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Rectification Properties of Metal-Silicon Contacts*

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Area contacts of twenty different metals were made on n and p silicon. The contacts were applied by the use of jet plating techniques, with the exception of alkali metal contacts which were pressure contact or mercury amalgam contact. A qualitative correlation is shown to exist between the work function of the metals and the rectification of these metals on n and p silicon. I-V characteristics taken on eleven of these metal-silicon contacts lend further support to this picture. Consideration of a quantitative work function model is made difficult due to the many errors and interpretations involved in using metal work function values.

Transistor structures were made and studied for several of the metal-silicon contacts. From analysis of this transistor data it is found that an excess current three orders of magnitude greater than theory predicts, must be present in the diodes made from these metals. This excess current is not adequately explained by any presently known mechanism.

INTRODUCTION

IN the past, a considerable amount of work has been reported on the study of metal-semiconductor contacts. Much of this work was directed toward finding a correlation between the work function of the metal and the sense of rectification of the metal-semiconductor contacts. The results have been quite varied. Brattain[1] reported finding a correlation with evaporated contacts made on n- and p-type silicon. Meyerhof,[2] working with metal contacts on Si and Ge, found essentially no dependence of work function for metal point contact silicon rectifiers. Borneman and his co-workers[3] have studied the electroplated metal contacts on Ge and found no apparent work function correlation on germanium. They reported that, in all cases, regardless of either the type of metal or the type of germanium used, the contact exhibited a barrier to electrons only. This lends strength to the hypothesis of Bardeen, namely, that the surface states on Ge are the dominant influence in the formation of the barrier at a metal-germanium interface and that the work functions of the metals would then have little or no influence on the adjusting of the barrier height on Ge.[1]

The generally accepted view of rectification in the case of a metal-semiconductor contact due to a pure work function difference model is illustrated in Fig. 1 which applies specifically to a p-type semiconductor in contact with a low work function metal in equilibrium. From Fig. 1 the barrier height is seen to be of the form[4]

$$\phi_{0p}=\phi_p-\phi_m+\phi_h, \tag{1}$$

and by analogy the barrier height of a high work function metal on an excess semiconductor is

$$\phi_{0n}=\phi_m-\phi_n+\phi_e. \tag{2}$$

For such a model, theory predicts that the total current density at the contact, J, should be of the form

$$J=J_s(e^{qV/kT}-1), \tag{3}$$

where the saturation current density J_s consists of the two current components, one due to the minority carrier saturation current and the other to majority carrier saturation current. Considering the metal to p-type semiconductor contact the hole saturation current density, J_{ps}, should then be of the form

$$J_{ps}=AT^2e^{-q\phi_0/kT} \tag{4}$$

and the electronic saturation current density of the

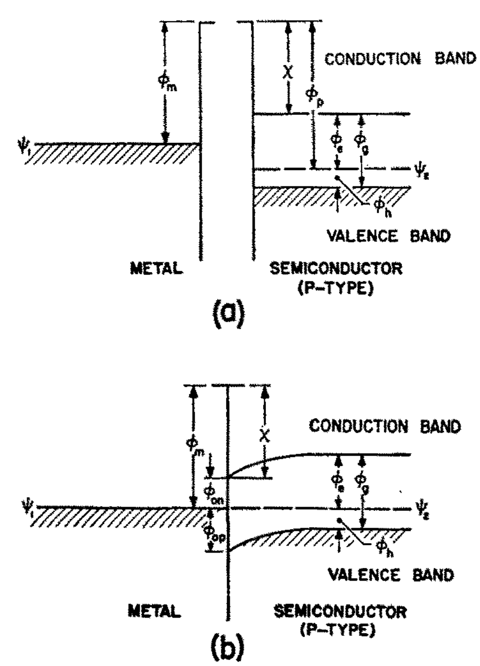

FIG. 1. Energy level diagram for metal and p-type semiconductor in electrical and thermal equilibrium (a) before contact, (b) after contact.

* This work was performed under Bureau of Ships contract NObsr-64670.
[1] J. Bardeen, Phys. Rev. 71, 717 (1947).
[2] W. E. Meyerhof, Phys. Rev. 71, 727 (1947).
[3] Borneman, Schwarz, and Stickler, J. Appl. Phys. 26, 1021 (1955).
[4] For definitions of symbols see glossary of symbols.

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form[3]

$$J_{ns}=\frac{4kT\mu_n n_{eq}}{\pi a}. \quad (5)$$

For a metal n-type semiconductor contact the expressions Eqs. (4) and (5) are reversed with a reversal of the n and p's. The ϕ_0 in Eq. (4) is either ϕ_{0p} or ϕ_{0n} given in Eqs. (1) and (2), respectively, which is the barrier height of the contact to the majority carriers. This indicates that the total majority current density, J_p, across the interface is a function of this work function difference between the metal and the semiconductor for the pure work function difference model of the contact.

In the case of metal-silicon contacts, made by jet electroplating techniques, a correlation between the work function of the metals and the rectification of these contacts on n and p silicon has been found. Qualitative results indicate good correlation between the work function of the metals and the sense of rectification of these contacts on both types of silicon. The quantitative results have further substantiated these earlier observations although the results indicate that the rectification picture is not solely explained by the work function difference model.

To further investigate the properties of metal-silicon contacts, transistor structures were made with some of the metals. From the current gain α_{ce}, of these transistors, the injection ratio of minority to majority current of the contacts can be calculated by the following equation[5] (for an n-p-n transistor),

$$\alpha_{ce}=\frac{1}{1+(J_{ps}4W/J_{ns}\pi a)}, \quad (6)$$

where J_{ps} and J_{ns} are given by Eqs. (4) and (5). These equations thus relate the diode and transistor data, and should show agreement for contacts that are behaving properly.

EXPERIMENTAL MATERIALS AND TECHNIQUES

The metal-silicon contacts were jet electroplated according to the method described in detail by Tiley and Williams.[6] Briefly, the method involves directing a jet of solution of a metal salt through a glass nozzle onto the silicon sample, which is held perpendicular to the stream. A columbium holder supporting the silicon wafer permits electrical contact to be made to the sample. The electrical circuit is completed by a platinum ribbon in the salt solution which serves as the second electrode.

In order to insure the best possible adherence of the metal to the silicon it was found necessary to give each silicon wafer a 3 HNO_3:2 HF chemical etch and then an H_2O rinse just prior to plating. Jet etching of silicon can be accomplished by use of a fluoride solution. However, it was found that it was not possible in most cases to use a metal salt solution to first electrolytically etch and then plate the metal by reversing polarity as is done for germanium.[3] This explains the use of the chemical etch prior to plating on silicon. The plating thickness could be regulated by varying either the

TABLE I. Composition of solutions used to plate various metals on silicon.

Metal	Solution components	Grams/liter	Solvent
Zinc	$ZnCl_2$	13.6	
	$SnCl_2$	0.016	
	$PbCl_2$	0.002	Ethylene glycol
Indium	$In_2(SO_4)_3$	17.26	
	H_2SO_4	4.52	H_2O
Tin	[a]$SnCl_2$	22.32	
	NaF	14.93	
	$NaHF_2$	7.73	
	NaCl	4.93	
	$Na_4Fe(CN)_6$	0.36	H_2O
Lead	$Pb(BO_2)_2\cdot H_2O$	180.3	
	H_3BO_3	180	
	HF	460	H_2O
Cadmium	$CdCl_2$	18.32	Ethylene glycol
	NH_4Cl	2.66	
Antimony	SbF_3	10.0	Ethylene glycol
	HF	57.5	
Copper	$CuSO_4$	8.0	
	H_2SO_4	16.36	H_2O
Bismuth	BiOCl	20.0	
	HCl	73.2	H_2O
Nickel	$NiSO_4\cdot 7H_2O$	105	Ethylene glycol
Cobalt	[a]$CoSO_4\cdot 7H_2O$	151	
	NaF	4.7	H_2O
Iron	$Fe(NH_4)_2$-$(SO_4)_2\cdot 6H_2O$	29.4	H_2O
Silver	$AgBF_4$	10.66	
	NaF	0.07	H_2O
Gold	$AuCl_3$	10.0	
	NaCl	2.9	H_2O
Rhodium	$RhCl_3\cdot 4H_2O$	4.0	
	H_2SO_4	34.80	H_2O
Platinum	[a]$Pt(NH_3)_2(NO_2)_2$	6.0	
	NH_4NO_3	2.0	Ethylene glycol
	H_2SO_4	0.174	

[a] These solutions also include a small percentage of wetting agents.

[5] By definition $\gamma=1/1+(J_{p0}/J_{n0})$ where J_{p0} and J_{n0} are the transistor (npn) emitter hole and electron current components. From Shockley's equations, J_{p0} is equal to the diode J_{ps} and $J_{n0}=(kTq\mu_n n_{eq})/W=J_{ns}\pi a/4W$. The latter expression is valid since the area of the transistor and diode contacts are essentially the same. Substituting for J_{p0} and J_{n0} into the expression for γ yields Eq. (6).

[6] J. W. Tiley and R. A. Williams, Proc. Inst. Radio Engrs. 41, 1706 (1953).

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current density or time of plating. After plating, a chemical etch was used to clean the sample and to give a sharply defined region of metal contact.

It was found that a 0.2 N sodium fluoride solution plus the addition of HF in a sufficient amount to give a *p*H of 3 was very good for electrolytic etching of *n*- and *p*-type silicon. Actually, the concentration of this solution is not very critical in the etching of *p* silicon, and it has been found that a solution of 0.4 N sodium fluoride without HF works equally as well on it. However, for etching of *n* silicon, the solutions' concentration is very critical; it is also necessary to flood the silicon with light to assure formation of smooth flat bottomed etch pits. The necessity of the light in the etching of *n* silicon is better understood if one realizes that the electrolytic etching process is dependent on the hole concentration supplied to the surface of the silicon. In *n* silicon there is normally a deficiency of holes and the light generates many hole-electron pairs. These etching solutions were used with the jet technique in the fabrication of silicon surface barrier transistors in order to get the desired base thickness, *W*, however, even in this case a chemical etch was used after the jet etching, just prior to the plating.

Table I lists the metals plated as well as the composition of the solutions from which they were deposited. In general, the metal deposits obtained were well defined, adherent dots. The exact physical nature of the plated deposits depended strongly on the plating current density and composition of the solution.

The silicon orientation appeared to have little, if any, effect on the physical nature of the metal deposit or the electrical properties of the contacts.

TABLE II. Comparison of rectification for metals on 2.5 ohm cm *n*- and *p*-type silicon to the work function of the metals.

Metal	Rectification of Metals on Silicon Property of broad-area metal contacts on *n*-type silicon	*p*-type silicon	Work function[a] ϕ_m (ev)
Potassium	Ohmic	Rectifying	2.15
Sodium	Ohmic	Rectifying	2.27
Lithium	Ohmic	Rectifying	2.39
Magnesium	Ohmic	Rectifying	3.46
Aluminum	Ohmic	Rectifying	3.74
Zinc	Ohmic	Rectifying	3.74
Indium	Ohmic	Rectifying	4.00
Lead	Ohmic	Rectifying	4.02
Tin	Ohmic	Rectifying	4.11
Cadmium	Rectifying	Rectifying[b]	3.92
Antimony	Rectifying	Rectifying[b]	4.08
Cobalt	Rectifying[b]	Rectifying	4.18
Bismuth	Rectifying[b]	Rectifying	4.28
Silver	Rectifying[b]	Rectifying	4.28
Copper	Rectifying[b]	Rectifying	4.47
Nickel	Rectifying[b]	Rectifying	4.84
Iron	Rectifying	Ohmic	4.36
Gold	Rectifying	Ohmic	4.58
Rhodium	Rectifying	Ohmic	4.65
Platinum	Rectifying	Ohmic	5.29

[a] H. B. Michaelson, J. Appl. Phys. 21 536 (1950).
[b] Lower saturation current observed on this type silicon.

EXPERIMENTAL RESULTS AND DISCUSSION

Rectification characteristics have been measured for some 20 metals on approximately 2.5 ohm cm silicon, both *n* and *p* type. With the exception of sodium, potassium, lithium, and magnesium, all metal-silicon contacts were made by electrochemical plating. The other contacts were made using pressure contacts or mercury amalgam contacts.

Table II shows these metals and their rectifying properties on *n* and *p* silicon, as well as the work function of the metals. As can be seen from the table, a qualitative correlation exists between the rectifying properties of the metal-silicon contacts and the work function of the metals. Those metals with high work function values ($\phi_m \geq 4.5$ ev) rectify only on *n* silicon, those metals with low work function ($\phi_m < 4.1$ ev) rectify on *p* silicon only, and those metals with intermediate work function values (4.1 ev $\leq \phi_m \leq$ 4.5 ev) rectify on both *n* and *p* silicon. It may be noted that a few metals, i.e., cadmium, nickel, and iron, are somewhat out of line according to their work function values, but such deviations may easily be attributed to possible error in work functions.

A few predictions can be made from the qualitative results:

(1) Metals having high work functions should be best for producing injection on *n* silicon.

(2) Metals having low work functions should be best for producing injection on *p* silicon.

(3) Metals having very low work functions ($\phi_m \leq 3.0$ ev) may even be expected to exhibit the phenomena of extraction on *n* silicon.

To further substantiate these predictions as well as examine the quantitative aspects of a work function model of rectification on silicon, quantitative data was required. For this purpose careful I–V data were taken for a number of these metal-silicon contacts and injection of the contacts was measured from transistor structures.

Quantitative measurements of diode characteristics on 2.5 ohm cm *n* and *p* silicon, with lieftime $\tau > 10$ μsec, have been made on eleven of the aforementioned metal-silicon contacts. The geometry of the wafers was $150 \times 150 \times 20$ mils with an ohmic base tab being soldered to one corner of the wafer. The area of electrical contact for those metals which formed diodes was determined from measurement of capacitance *vs* voltage curves.[7] These areas varied between 10^{-3} and 5×10^{-3} cm², and agreed closely with the visual measurements of the area of contact.

The I–V curve for a typical zinc *p*-silicon contact is shown in Fig. 2. The forward and reverse curve as seen here deviate from the relation Eq. (3). In Fig. 3 are shown typical reverse I–V curves representative of

[7] R. F. Schwarz and J. F. Walsh, Proc. Inst. Radio Engrs. 41, 1715 (1953).

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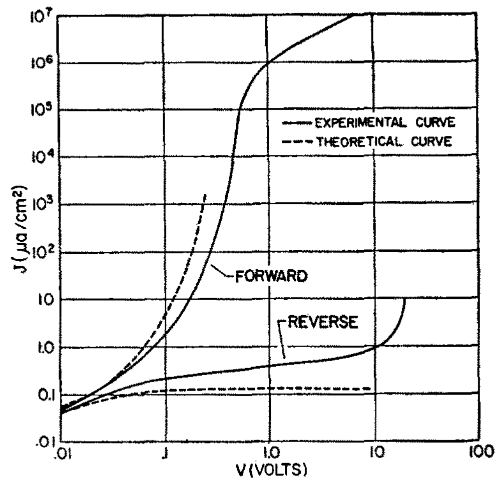

FIG. 2. I–V curve of a plated zinc contact on 2.5 ohm cm p-type silicon.

a large number of diodes measured for each metal contact.

In all cases for these diodes the saturation current density, J_s is at least three orders of magnitude higher than the minority carrier diffusion current density as given by Eq. (5). Considering 2.5 ohm cm p silicon, Eq. (5) predicts a minority carrier saturation current density of about 10^{-10} amp/cm^2. The actual measured values of J_s are given in Table III. An experimental measure of the minority carrier current is given by a curve of I_c *versus* V_e for a zinc silicon transistor. Essentially I_c is a measure of the minority current injected by the emitter contact into the bulk; the curve of I_c *versus* V_e should therefore give the forward I–V relationship of the bulk injected minority current of the emitter contact. A contact behaving normally should inject a current which follows a relationship expressed by Eq. (3). Relationships recorded for I_c *versus* V_e for several zinc p-silicon SBT's follow this theoretical equation so closely that the values of

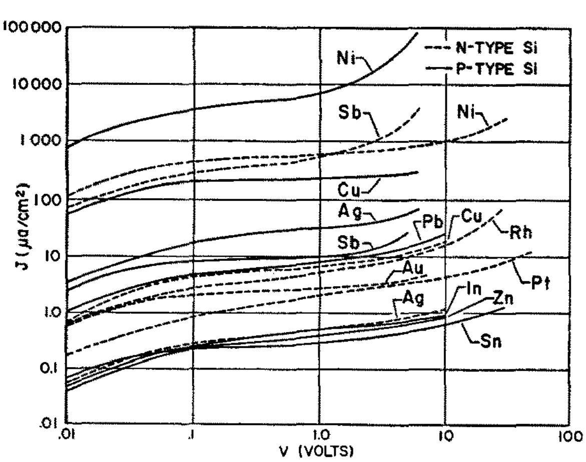

FIG. 3. Reverse diode curves of metals plated on 2.5 ohm cm n- and p-type silicon.

injected current calculated for the geometry of the particular contacts concerned are in almost complete conformity with experimental measurements. These data for a typical transistor are displayed in Fig. 4. Thus the minority carrier current can be said to conform to theory, with the exception of a component due to surface recombination that can not be more than a factor of two greater than the theoretical minority carrier saturation current. Therefore, it should be valid to say that J_s is essentially given by the relation Eq. (4). Thus, if it is assumed that the measured saturation current is all majority current, then a value of barrier height of the contacts can be calculated from Eq. (4) provided the constant A is known.

The constant A is given a value of 120, this value being used by Borneman and colleagues for metal-germanium diodes. The ϕ_0 values recorded in Table III are calculated from the reverse I–V curves shown for

TABLE III. Barrier heights, ϕ_0, as calculated from diode and transistor data for the metal contacts of work functions as listed. Values of saturation current density for the contacts were taken at 0.1-volt reverse bias.

Metal	Type Si	Saturation current density (J_s(μa/cm²))	Barrier Height ϕ_0(ev) From diode J_s	From transistor α_{ce}	Work function ϕ_m(ev)
Zinc	P	0.20	0.82	1.1	3.74
Indium	P	0.23	0.82	1.1	4.00
Lead	P	4.50	0.74	0.9	4.02
Tin	P	0.22	0.82	1.0	4.11
Antimony	P	8.00	0.73		4.08
Antimony	N	270	0.63		4.08
Silver	P	17.0	0.71		4.28
Silver	N	0.27	0.81		4.28
Copper	P	190	0.64		4.47
Copper	N	4.10	0.74		4.47
Nickel	P	3500	0.57		4.84
Nickel	N	420	0.62		4.84
Gold	N	2.05	0.76		4.58
Rhodium	N	2.60	0.75		4.65
Platinum	N	0.80	0.79	0.8	5.29

the contacts in Fig. 3. Values of J_s taken for calculation of ϕ_0 were those at 0.1 V bias in the reverse direction. These values are listed in Table III along with ϕ_m for the metals.

Transistor structures were made using the metal contacts zinc, indium, tin, and lead. These transistors had a base width $W=10^{-3}$ cm and emitter and collector radius $a=2.5\times10^{-2}$ cm. Curves of α_{ce} measured as a function of I_e, showed α_{ce} to be nonlinear with I_e tending to zero as I_e decreased in the microampere range and asymptoting to $\alpha_{ce}=0.95$ as I_e reaches values in the tens of microamps. A typical curve for such a transistor using zinc contacts on p silicon is shown in Fig. 5. This is as one would predict from the forward curve of the diode in Fig. 2, and the previously discussed data that the minority diffusion current essentially obeys theory. Values of α_{ce} may then be calculated from the diode curve in Fig. 2 using Eqs. (3), (5), and (6) and using the values of W and "a"

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previously mentioned for the zinc transistor. Equation (6) is modified to the extent that the ratio of hole and electron saturation current in the denominator is replaced by the voltage dependent current ratio found for the forward diode curve. Thus from the forward diode curve one obtains J_n and J_p as a function of V_e whereas Eqs. (3) and (5) give J_n as a function of V_e. If one calculates α_{ce} for all the points of the forward diode curve it will be seen that a curve of α_{ce} *versus* I_e will result. This has the same form as the transistor curve in Fig. 5. It is therefore felt that for the contact on p silicon, a true description of the contact is obtained by calculation of ϕ_0 from the limiting value of transistor α_{ce} and not from the diode data. However, for the contacts on n silicon and for the contacts copper and nickel on p silicon the values of ϕ_0 calculated from diode data are considered to be a good approximation to the barrier height. In support of this is the fact that, with the exception of platinum, no α_{ce} could be measured for transistors made using these contacts, not even for emitter currents up to several milliamperes. For the platinum contact on n-silicon values of α_{ce} were obtained from transistor data which gave a value of ϕ_0 in good agreement with that calculated from diode saturation current. The forward curves of the diodes on n silicon were also found to follow more closely the theoretical diode curve. The values of ϕ_0 calculated from transistor data are listed in Table III.

Other investigators also have found reverse saturation currents for silicon diodes, measured for both grown and alloy junctions, to deviate considerably from theory. Several mechanisms have been postulated to explain these deviations of diode curves, however, none are completely satisfactory.

Consider first the effect of high surface recombination velocity on the diode. Calculations made in our laboratories have shown that for the values of S normally found for the contact geometry used, S can increase the saturation current of a diode by at most a factor of two. The effect that high S has on a transistor can be obtained from the work of Webster.[8] It was found that S changes α_{ce} at most by a factor of about $\frac{1}{2}$ and that this maximum change occurs generally with currents in the milliampere range for the resistivities of silicon in question. Consequently surface recombination does not adequately explain the effects measured for these diodes and transistors.

The effect of channel leakage currents on I–V curves of silicon PN junctions was investigated by Bath and Cutler.[9,10] The analysis carried out by these investigators predicts an I–V curve close in form to measured curves. However, quantitative application of this analysis to the data reported here or to experimental

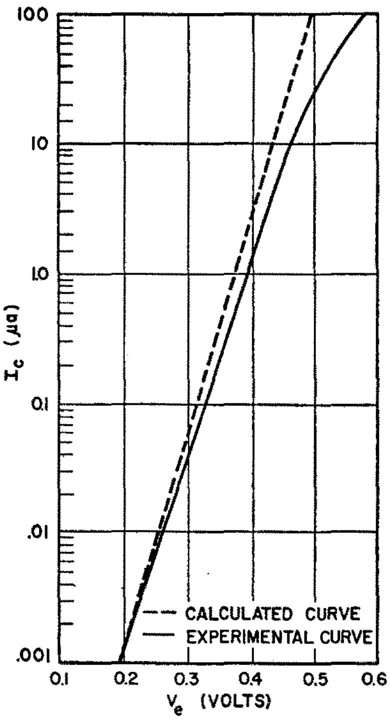

FIG. 4. A typical curve of collector current, I_c, *versus* emitter voltage, V_e, in the nonlinear range of α_{ce} for a zinc plated silicon surface barrier transistor on 2.5 ohm cm p-type silicon.

data on pn junctions gives current magnitudes in the forward direction which are too high.

Recently Pell and Roe[11] have published a paper in which they consider excess current arising from generation of carriers due to midband levels in the space charge region of a junction. Using these results, Dr. Schwarz of our laboratory has calculated this effect with regard to the particular diode structures discussed in this paper. In considering the most favorable condition of the generation levels lying at midband, the calculated reverse currents come out an order of magnitude lower than those measured experimentally. Also, the shape of the calculated curves do not show as much saturation as those measured. There is some question however as to the values to be used for trapping density and trapping cross sections for holes

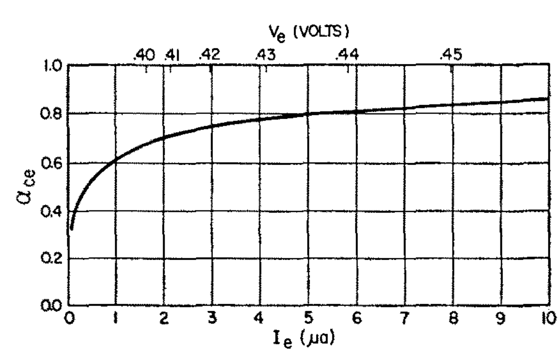

FIG. 5. Current gain, α_{ce}, *versus* emitter current, I_e, for a typical zinc plated silicon surface barrier transistor on 2.5 ohm cm p-type silicon.

[8] W. M. Webster, Proc. Inst. Radio Engrs. 42, 914 (1954).
[9] M. Cutler and H. M. Bath, J. Appl. Phys. 25, 1440 (1954).
[10] H. M. Bath and M. Cutler, 1955 Institute of Radio Engineers, AIEE Semiconductor Device Research Conference, Philadelphia, Pennsylvania.
[11] E. M. Pell and G. M. Roe, J. Appl. Phys. 27, 768 (1956).

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and electrons in calculating the curves. Thus, as it stands, this model of generation of carriers in the barrier does not appear to explain the experimental curves reported in this paper. Further consideration will be given to this model. These considerations will require lifetime *versus* temperature data on silicon.

CONCLUSIONS

A qualitative correlation has been shown to exist between the work function of the metals and the rectification of these metal contacts on n and p silicon. The I–V characteristics taken for some of these metal-silicon contacts lend further support to this picture.

Quantitative consideration of a work function model of rectification is made difficult for several reasons. First, as mentioned, the measured work functions for metals are subject to many errors and interpretations and lend themselves to forming only a qualitative picture. Second, when considering those metals which rectify on both n and p silicon, the sum $(\phi_{0n}+\phi_{0p})$ is expected from a work function picture to be more or less constant and equal to the gap width. This sum is found, however, to be 1.18 ev for Ni, 1.36 ev for Sb and Cu, and 1.51 ev for Ag. In terms of saturation current densities, these differences are too large to be due to errors in the experiments. The excess current found to be present in some of the diodes and causing great nonlinearity in the transistor curves near zero emitter current cannot be explained by such mechanisms as high surface recombination velocity or channeling. The mechanism of space charge generation in the barrier region as presented by Pell and Roe also does not, in its present form, explain these results; however, this mechanism deserves further consideration.

The results herein have been mostly experimental; a complete theoretical treatment of the rectification picture of metal-silicon contacts remains to be done.

ACKNOWLEDGMENTS

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GLOSSARY OF SYMBOLS

A	a constant in Richardson equation
a	radius of circular metallic contacts
e	napierian base
I_e, I_c	dc emitter and collector currents
J	total current density crossing the diode barrier
J_p	hole current density
J_n	electron current density
J_{ps}	hole saturation current density crossing the diode barrier
J_{ns}	electronic saturation current density crossing the diode barrier
J_s	total reverse saturation current density crossing the barrier of the diode
k	Boltzmann's constant
n_{eq}	equilibrium value of electron concentration in the bulk
q	magnitude of electronic charge
T	absolute temperature
V	voltage applied across the barrier
V_e	emitter to base voltage, emitter negative
W	base width of a transistor
α_{ce}	grounded base current gain
γ	ratio of minority carrier current to total current crossing the emitter
μ_p	mobility of electrons
ϕ_{0n}	barrier height at metal interface to electrons (measured from Fermi level)
ϕ_{0p}	barrier height at metal interface to holes (measured from Fermi level)
ϕ_0	barrier height at metal interface to majority carriers (measured from the Fermi level)
ϕ_p	work function of p-type semiconductor
ϕ_n	work function of n-type semiconductor
ϕ_g	width of the forbidden region
ϕ_h	potential necessary to move a hole from the Fermi level to the highest valence level
ϕ_e	potential necessary to move an electron from the Fermi level to the lowest conduction level
χ	potential necessary to remove an electron from the bottom of conduction band to some point at infinity outside of the semiconductor
ψ_1	Fermi level in the metal
ψ_2	Fermi level in the semiconductor

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