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RESEARCH AND DEVELOPMENT PROGRAM TO PRODUCE A SILICON CARBIDE COLD CATHODE (HOT ELECTRON) EMITTER

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INTRODUCTION

General Comments on Electron Emission

The emission of electrons from solids is a subject of great technological importance and there is little possibility of it becoming less so in the forseeable future. However, the general trend or evolution from thermionic emitters and towards "cold" solid state emitters will no doubt continue. Of course technologically the most common emitter has been the thermionic emitter and continued work with thermionic emitters has brought about a refinement to where the emission current density is approaching the theoretical limit.

There are four commonly used methods of electron emission: thermionic emission, the escape of electron from a solid surface because of energy imparted (to the electrons) by heating the solid; photoemission, the ejection of electrons because of excess energy imparted by high energy photons; field emission, where electrons are able to leave the solid because of a narrowed and lowered surface barrier in the presence of a high electric field; and secondary emission, the ejection of electrons when the solid is bombarded with high energy electrons (energy transfer is from the primary to the emitted electron).

The most widely used of these methods is thermionic emission primarily because of the large current densities obtainable via relatively simple "brute-force" methods. The major drawbacks to thermionic emission are the large amounts of power required to heat the emitter and the reaction of the hot emitter surface with gas constituents in the vacuum. This latter limitation makes the thermionic emitter of questionable value as an electron sources for low pressure gauges or any low pressure mass analysis device.

The drawbacks to photoemission are the requirements for a high intensity ultraviolet source and an appropriate (low) surface barrier. The equations describing the field emission of electrons indicate that this method of emission is capable of providing large current densities. However, the application of the high fields (recall that in field emission the current density $j \propto E^2 \exp(-A/E)$ where A is a constant and E is the electric field) necessary to obtain these currents presents a practical problem in preparing and maintaining surfaces that can withstand fields near breakdown.

Secondary emission using either electrons or ions for the primary particles is a relatively clean way of getting electrons though in practice the emitted current densities are not very high. Secondary emission is used (and quite successfully) in low pressure devices where a "cold cathode" discharge provides the source for primary particles. Two major problems are evident, more or less, depending on the pressure, the liberation of gas from the cathode and the problem of sustaining a discharge at low pressures.

Hot electron emission in comparison with these more popular emission mechanisms has the advantage that the emitting surface is cold (temperature wise) and the power requirements are relatively low. The major disadvantage is the low level of emitted current. For applications in vacuum instruments there are some additional advantages such as the emission current being insensitive to pressure (at low pressure) and a surface that is relatively inert regards reactions with the residual gas. Though there is not sufficient information yet available for a definitive statement, there may be other advantages to a hot electron emitter such as only a slight temperature dependence of the emission current and narrow energy spread for the emitted electrons. These latter properties depend on the details of the actual emitter and must be taken up in that context.

Hot Electron Emitters*

A hot electron emitter is a solid state device that emits electrons excited to high energies (say in excess of 6 eV) in the solid sufficient to overcome the surface barrier without any additional energy input. The term hot electrons comes from semiconductor physics where charge carriers of high energy (higher) than the Fermi energy including the Maxwell-Boltzmann modification) are termed hot carriers. An electron of 6 eV energy has an

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*The word hot used in this report has two meanings 1) the physical temperature of a piece of material and 2) the energy state for electrons in a solid. This should present no problem in interpretation; the context should make clear the meaning. For example, the statement "Hot electron emitters are not hot." is understood to mean that solid state devices that emit electrons via the mechanism of hot electron emission are physically cold.

equivalent temperature of 70,000 deg K. Hot carriers can be created only in regions of high electric field where the electron can gain this rather high energy between collisions with the ion cores. The emission of these hot electrons depends (once they are excited) on the lack of losses that would take away enough energy to drop them back into the Fermi sea and their ability to overcome the surface barrier.

The problem is best understood by breaking it up into three separate problems. Refer to Fig. 1 where we give a generic name to each of these regions and also physically describe the region for a reverse biased semiconductor junction emitter.

First, the electrons have to be excited to several eV of energy and this is accomplished in the generation region indicated where there must of necessity be a high electric field. The electroncs that leave this generation region and for our purposes we confine our attention to hot electrons which we define as those possessing the minimum energy necessary to surmount the barrier enter the transport region and there loose energy on their way to the surface. These hot electrons encounter a barrier at the surface which is a potential barrier of finite height and width. Those that surmount this barrier are emitted from the solid.

We can at the outset put some very general restrictions on the properties for this kind of a device. Working backwards we first note that surface barriers are the order of or greater than 5 eV for untreated surfaces of metals or semiconductors so we require that the electrons be accelerated to

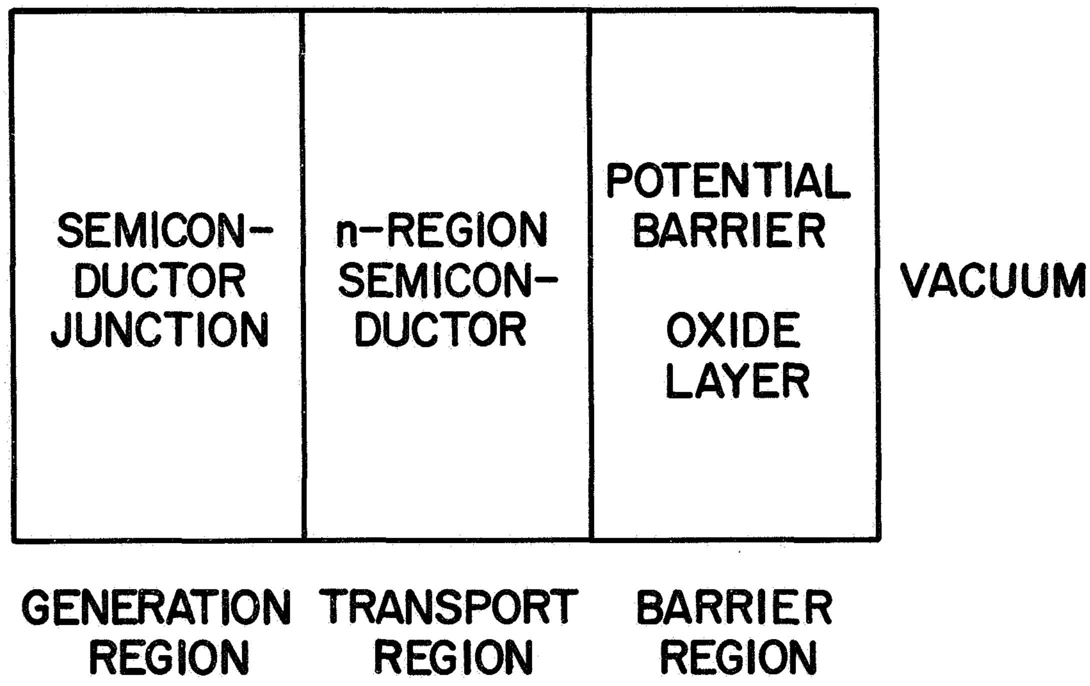

Fig. 1. The Hot Electron Emission Problem.

at least 5 eV in energy in the generation region to be considered as possible emitters. This requires further that the device be a semiconductor capable of sustaining sufficiently high fields to generate hot carriers, in excess of 5 eV in energy, in the generation region. This requirement alone allows us to make an operationally definitive but not necessarily exclusive statement that any semiconductor junction where we can produce at least an avalanche breakdown in the reverse direction is a suitable candidate for consideration as a hot electron emitter. Given such a device which surely approaches the limits of present technology we make an emitter by creating an appropriate transport region and the requirement on the transport region is that its thickness be the order of or less than the mean free path for the electrons which is ∿ 1000 Å. In order to have a more detailed understanding of this phenomenon of hot electron emission we need to better understand what goes on in these three regions so in the next section we present a simple model for a junction, a discussion of electron loss mechanisms in the transport region and barrier penetration.

THEORY

Junctions

Abrupt junction. - Let us consider now a semiconductor crystal containing a p-n junction and further assume that the junction region is very narrow. This is called an abrupt junction. In actual practice it is possible only to approach the situation of an abrupt junction and a junction that is spread out in the crystal is called a graded junction. The abrupt junction is a much simpler situation to handle mathematically and the model developed here shows most of the features of both abrupt and graded junctions. This simple model is in any case sufficient for our purposes.

Assume that we have an abrupt p-n junction as shown in Fig. 2. On the n-side of the junction there are n_{no} free electrons and p_{no} free holes and on the p-side p_{po} free holes and n_{po} free electrons. The number of electrons on the n-side is much greater than on the p-side and vice versa for the holes so

$$(1) \qquad n_{no} >> n_{po} \qquad\qquad p_{po} >> p_{no}$$

The notation here is simply that the letter n or p denotes the carrier, electron or hole, and the first subscript n or p denotes the side of the junction and the second subscript o indicates initial condition. The C_d and C_a indicate donor and acceptor concentration.

If we instantaneously create the situation (the abrupt junction) describe above there will be a diffusion of electrons into the p-region and holes into the n-region depleting the region surrounding the junction of majority carriers, that is, some electrons will be lost from the n-region and some holes from the p-region. As this depletion continues the ionized donor and acceptor atoms near the junction set up an electric field so as to oppose the continued diffusion of majority carriers. In the equilibrium condition then there is a depletion of majority carriers from the junction region and a space charge layer built up in which there is an electric field. The situation is shown in Fig. 3.

Potentials. - The difference in potential across the dipole layer created by this diffusion is related simply to the dipole moment (per unit area) by

$$(2) \qquad \phi = 4\pi D$$

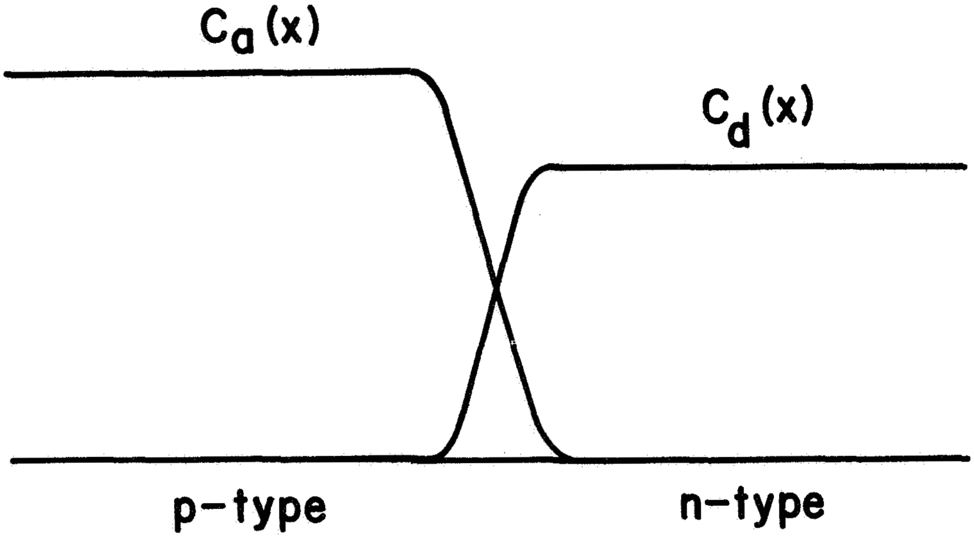

Fig. 2. Impurity Atom Concentrations in the Neighborhood of an Abrupt p-n Junction. C_d is Donor and C_a Acceptor Atom Concentrations.

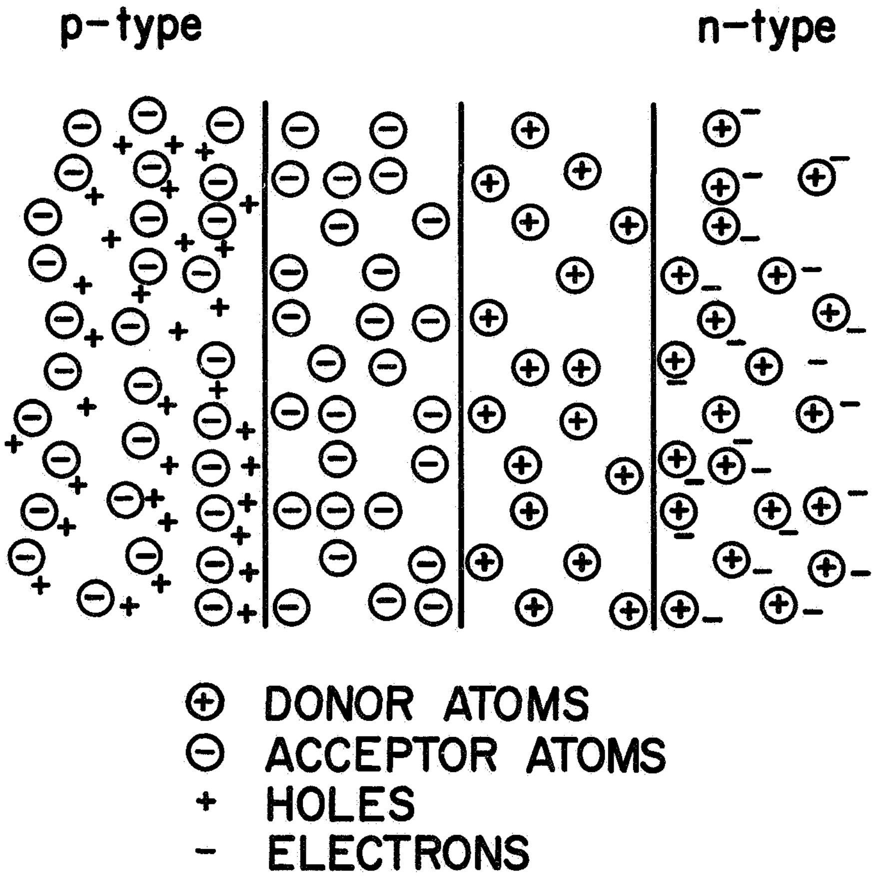

Fig. 3. Illustrative Diagram Showing the Formation of Space Charge Layers by Diffusion of Impurity Atoms.

where ϕ is the potential difference at the boundary and D is the dipole strength. The Fermi level must be at the same potential across the junction. Far from the junction the p- and n-regions must behave like separate p and n crystals and in a p-type crystal the Fermi level moves toward the valence band and in an n-type crystal toward the conductance band. Thus across a junction depletion region the bands bend so as to oppose by creating an electric field the depletion of majority carriers from the region immediately surrounding the junction as we saw in the physical picture of the previous section. The band situation is shown in Fig. 4.

The internal contact potential ϕ is determined by the equilibrium electron or hole densities far from the space charge region. The equilibrium electron density is

$$n_{no} = 2\left(\frac{2\pi m_e^* kT}{h^2}\right)^{3/2} \exp\left(\frac{E_F - E_{cn}}{kT}\right) \tag{3}$$

and the equilibrium hole density is

$$n_{po} = 2\left(\frac{2\pi m_e^* kT}{h^2}\right)^{3/2} \exp\left(\frac{E_F - E_{cp}}{kT}\right) \tag{4}$$

The double subscript on E such as E_{cn} is that the first subscript refers to the band, conduction or valence, and the second subscript to the side, p or n. Solving these equations for E_{cn} and E_{cp} we have

$$E_{cp} - E_{cn} = kT \ln \frac{n_{no}}{n_{po}} \tag{5}$$

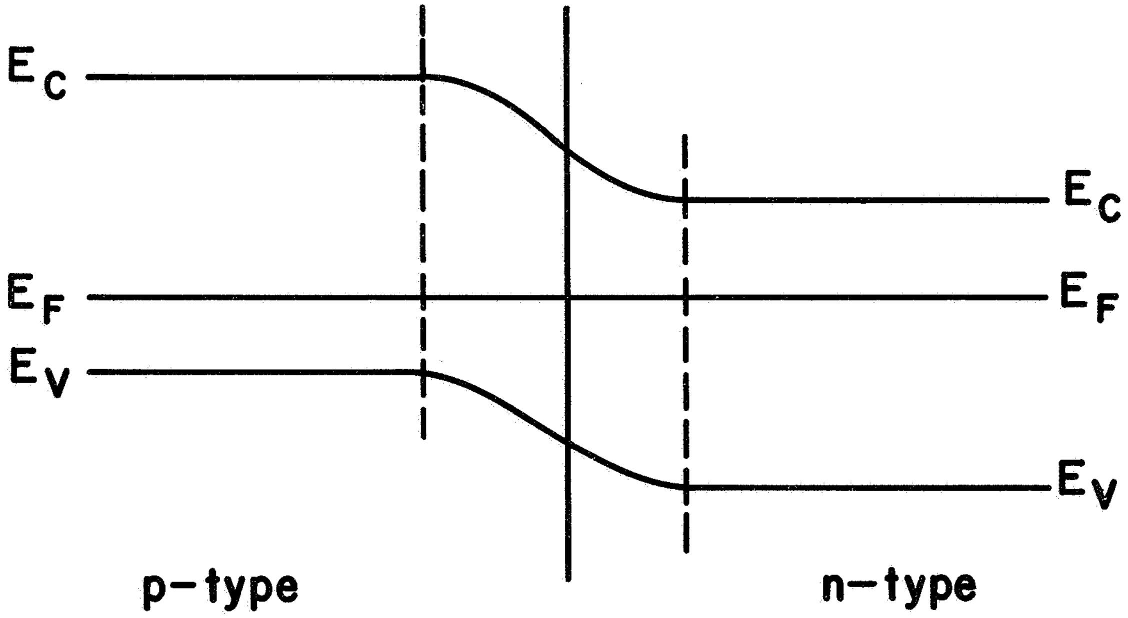

Fig. 4. Potential Diagram Showing Band Situation Near a p-n Junction (No Applied Voltage).

$$\phi = kT \ln \frac{n_{no}}{n_{po}} \tag{6}$$

Now we want to consider the effect of an applied voltage on a semiconductor containing a p-n junction. Since the carriers are depleted from the junction region, most of the applied voltage will appear at the junction. If the voltage is applied to the device in such a way as to flatten out the bands and effectively reduce the inner potential, the junction is said to be biased in the forward direction. In this situation the impedance of the junction is reduced with the potential barrier being given by $\phi - V_o$ where V_o is the applied voltage. This is assuming all the voltage appears across the junction which is generally the case. If the sign of the applied voltage is reversed with the negative voltage applied to the p-region then this is the reverse direction and the effective potential is the same expression $\phi - V_o$ where V_o is now a negative quantity. Also in this situation the impedance is increased.

Junction model. - Now we can proceed to set up a mathematical model for the junction. The first point to consider is how the space charge varies as we approach the junction from the p or n sides. Far from the junction the net charge density is zero on both sides and on the p-side just before the junction it is $-eC_a$ and on the n-side eC_d. As the junction is approached from the p-side the charge density goes quickly from zero to $-eC_a$ with the same situation obtaining as we approach from the n-side with the charge density quickly approaching eC_d. This is assuming that all donors and acceptors very close to the junction are ionized, that is, that $e(\phi - V_o) >> kT$ which is most always the case. This situation is shown in Fig. 5.

With the notation shown in the diagram we can now write down the Poisson's equation for the solid assuming that the transition region is sufficiently narrow so that it can be approximated by a straight (vertical) line thus

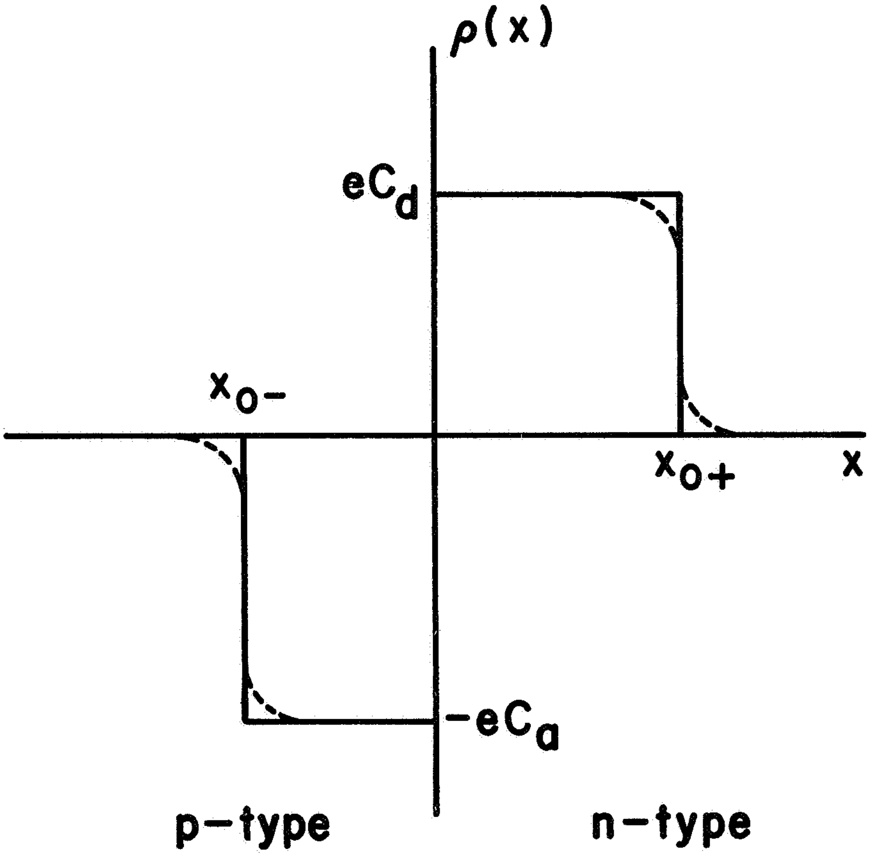

Fig. 5. Charge Density Distribution for the Abrupt Junction Model; Assumed (Solid Curve) and Actual (Dashed Curve).

$$
\begin{aligned}
&\frac{d^2\phi_+}{dx^2} = -\frac{4\pi eC_d}{\kappa} && 0 < x < x_{o+} \\
&\frac{d^2\phi_-}{dx^2} = \frac{4\pi eC_a}{\kappa} && -x_o < x < 0 \\
&\frac{d^2\phi_-}{dx^2} = 0 && x > x_{o+} \text{ and } x < -x_{o-}
\end{aligned}
\tag{7}
$$

Beyond the space charge region the potential is a constant so that $\phi_+(x)$ for $x > x_{o+}$ is a constant and $\phi_-(x)$ for $x < x_{o-}$ is a constant. Also the difference in these potentials is just $\phi - V_o = \phi - V_o = \phi_+(x_{o+}) - \phi_-(-x_{o-})$. At the junction the electric field must be continuous since there is no surface charge (Gauss's theorem) so that

$$
-E_+(o) = \left(\frac{d\phi_+}{dx}\right)_o = \left(\frac{d\phi_-}{dx}\right)_o = -E_-(o) = -E_o \tag{8}
$$

where the $E_+(o)$ and $E_-(o)$ indicate the fields in the $(o < x < x_{o+})$ and $(-x_{o-} < x < o)$ regions and E_o the common value at the junction. With these boundary conditions we can proceed to integrate Eq. (7). The first integral is

$$
\begin{aligned}
&\frac{d\phi_+}{dx} = -\frac{4\pi eC_d}{\kappa}x + A = -E_+(x) && (0 < x < x_{o+}) \\
&\frac{d\phi_-}{dx} = \frac{4\pi eC_a}{\kappa}x + B = -E_-(x) && (-x_{o-} < x < 0)
\end{aligned}
\tag{9}
$$

Outside the space charge region the field must be zero so $d\phi_+/dx = 0$ at x_{o+} and $d\phi_-/dx = 0$ at $-x_{o-}$ thus the constants are

$$A = \frac{4\pi e C_d}{\kappa} x_{o+} \quad \text{and} \quad B = \frac{4\pi e C_a}{\kappa} x_{o-} \tag{10}$$

and so Eq. (9) becomes

$$-E_+(x) = \frac{d\phi_+}{dx} = \frac{4\pi e C_a}{\kappa} (x_{o+} - x) \tag{11}$$

$$-E_-(x) = \frac{d\phi_-}{dx} = \frac{4\pi e C_a}{\kappa} (x + x_{o-})$$

If we set $x = 0$ in these field equations we find a relation between the densities and the widths of the space charge region

$$E_o = - \frac{4\pi e C_d x_{o+}}{\kappa} = - \frac{4\pi e C_a x_{o-}}{\kappa} \tag{12}$$

so that

$$\frac{C_a}{C_d} = \frac{x_{o+}}{x_{o-}} \tag{13}$$

and the ratio of the widths of these space charge layers is inversely proportional to the charge density.

Integrating the first of Eq. (11), $\phi_+(x)$ can be written as

$$\phi_+(x) = \frac{-2\pi e C_d}{\kappa} (x_{o+} - x)^2 + C \tag{14}$$

where a constant due to the $(x_{o+} - x)^2$ term has been taken up with the usual constant of integration. Similarly we have

$$\phi_-(x) = \frac{2\pi e C_a}{\kappa} (x + x_{o-})^2 + D \tag{15}$$

Since the potential must be continuous at $x = 0$ we take the arbitrary potential zero to simplify evaluation of the constants.

$$C = \frac{2\pi e C_d x_{o+}^2}{\kappa} \quad \text{and} \quad D = - \frac{2\pi e C_a x_{o-}^2}{\kappa} \tag{16}$$

and the potential has the form of

$$\phi_+(x) = \frac{2\pi e C_d}{\kappa} [x_{o+}^2 - (x_{o+} - x)^2] \tag{17}$$

$$\phi_-(x) = \frac{2\pi e C_a}{\kappa} [(x + x_{o-})^2 - x_{o-}^2] \tag{18}$$

in the vicinity of the junction.

We can now specify the width of the junction in terms of the material parameters for the semiconductor. The effective inner potential $(\phi - V_o)$ defined above can be written as

$$\phi - V_o = \frac{2\pi e}{\kappa} [C_d x_{o+}{}^2 - C_a x_{o-}{}^2] \tag{19}$$

and x_{o+} and x_{o-} are related by Eq. (13) so we can solve for x_{o+} and x_{o-}

$$x_{o+} = [\frac{\kappa(\phi - V_o)}{2\pi e} \quad \frac{C_d}{C_a(C_d + C_a)}]^{\frac{1}{2}} \tag{20}$$

$$x_{o-} = [\frac{\kappa(\phi - V_o)}{2\pi e} \quad \frac{C_d}{C_a(C_d + C_a}]^{\frac{1}{2}} \tag{21}$$

and the total width of the space charge region $x_o = x_{o+} + x_{o-}$ is

$$x_o = [\frac{\kappa(\phi - V_o)}{2\pi e} \quad (\frac{1}{C_d} + \frac{1}{C_a})]^{\frac{1}{2}} \tag{22}$$

Substituting in Eq. (12) for the field at the junction we find

$$E_o = [\frac{8\pi e(\phi - V_o)}{\kappa} \quad (\frac{1}{C_d} + \frac{1}{C_a})^{-1}]^{\frac{1}{2}} \tag{23}$$

Of course the field is also given by the simple relation $E_o = 2(\phi - V_o)/x_o$.

<u>Zener diode</u>. - When a very high reverse bias is applied to a p-n junction there is a very sharp bending of the bands as illustrated in Fig. 6. In this situation the potential energy barrier separating electrons in the valence band of the p-region

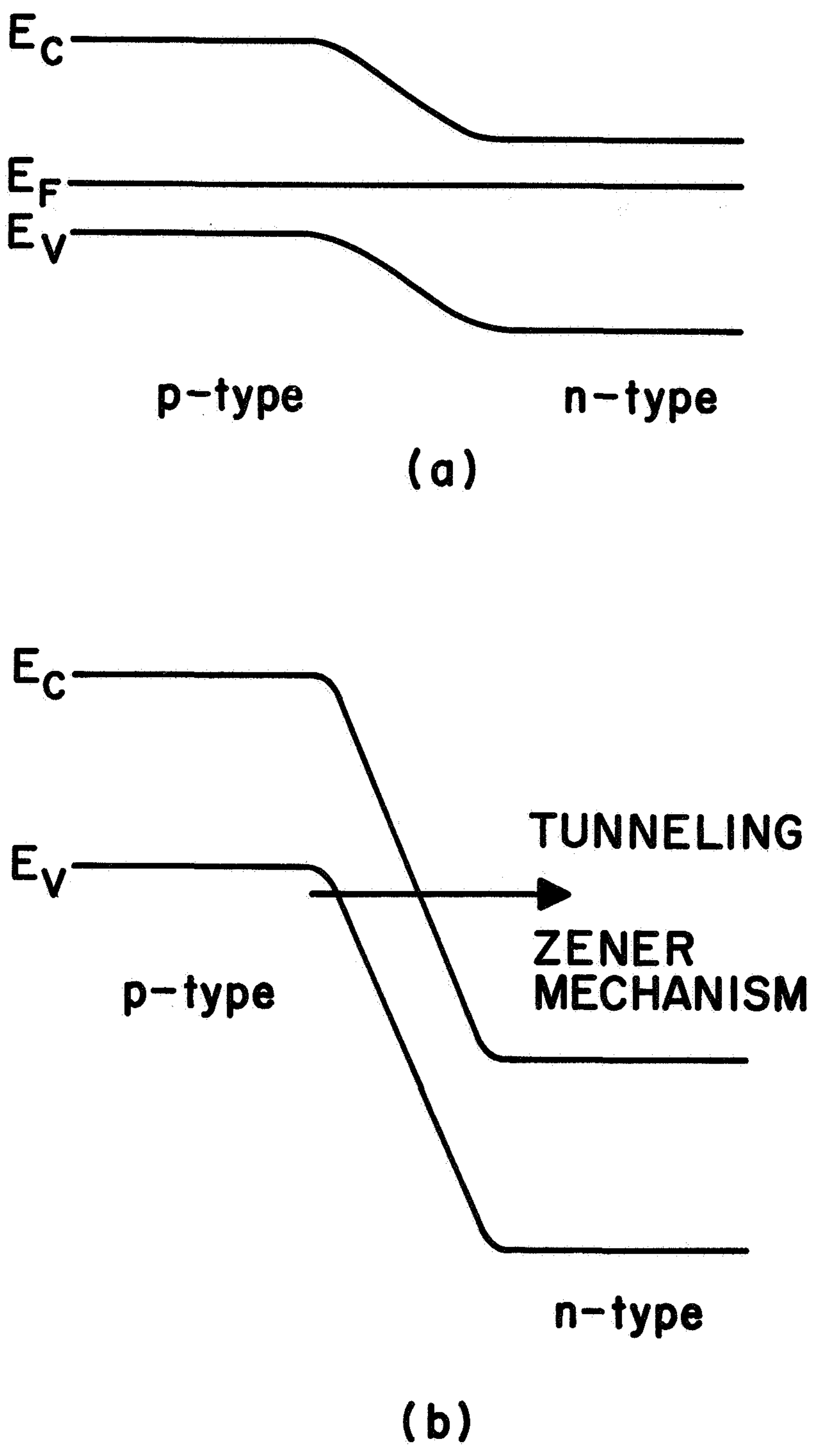

Fig. 6. Band Diagram for a Zener Diode with (a) No Voltage Applied and (b) Reverse Bias.

from empty states in the conduction band in the n-region becomes very narrow and tunneling of electrons from the p- to the n- region may occur. This reverse bias electron tunnel current is the Zener current. The phenomenon can be looked on as internal field emission and is analogous to the problem of field emission from a metal where electrons inside the metal have to penetrate (tunnel through) a surface potential barrier. In the barrier penetration problem, a special case of which we shall take up shortly, the transmission is proportional to an exponential containing the barrier width and square root of the barrier height in voltage. Thus we see there are two requirements for the Zener mechanism, the bands must be bent sufficient so electrons in the valence band are opposite allowed states in the conduction band and the barrier width reduced sufficient to allow appreciable transmission. Both these requirements are met with a narrow junction and a high reverse bias voltage. Looking back to Eq. (22) we see that the narrowest junctions, those most suitable for use as a Zener diode, are those where the material is highly doped and in these high fields exist even before application of voltage.

Avalanche diode. - Another method of obtaining high reverse bias currents is to use the avalanche mechanism. If the electrons which are providing the current in a reverse bias junction can between collisions acquire sufficient energy from the electric field to create electron-hole pairs by impact ionization (of atoms) an avalanche effect will be initiated leading to breakdown in the junction. The condition for avalanche breakdown in a junction then is that the electrons acquire sufficient energy between collisions for impact ionization. If the impact ionization energy is E_i then the critical field for avalanche breakdown is

(24) $$E_c = \frac{E_i}{\lambda}$$

where λ is the mean free path. In most crystals λ is the order of 10^{-5} cm and E_i is the order of 10 eV so we require fields of order 10^6 V/cm. The actual breakdown voltage for a junction can be determined from Eq. (23) if V_b replaces V_o and $V_b >> \phi$ so that the field is given by

(25) $$E_b \simeq \frac{E_i}{\lambda} = [\frac{8\pi e V_b}{\kappa} (\frac{1}{C_d} + \frac{1}{C_a})^{-1}]^{\frac{1}{2}}$$

and solving for V_b we have

(26) $$V_b = \frac{\kappa E_i^2}{8\pi e^2 \lambda^2} (\frac{1}{C_d} + \frac{1}{C_a})$$

Since the mean free path (electron-ion core collisions) is inversely proportional to temperature the avalanche breakdown voltage increases with temperature. Contrariwise, the Zener mechanism is relatively insensitive to temperature because the electrons traverse the entire junction without suffering a collision.

The actual breakdown mechanism depends on the material and the junction. Those devices with abrupt junctions and high doping levels will generally break down via the Zener mechanism while for graded junctions or abrupt junctions with small doping the breakdown mechanism will be avalanche. Experimentally the temperature dependence determines the mechanism.

Electron Transport in Semiconductors

After the electrons are excited to high energies in the generation region most of their kinetic energy is manifest in a high velocity component directed toward the emitting surface. Only electrons with energies greater than ~ 5 eV can overcome the barrier at the surface and escape from the material so in determining the predominant electron loss mechanism in this region, we must keep in mind that we are looking for electron losses operating at energies > 5 eV. In this section then we give a survey of the electron loss mechanisms that can operate on electrons in transport.

In this discussion we must realize at the outset that the electron loss mechanisms leading to resistivity as we generally speak of it in connection with problems in the conductivity metals, are not necessarily the ones of interest here. In normal conduction phenomena an electron collision where there is momentum transferred but in which momentum is conserved does not lead to resistivity because the current is not affected (remember current is basically number x charge x velocity). Such a collision, however, may reduce the energy of the primary electron sufficient to make it impossible for this electron ever to be emitted from the material. For example, if a 6 eV electron traveling in a specified direction collides with a thermal electron and the two electrons end up moving off in the same direction each with 3 eV energy the total current has not changed but the probability of the original electron overcoming a 5 eV barrier has gone from unity to zero.

Also we must consider loss mechanisms other than those typical for conduction electrons because the electrons we are concerned with have higher energies than typical conduction electrons and for most collision processes there is a strong dependence of free path length or characteristic collision time on energy.[†] For example, conduction electrons in metals typically have mean free paths of ∿ 1000 Å while the free path length for electron-electron collision can be 100 Å or less in the 5 - 10 eV range (ref. 2).

With this general introduction then we proceed to a brief discussion of the several electron loss mechanisms we need to consider. Generally the electrical resistivity of a material depends on the departure from or disturbances to the perfect lattice. Thus in transport problems we consider (1) electron scattering by vibrating host atoms (electron-phonon interactions), (2) scattering by impurities and lattic imperfections, that is, disruption of the uniform periodic lattice by imperfections therein and (3) electron-electron interactions. The relative importance of these is the order given with the electron-phonon interactions being by far (by several orders of magnitude) the more important.

To this usual list we need add only one other for our case, (4) plasma oscillations. We now take up each of these in turn and consider their relative importance regards energy losses for hot electrons.

Plasma oscillations (ref. 2). - "Plasma" type interactions characteristically involve an energy loss on the part of the high energy electrons in excess of 10 eV and have an associated free path length of order 200 Å. Since the electrons injected into

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[†] The expressions, "mean free path", "free path length" and "characteristic collision time" all refer to a time or distance between collisions. In this report the term "mean free path" refers only to the processes leading to resistivity in metals.

the transport region originate in an avalanche or at best a Zener junction few of the electrons are expected to have sufficient energy to enter into plasmon interactions with this attendent large energy loss. Because this type of interaction is not totally beyond the realm of possibility it should be considered for each case, that is each device. The free path length and loss per interaction are such as to drastically reduce the probability of electron emission if this mechanism operates.

Impurity and lattice imperfections. - We can get some idea of the relative importance of this mechanism for our situation with a simple order of magnitude calculation and logical argument. The initial assumption is that one (electron-electron) interaction produces sufficient energy loss to remove the carrier from consideration as a possible emitter. We can estimate an effective cross section σ_{eff} that would be necessary for this process to be significant and so we define $\sigma_{eff} \sim \frac{1}{C_i L}$ where C_i is the impurity concentration and L is the maximum path length available for the interaction or the thickness of the transport region. The maximum value for L is 1000 Å, the maximum value of the mean free path for the electrons; the transport region must be of order or less than this value. The maximum concentration we could expect is $10^{19}/cm^3$* so $\sigma_{eff} \sim 10^{-14}$ cm^2. What this calculation tells us is that in order for impurity scattering to have any influence the cross section for the impurity atoms must be at least 10^{-14} cm^2. This is an order of magnitude larger than the geometrical cross section of a lattice site which is 10^{-15} cm^2 so we can neglect impurity atom scattering. Now assuming further

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*This concentration amounts to approximately one impurity atom for every one thousand host atoms sufficient to drive the valence band to the close proximity of or into the Fermi level for most semiconductors assuring at least an avalanche and probably a Zener junction.

that the electrical extent of a lattice defect and hence its cross section, is roughly equal to that for impurity atoms we can neglect scattering at lattice imperfections also (assume lower concentrations).

Electron-electron interactions. - In any electron-electron interactions that we want to consider, that is, where one electron is "hot" and the other is not we would expect that the primary electron would be scattered into a lower energy state and removed from consideration regards emission. For electrons near a band edge and here we assume that the hot electrons are close (within 1 or 2 eV) to the bottom of the valence band the collision frequency is (ref. 3)

$$\frac{1}{\pi^4} \frac{e^2}{a^2} \frac{(kT)^2}{\hbar E_q^3} \tag{24}$$

where a is the spacing of the electron gas and the other symbols have their usual meaning. A "hot" electron that enters into an electron-electron interaction is assumed to be scattered into a lower energy state, either into the Maxwell modified Fermi distribution in the valence band or into the conduction band. Taking kT for 6 eV electrons and calculating a on the basis of a concentration of 10^{19} 1/cm^3 and taking $E_q = 2.8$ eV we obtain a time between collisions of $\tau_{ee} \sim 4 \times 10^{-13}$ sec. Again using 6 eV electrons, calculating the velocity and using this τ_{ee} we find that the free path length for this kind of collision is 6000 Å.

This is still a bit large for consideration as a loss mechanism since the transport region must be 1000 Å or less.

However, this mechanism should be seriously considered for each particular situation because it is close (within an order of magnitude) to the mean free path.

Electron-phonon interactions. - Electron-phonon interactions physically are the scattering of electrons by the vibrating host atoms with the scattered electron going into another momentum state with a coincident absorption or emission of a phonon.

It is this interaction that predominates in the classical resistivity of metals and therefore defines the mean free path.[†] The energy per interaction is of order 0.1 eV for the energy range we are interested in with one interaction every few lattice sites. There is also a strong dependence of the energy loss per interaction on electron energy with the loss increasing for high energy electrons. With this kind of situation it is clear that this loss mechanism obtains and is no doubt primarily responsible for the attenuation of hot electrons in transport through the lattice. Because this loss mechanism is well understood we shall be content with this simple argument.

In looking for the predominant interaction leading to energy losses for hot electrons in the transport region we have shown that the classic loss mechanism leading to electrical resistivity in metals should predominate with the electron-electron interactions also possibly playing a role. The exact mechanism and its magnitude need be worked out for each particular case though we would expect on the basis of the above to find the limiting loss mechanism among these later two.

[†] The mean free path as it is used in describing the resistivity in metals and defined classically by Wilson is an operational definition and does not prescribe the mechanism for energy loss.

Barrier Penetration

The last thing the electrons must do in order to leave the solid is penetrate the surface barrier. On the basis of what we have done so far it would appear that in most devices, at least some of the "hot" electrons will reach the surface barrier with sufficient energy to pass the barrier, in a classical sense, with only a discrete loss in energy. The barrier height of say 5 eV is about the same energy as many of the hot electrons so we should look into the attentuation introduced by the barrier for electrons with energy nearly equal to the barrier height.

The model for barrier transmission we shall use is the usual simple one for barrier transmission shown in Fig. 7. This is a square barrier of height U_o and width b with a particle of energy E incident from the right. By appropriate matching of the free particle wave functions we can obtain an expression for the transmission of the barrier.

$$(25) \qquad T = e^{-2\left[\frac{2m}{\hbar^2}(U_o - E)\right]^{\frac{1}{2}} b}$$

This expression is most realistic since it provides greater transparency for small mass, less difference between the barrier height and the energy of the incident particle and a narrower barrier. We can work out some more convenient relations for seeing the effect of this transmission on the emitted current of electrons by putting in the constants m and $\hbar$. If this is done we find a numerical relation

$$(26) \qquad T = \frac{1}{e^{1.1\mathrm{x}10^{8}\Delta E^{\frac{1}{2}} b}}$$

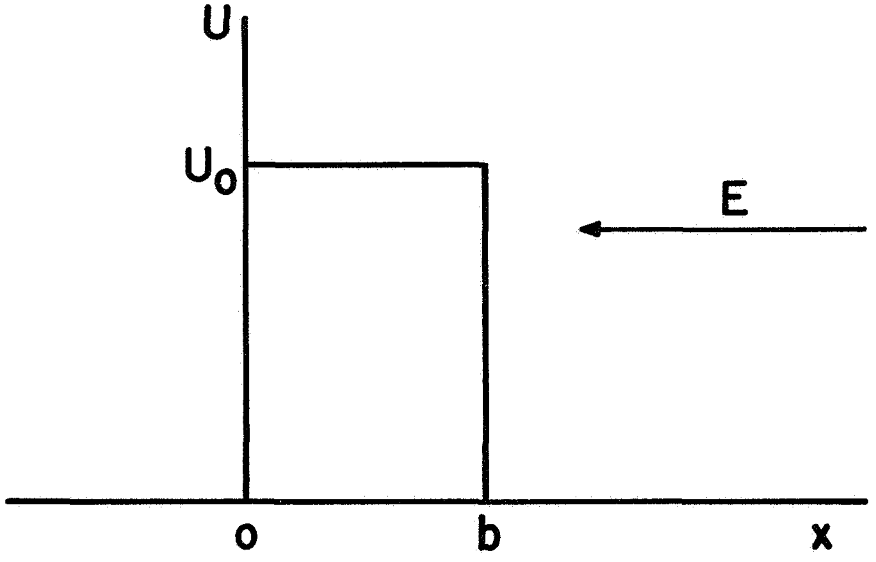

Fig. 7. Model for Barrier of Fixed Height and Width.

where ΔE is the energy difference measured in eV and b is the width in cm. If we measure b in Angstrom, we can use an even simpler approximate relation

$$T = \frac{1}{e^{\Delta E^{\frac{1}{2}} b}} \tag{27}$$

We can also write this in another form.

$$\Delta E^{\frac{1}{2}} b = \mathrm{Ln}\frac{1}{T} \tag{28}$$

Now we can plot (Fig. 8) T versus $\Delta E^{\frac{1}{2}} b$ on log linear paper which will be a straight line and see what combinations of barrier height and width give reasonable transmission. For example with an oxide layer 20 Å thick which is about the smallest we can expect the energy of the incident electron need be only 0.25 eV below the barrier height to reduce the transmission to 10^{-5}. Thus our first approximation is to take the barrier as a classical one, that is, electrons with energy greater than the barrier height get over and those below do not.

EXPERIMENTAL

Brief Historical Survey

Almost all of the few papers on electron emission from reverse biased semiconductor junctions have been published since 1960 (ref.s 4-12). Most of the early work was on silicon devices but more recently emphasis has been on silicon carbide. Generally speaking the hot electron emission was observed from the edges of junction devices before any formal attempt was made on devices specifically prepared to study hot electron emission.

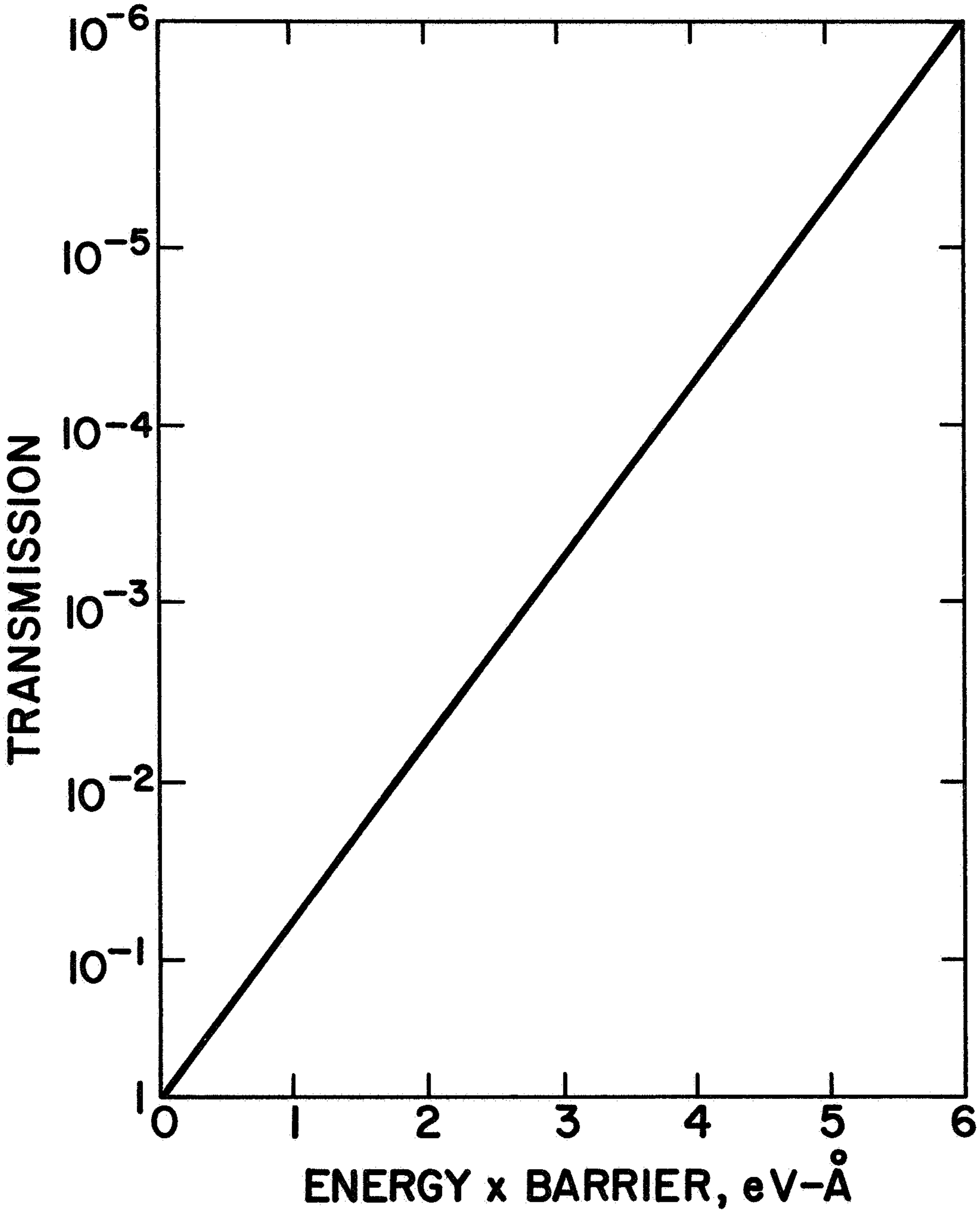

Fig. 8. Graph of Transmission Versus the Parameter Energy Difference x Barrier Width.

Typical of the first efforts were those of Patrick and Choyke (ref. 4, 9) who measured hot electron emission from SiC over a range of 10^{-12} to 10^{-6} amp and Bartelink, Moll and Meyer (ref. 7) who measured emission currents as high as 10^{-9} amp from silicon. The best reliable emission currents reported have been of order 10^{-7} amp (ref. 12). Some of the higher currents were obtained under pulsed operation.

First Simple Experiments

Our first experiments were to measure the hot electron emission current from the edge of commercial light emitting diodes. The configuration and details of the Norton and General Electric packages which we used are shown in the accompanying two figures (Fig. 9 and Fig. 10). These two packages formed the basis for our various mounting schemes used throughout this work.

One problem we encountered early on and this is peculiar to SiC rather than hot electron emission was that the crystals crack quite easily under rapid heating or cooling. In many respects the SiC crystals behaved as one might expect a piece of glass to behave under the same circumstances. This cracking problem plagued us throughout the work and in the case of SiC care must be taken to heat and cool the crystals slowly. A rate of 10°C/min appears to be satisfactory.

Our basic experimental apparatus which is shown schematically in Fig. 11 is relatively simple. The diodes are run in the reverse direction (there is usually no light emission in this direction) and the emitted electrons are collected by a plate placed close (1 - 2 mm) to the diode. The field in the junction

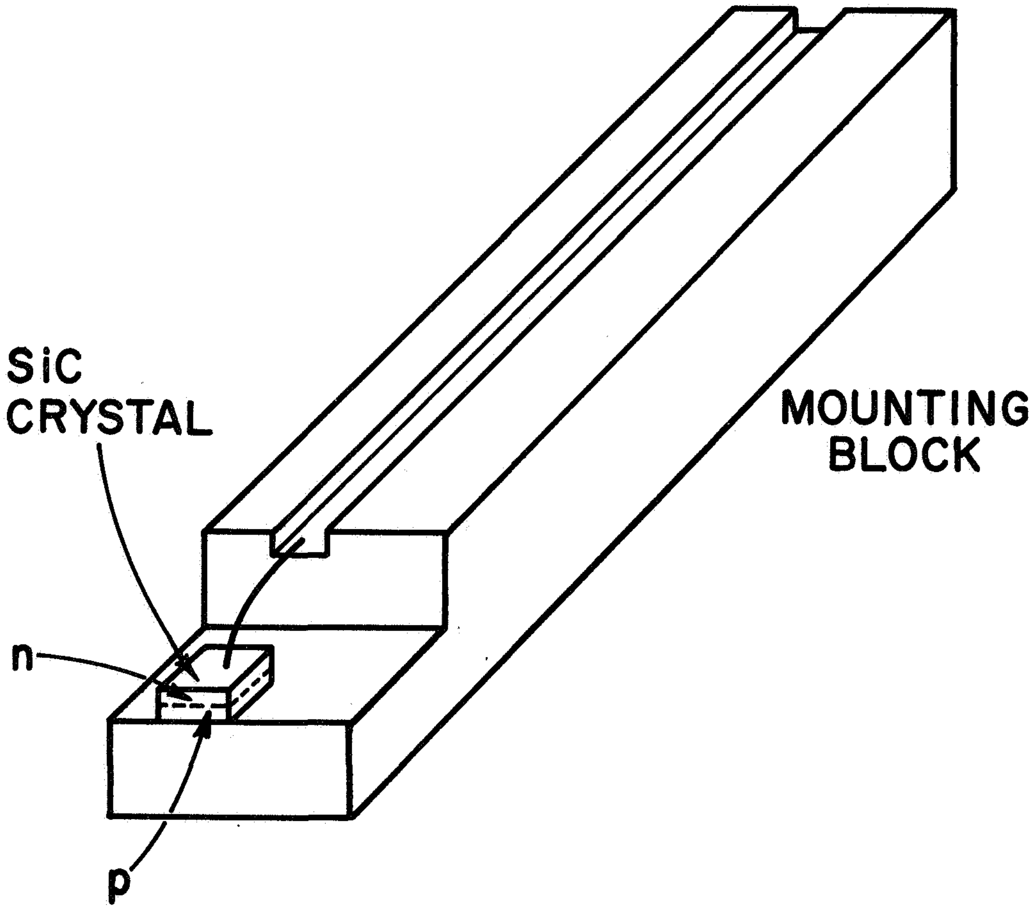

Fig. 9. Norton Standard Package - Light Emitting Diode.

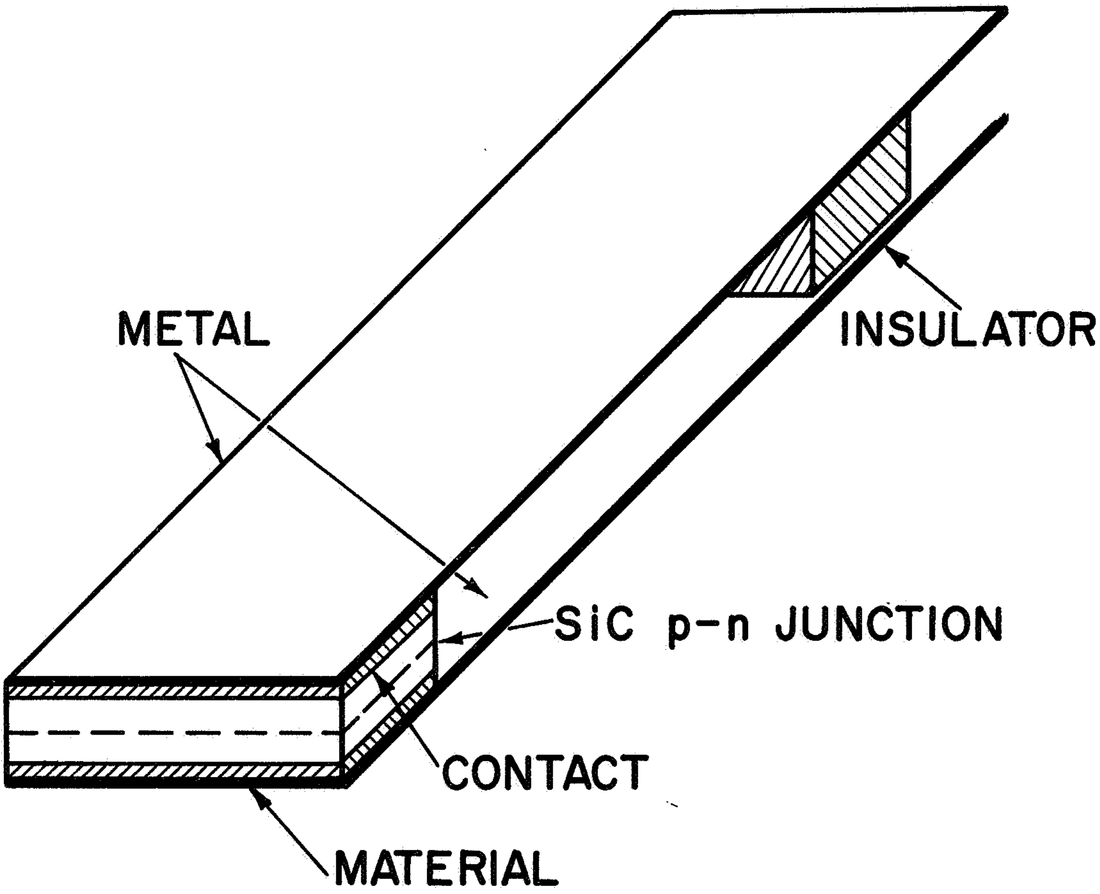

Fig. 10. General Electric Standard Package - Light Emitting Diode.

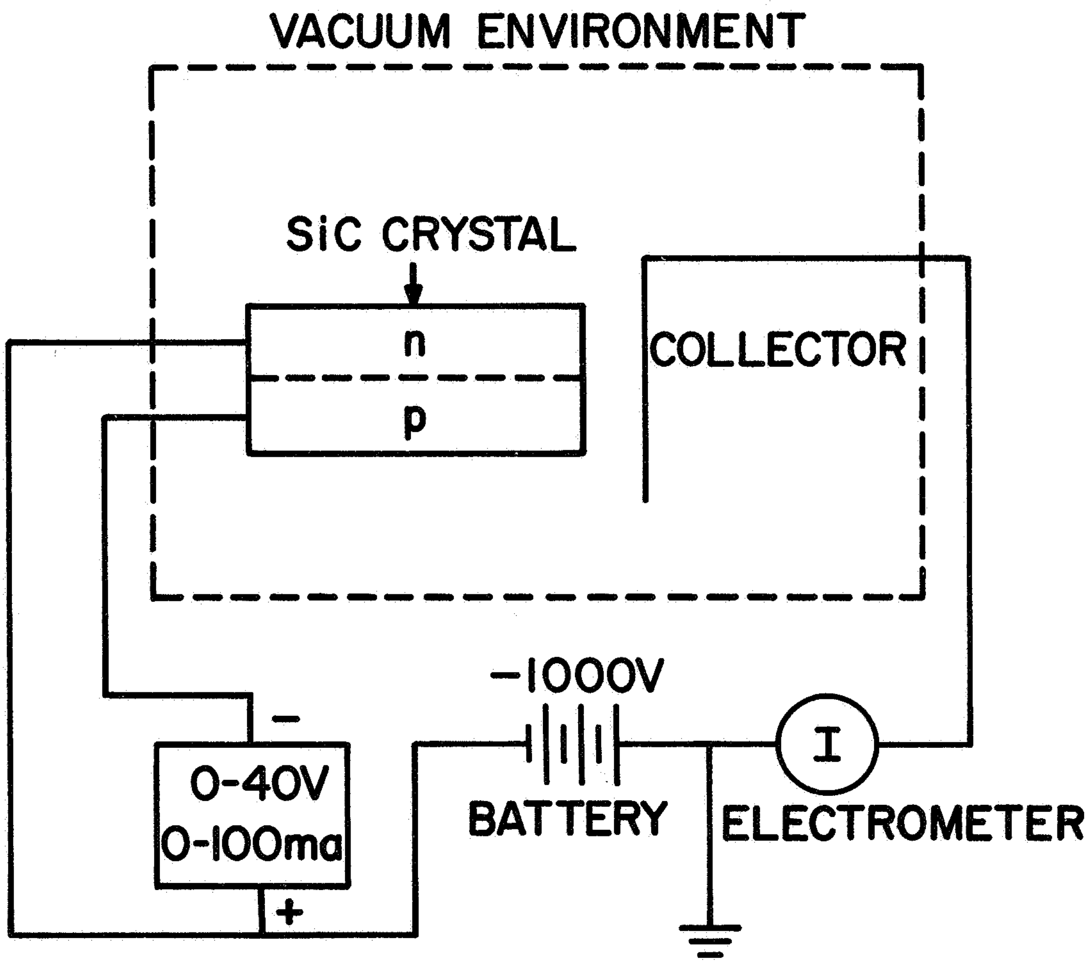

Fig. 11. Schematic Diagram of Basic Apparatus.

is of order 10^6 V/cm and the field applied by the plate must be or order 10^4 V/cm. The high field in the junction and the fact that the electrons are emitted in close proximity to the junction requires this high collecting field. If a high collecting field is not present the electrons will return to the n-region of the crystal, that is, after being emitted they will turn slightly and reenter the n-side of the crystal.

The vacuum environment was via a commercial oil diffusion pumped glass bell jar system that operated in the 10^{-5} to 10^{-6} Torr range.

Looking to the adjacent table (Table I) which is a summary of the data on edge emission from these standard package light emitting diodes we see extremely low emission currents and low efficiencies. The best (most efficient) devices were two of the General Electric SSL-11 diodes that were run at a comparatively low junction current. If we assume that the applied voltage is directly related to the voltage across the junction then as we would expect on the basis of the theory developed in the previous sections those junctions sustaining a higher voltage (those able to "heat" the electrons more) to give a better emission, and this is the case.

Reduce the Thickness of the n-Region

Ion bombardment. - One method of removing small amounts of material from SiC (say from 100 to 10,000 Angstrom) is to use positive ion bombardment. We attempted to do this with the intent of developing a technique for removing small amounts of

TABLE I

SUMMARY OF EDGE EMISSION DATA

Diode	Voltage	Current	Emission	Efficiency†
1200B2	40V	30ma	1×10^{-13} amp	3×10^{-12}
1166A1	36	25	1×10^{-13}	4×10^{-12}
1160A1⊥	34	30	2×10^{-14}	6×10^{-13}
1255A1⊥	29	30	5×10^{-12}	2×10^{-10}
1190B1B	34	30	3×10^{-14}	1×10^{-12}
SSL-11#257	35	2.6	3×10^{-12}	1×10^{-9}
SSL-11#256*	15	20	10^{-12}	$\times 10^{-10}$
SSL-11#272	35	4.2	1.2×10^{-11}	3×10^{-9}
SSL-11#273*	18.5	40	6×10^{-13}	1.5×10^{-11}

The diodes with SSL-11 in the designation are General Electric, the others Norton.

⊥ After etch in CP-4

* Unpolished side

† This definition of efficiency is very much an operational one. It is the emitted current over the junction current.

material from the crystal, that is, to reduce the electron transport distance in the n-region. There has been some work done on sputtering of SiC (ref. 13) and by inference from work on II - VI and III - V compounds (ref. 14) we would hope to remove Si and C together. Surely this is the case for the [0001] direction in SiC and probably also for other directions. The details of the mechanism are not completely clear but it is safe to say that we do not expect to have an excess of one constituent on the surface after ion bombardment.

Every attempt to bombard a crystal with ions resulted in a degradation of the junction character. Of course the ions were incident on the emitting edge (the edge facing the collector in Fig. 11). After even a very mild bombardment of 75 ma-sec at the typical cleaning voltage of 400 V (2.5 ma for 30 sec) which should remove less than 1000 atomic layers* we typically observed a 10 - 20 percent drop in voltage across the junction and a decade loss in emission current. Further bombardment of the same sample or more extensive bombardment doses on a fresh sample always resulted in further or increased degradation. After several attempts where in each case the junction was degraded ion bombardment was abandoned.

Apparently, the damage introduced by the ions or the occluded argon served to lower the conductivity. Again by inference with work on metals we expect the damage to be 1000 to 10,000 Angstrom below the surface (ref. 15). And this is

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*A dose of $\sim$ 100 u amp-sec per cm^2 gives about one ion for each surface atom and with somewhere between 1 and 10 (and closer to 1) ions necessary for each sputtered atom we can make a good estimate of the number of layers removed.

greater than the maximum thickness of the n-region which must be of order or less than 1000 Angstrom. No attempt was made to anneal out the ion bombardment induced damage as the annealing temperature is around 1000°C and the diode package would stand no where near this temperature (maximum less than 200°C).

Polishing, lapping or machining. - Mechanical methods for preparing crystal surfaces is most inappropriate because all of these methods leave scratches the order of 100 to 1000 Angstrom which is the same size as the thickness of the n-region we would like to prepare.

Bias cut junctions. - An ideal emitter would be a p-type material with a very thin n-type layer and a doping so as to produce a Zener diode with a thin contact on the n layer such that the combined thickness of the n-region and the contact was less than 1000 Angstrom. In this way "hot" electrons created in the junction would pass through the n-region and the contact and into the vacuum without suffering appreciable energy loss.

Now as an approximation we made up samples with a cut across the junction to expose a thin n-region. This technique was so successful in increasing the emission current up to acceptable working levels that most of the rest of the experimental work was done on similar samples. A drawing of this configuration for the emitters is shown in Fig. 12. And in Fig. 13 this kind of an emitter is shown on a mounting block. In this device the n-region is so highly doped that the voltage applied at the contacts is essentially all present across the junction. Looking at the insert in Fig. 12 we can make an estimate of the area where the electrons are being emitted. Assuming that an effective path length of 1000 Å in the n-region is the maximum that an hot electron can travel a strip of n material

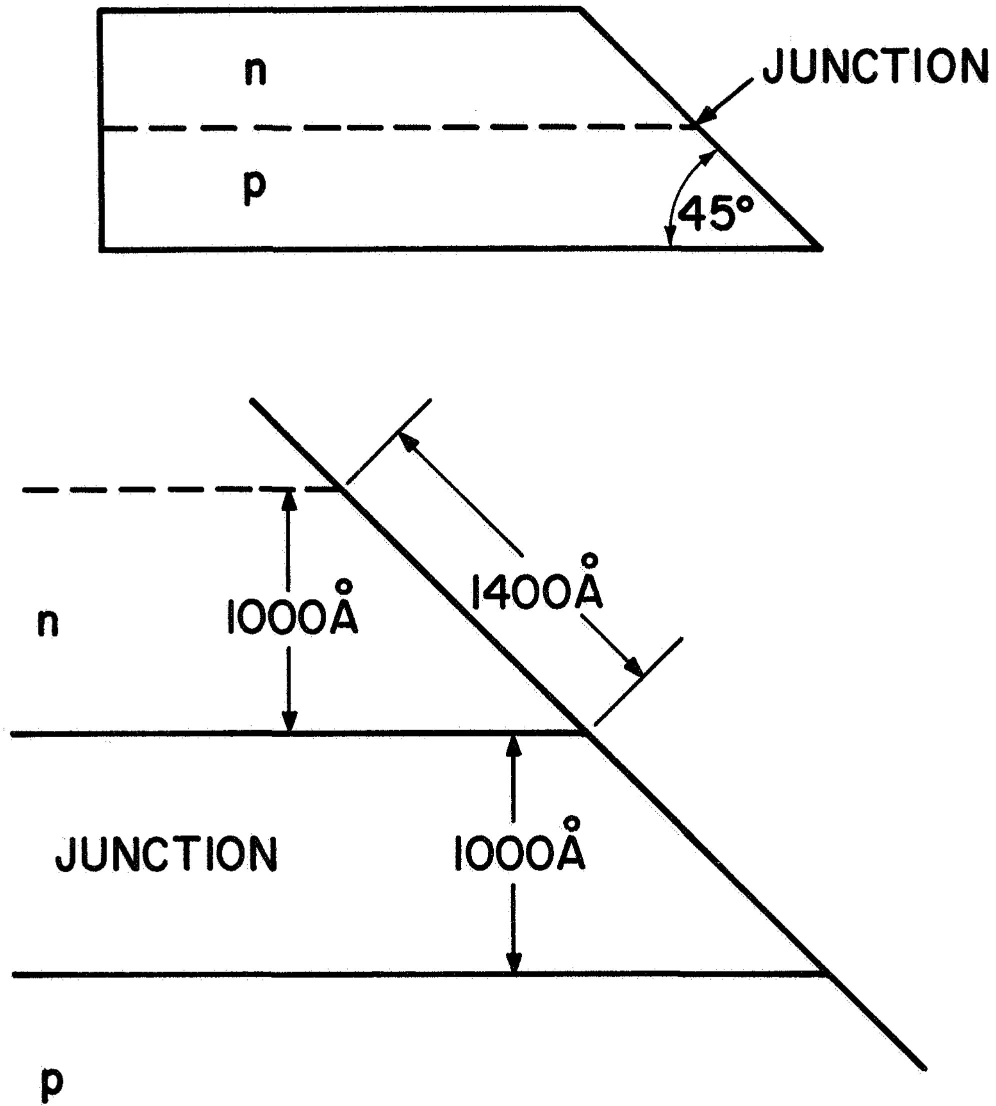

Fig. 12. Bias Cut Diode Configuration.

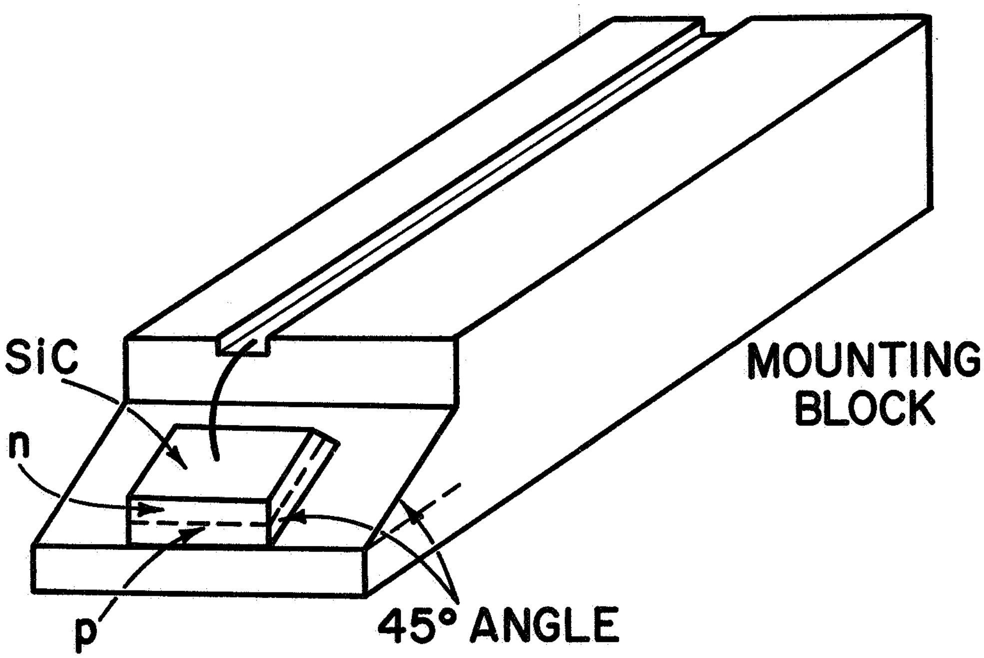

Fig. 13. Norton Diode Modified for Electron Emission.

roughly 1400 Angstrom wide should be emitting electrons. Since we most likely have an avalanche junction electrons should also be coming from the junction itself and assuming a junction width of 1000 Å and a field of between 10^5 and 10^6 V/cm there should be hot electrons most of the way across. For the sake of argument let us assume a total emitting area from the junction of 600 Å thus we have a strip of width 2000 Å for emission. Since most of the devices we used were 2 mm long the surface area for emission was 4×10^{-6} cm^2.

In Table II is a summary of data on the maximum emission obtained on these edge cut diodes subjected only to wash in acetone or alcohol or a CP-4 etch. This Table shows data typical of the many diodes checked and further is limited to very mild etches and cleanings[†]. Note however, that diode No. 1334 had a relatively high emission current and efficiency.

Lowering of the Surface Barrier

Heating. - Using this same package as shown in Fig. 13 we attempted some mild heating of the sample. We were limited in temperature by the contact material which for the Norton diodes was a lead-indium alloy and for the General Electric diodes a gold epoxy.

[†] Typical CP-4 etches were for under 5 sec. The CP-4 etch is 100 parts nitric acid, 44 parts glacial acetic acid and 16 parts 48% hydrofluoric acid.

TABLE II

SUMMARY OF EMISSION FROM 45° CUT DIODES

Diode No.	Voltage	Current	Emission	Efficiency
1317 EV	29V	30 ma	6.2×10^{-9}amp	3×10^{-7}
1342 EV	28	40	1.1×10^{-10}	3×10^{-8}
1334	23	60	2.6×10^{-7}	4×10^{-6}

Heating of the crystals was accomplished by electron bombardment from either a hot filament or a plasma. The electron bombardment was always carried out so that electrons did not strike the SiC but rather some part of the mount. Considerable care had to be taken to slowly heat and cool the crystals, otherwise they cracked. Temperatures were measured with a thermocouple.

We ordered from Norton some special diodes mounted on tungsten blocks with materials so as to withstand 700°C. Unfortunately, however, neither of these devices was operated over 200°C. With the first one a series of minor disasters such as solder melting at 100°C, leads coming off and the diode coming loose from the mounting block eventually culminated with a breakdown in the diode junction. And on the other diode we cracked the crystal early in the experiment (before exceeding 250°C).

In normal operation on a reasonably efficient (large) heat sink at approximately 30 V and 20 - 60 ma the temperature was 80 to 120°C. And the data shown in Table II was taken after running the devices for several hours in vacuum. In almost every case the initial emission current was very low, in the 10^{-12} amp or lower range but during the first hour of operation there was a rapid rise of several orders of magnitude usually to the 10^{-9} or 10^{-10} amp range and after this a slow rise of another decade or so over several hours. Heating, other than that inherent in operation of the device, or etching in CP-4 served to reduce the time necessary to reach an equilibrium emission current. Sometimes the emission current rose slowly for many hours (10 to 20) so etch in CP-4 was most appropriate to hurry the process along. This situation is attributed to a dirty surface coming to equilibrium with its environment with the final state being determined by the temperature of the device and the vacuum.

A summary of our efforts to specifically improve emission by heating of the package shown in Fig. 13 is given in Table III.

Cesium adsorption. - In an attempt to directly lower the surface barrier we used a cesium ion gun to deposit a known amount of cesium on the surface. A simple schematic of the gun is shown in Fig. 14. This ion gun uses a zeolite (molecular sieve) in which an exchange reaction has been performed to place cesium in an alkali metal site. The bond arrangement in the zeolite is such that the cesium is liberated as an ion. This type of gun has two distinct advantages. First, cesium is not released into a vacuum chamber to do its destruction on working parts and second, controlled amounts of cesium can be deposited on desired surfaces simply by applying the proper voltages. In these experiments we obtained cesium ion beams in the 10^{-6} to 10^{-9} amp range which is most convenient for depositing monolayers on the metal. (Note that a dosage of 100 μ amp-sec is approximately equivalent to a monolayer coverage on 1 cm^2.) We had two very successful exposures the results of which are summarized in Table IV. Based on this data and some other less successful runs, that is, cases where we had a small fraction of or large number of monolayers deposited we see that the cesium has an effect other than lowering the work function namely reducing the voltage across the junction, most likely by a leakage path around the edge of the diodes.

This reduction in voltage across the junction had a disastrous effect on the emission current and forces the conclusion that the total effect of cesium adsorption is not beneficial. Further attempts at cesium adsorption were abandoned.

TABLE III

SUMMARY OF EMISSION FROM HEATED DIODES

Diode No.	Voltage	Current	Emission	Efficiency
1325B2*	26V	60ma	4.5×10^{-8}	7.5×10^{-7}
Heat† at 250°C for 10 min.				
	26	60	2×10^{-8}	3.2×10^{-7}
1349A1	28	25	3×10^{-12}	1×10^{-10}
Heat at 125°C for 20 min.				
	23	25	1×10^{-9}	4×10^{-8}
Heat at 200°C for 20 min.				
	23	25	1×10^{-10}	4×10^{-9}
Heat at 200°C for 20 min.				
	23	25	3×10^{-10}	1.2×10^{-8}

*This diode was previously used for cesium adsorption. It was etched and run and etched and run before this test.

†This stated time does not include heating and cooling time.

TABLE IV

SUMMARY OF EMISSION FROM CESSIATED SURFACES

Diode No.	Voltage	Current	Emission	Efficiency
1334	21V	60ma	8×10^{-9}	1.3×10^{-7}
After a dose of 600 μ amp-sec				
	18	60	2×10^{-8}	3.3×10^{-8}
1325B2	26	60	3×10^{-8}	5×10^{-7}
After a dose of 175 μ amp-sec				
	25	60	1.4×10^{-8}	2.3×10^{-7}

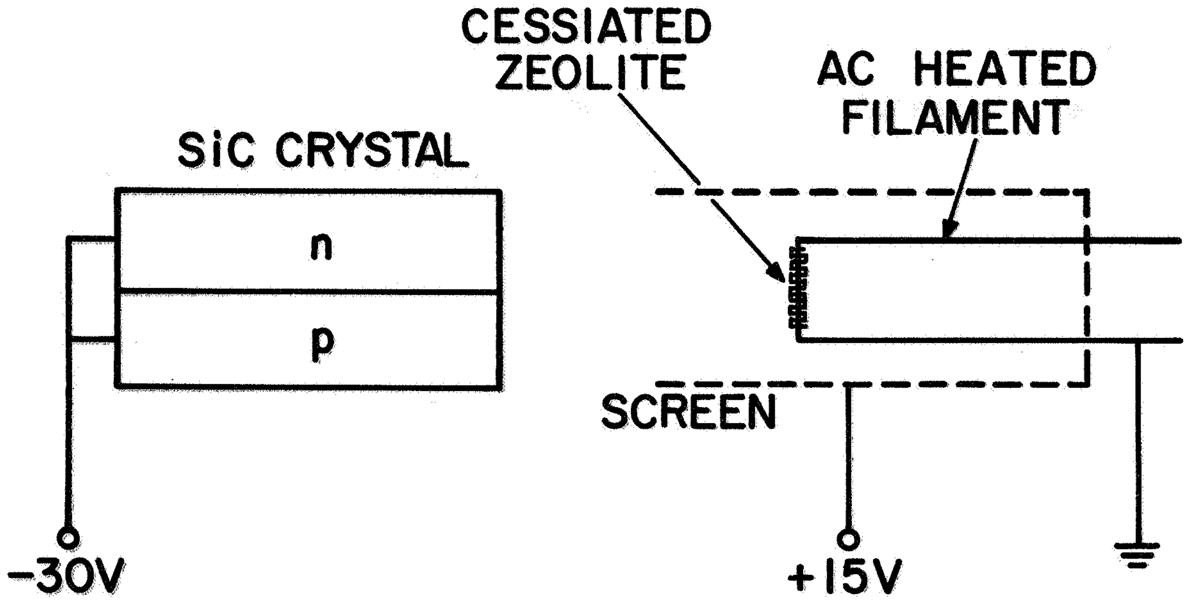

Fig. 14. Cesium Ion Gun.

<u>Tailoring the junctions</u>. - As far as tailoring the junctions to give a high voltage drop is concerned the concept is barely feasible since it is difficult enough to make the diodes let alone make them with specific impurity dopings. About all we know about the doping and the junction is that the junctions are approximately 1000 Å wide and the donor impurities are nitrogen at concentrations of approximately 10^{18} to 10^{19} per cm^3 and the acceptor impurities are boron or aluminum at approximately 10^{17} to 10^{18} per cm^3 concentrations.

DISCUSSION AND CONCLUSIONS

In the development of a model for the junction, we saw that for a junction operating in the avalanche condition the junction current is temperature dependent. There is a relatively large amount of power discipated in the junction which serves to raise the temperature of the whole device, and thus limit the current. It is this effect that in practice limits the current for a reverse biased junction running in avalanche. For a Zener diode local heating at imperfections causes "punch through" i.e., microscopic breakdown in the junction. Thus there is a clear finite limit to the junction current and the devices we have used have been operated near this limit. The junction current cannot arbirarily be increased, we have to look elsewhere for more emission.

The temperature surely affects the loss mechanism in the transport reason whatever mechanism is operating. If we assume the loss in the n-region is typical electron transport loss for condution electrons in metals (electron-phonon interactions), we expect at high temperatures* a resistance proportional to temperature. This is with a simple Einstein model for the lattice. In this theory the scattered electron is presumed to loose an amount of energy small compared with kT.

For the case of hot electron transport the energy loss per collision may be large compared with kT. If there were a large energy loss per scattering event then we would expect resistance to be proportional to the fifth power of the temperature as is the case for low temperatures.

Experimentally it should be rather easy to see if something (in this case the emission current) depends on the first or fifth power of temperature. Unfortunately, we were not able to make such a determination. There were other things going on that precluded such measurements. When the temperature of a piece of SiC is raised, in vacuum, there surely is a large change in the oxide layer thickness and probably content too. We expect the oxide layer to get thinner as we increase the temperature. There may well be regions (in temperature) between say 200 or 300°C and 1200°C where the surface condition is relatively stable and we could study the dependence of emission current on temperature without the surface changing but such was not the case in this work. In our attempts to measure emission efficiency as a function of temperature we always observed an increase in emission efficiency as the temperature was increased up to 200°C or so and then a decrease. The initial increase was presumed due to a thinning barrier layer and shortly (usually one or two data points) after the observed decrease in efficiency with temperature we destroyed the device. This kind of an experiment however, does appear possible with sufficient perserverence and would be very helpful in understanding the loss mechanism.

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*High temperatures in this context means high in relation to the Debye temperature. All of the devices we worked with were presumably in the high temperature range.

Though it appears, at this point, that electron-phonon interactions produce attentuation of the electron beam there has most assuredly not been sufficient work to rule out other loss mechanisms.

The effect of a finite barrier appears to be simple. If we take a barrier 5 Å wide (approximately one atom) which is as small as we could ever hope to get then electrons 1 eV below the barrier are attenuated by a factor 10^{-5}.

On the basis of the work in Theory and the geometric arrangement of Fig. 12 we can make an estimate of the maximum current we might be able to observe for this configuration. For convenience we make this calculation for 1 ma of junction current. If there is 1 ma of junction current through a junction 2 mm on a side. This is 1×10^{-3} amp/4×10^{-2} cm^2 or 2.5×10^{-2} amp/cm^2. A 2000 Å strip 2 mm long has an area of 4×10^{-6} cm^2 and so there would be 1×10^{-7} amp across the junction per ma of junction current in the device available for emission.

The maximum current we have observed is 4×10^{-9} amp per ma of junction current (Norton diode No. 1334, Table II) which is close to the calculated maximum value (4%) considering the sophistication of this calculation.

The several attempts to directly reduce the thickness of the n-region were unsuccessful because they introduced damage into the crystal to a depth comparable with or in excess of the desired thickness of this region.

Direct lowering of the work function by cesium adsorption may or may not have been successful. The total effect of cesium adsorption was not however in the desired direction. Unless these undesirable effects of leakage can be overcome, there is no reason to use cesium adsorption to lower the work function.

Heating the crystals like etching seems to be of some help though primarily in decreasing the time to reach equilibrium. There is a difference of opinion in the literature regards heating with some authors claiming necessity of heating to one or another temperature (some as high as 600°C) and others claiming this of no value (ref. 4, 11, 12). Our experience indicates that heating helps in rapidly attaining the maximum emission current but does not appreciably alter that maximum.

REFERENCES

1. Wilson, A. H.: The Theory of Metals. Cambridge University Press, 2d.ed., Cambridge, England, 1953.

2. Pines, D.: Collective Energy Losses in Solids. Rev. Mod. Phys., Vol. 28, 1956, pp. 184-198.

3. Peierls, R. E.: Quantum Theory of Solids. Oxford at the Clarendon Press, England, 1956, p. 133.

4. Patrick, L.; Choyke, W. J.: Electron Emission from Breakdown Regions in SiC p-n Junctions. Phys. Rev. Lt. Vol. 2, January 1959, pp. 48-50.

5. Goffaux, R.: Emission Electronique De Jonctions P-N L. J. de Phys. & Rad., Tome 21, Fev. 1960, pp. 94-96.

6. Gleichauf, P. H.; Ozarow, V.: Electron-Emission Microscope and Velocity Distribution Studies on Silicon Carbide p-n Junction Emitters. J. Appl. Phys. Vol. 32, March 1961, pp. 549-550.

7. Bartelink, D. J.; Moll, J. L.; Meyer, N. I.: Hot-Electron Emission from Shallow p-n Junctions in Silicon, Phys. Rev., Vol. 130, May 1963, pp. 972-985.

8. Senitzky, B.: Electron Emission from Silicon p-n Junctions. Phys. Rev., Vol. 114, Nov. 1959, pp. 874-879.

9. Patrick, L.: Electron Emission from Reversed Biased p-n Junctions in SiC. J. Appl. Phys., Vol. 32, Oct. 1961. pp. 2047-2048.

10. Fridel, I.; Kholuyanov, G. F.: Electron Emission from p-n Junctions in SiC Prepared by Nitrogen Diffusion. Soviet Physics - Solid State, Trans. Bull., Vol. 5, Jan. 1964, pp. 1418-1421.

11. Bok, J.: Klein, J.: Influence De L'Interaction Electron Electron Sur L'Emission D'Electrons Chauds A Partir Des Jonctions P-N Pett Profondes. J. Phys. Chem. Solids, Vol. 27, pp. 1295-1303.

12. Brander, R. W.; Jodkill, A.: Silicon Carbide Cathodes. 2nd Int. Conf. on SiC, to be published.

13. Dillon, J. A., Jr.: The Oxidation of Silicon Carbide. Silicon Carbide, Pergamon Press, New York, 1960, pp. 235-240.

14. Madelung, O.: Physics of III-V Compounds. John Wiley & Sons, 1964.

15. Brandon, D. G.; Bowden, P. B.; Boker, A. G.: Properties of Reactor Materials and the Effects of Radiation Damage. Butterworths, London, 1962.

16. Weber, R. E.; Cordes, L. F.: Alumenosilicate Alkali Ion Sources. Rev. Sci. Inst., Vol. 37, Nov. 1966, p. 112.