independent of the work function of the metal.

The thickness of the "metallic" layer would not have to be more than a few atomic distances in order to satisfy the electronic conditions, so that this model essentially assumes the existence of particular surface states<sup>37</sup> for the conduction electrons. Calculations in this general direction might throw further light on the mechanism of silicon point-contact rectifiers.<sup>38</sup>

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<sup>&</sup>lt;sup>35</sup> A. V. Joffe, J. Phys. USSR 10, 49 (1946).

<sup>&</sup>lt;sup>36</sup> This was kindly pointed out to the author by G. H. Wannier.

<sup>&</sup>lt;sup>87</sup> See for example, F. Seitz, *The Theory of Solids*, (McGraw-Hill Book Company, New York, 1940), sec. 70. <sup>38</sup> Note added in proof: Since this paper was sent in for

publication, J. Bardeen has kindly informed the author of his calculations on surface states, which appear in Phys. Rev. **71**, 717 (1947).



Silicon ground with No. 600 carborandum.



Silicon polished on 0000 emery paper.



Tungsten point pressed on ground silicon.



Tungsten point pressed on polished silicon.

FIG. 8. Photomicrographs of silicon surfaces and tungsten points ( $1000 \times$  magnification).