第六讲 Bell实验室与半导体

一、 Bell实验室

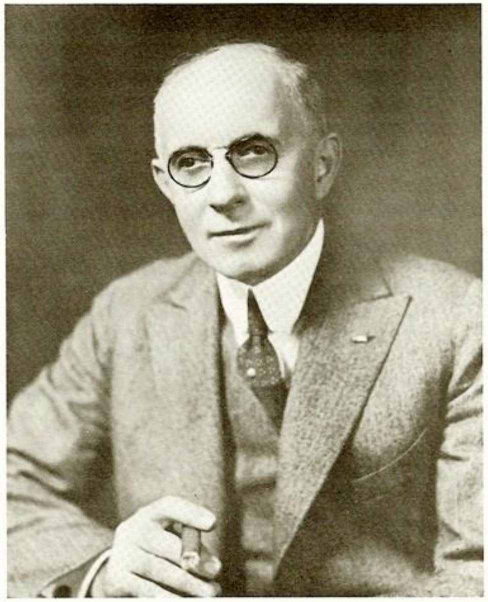
Bell Lab成立于1925年1月1日，原来是西方电子公司的一个研究部门， 在与AT&T合并后成为一个独立实体。

图是位于新泽西州Murray Hill的Bell Lab照片

一、 Bell实验室

实验室的第一任总裁是Frank Jewett。他是芝加哥大学的物理博士，曾是美国第一位Nobel奖获得者迈克尔逊的助手。他认为电话和其它通信方式的发展需要物理知识，需要发现新的方式和机理。因此，他在Bell实验室营造了一种激励原始创新的氛围。

Frank Jewett believed that the best science and technology result from bringing together and nurturing the best minds. He worked diligently to acquire an extraordinary collection of scientists and then provided them with the support to create the breakthroughs that defined the industry.



Frank B. Jewett, first President of our Chapter.

1939年他被选为美国科学院院长后辞去了在Bell的职位，但他的从原创的基础性工作出发进而进行技术创新和开发的思路和风格被坚持了下来。

Frank Jewett
PRESIDENT
1925–1940

一、 Bell实验室

AT&T主要开展电话和通信业务，因此Bell Lab主要研发也是围绕长距离通信这个核心进行的。前面已提到，在无线电话开始的时候，真空管得到了长足的发展和应用。但是传统的真空管效能差，可靠性低，使得通信技术的发展面临许多障碍。

随着对真空管的不断深入了解和开发，Bell Lab的研究人员认为通信技术发展受到阻碍的原因是真空管固有的缺陷造成的，只有找到可以取代真空管的新的器件才能从根本上解决问题。因此，Bell Lab就希望研究出完全不同的器件。而刚刚开始被认识的基于半导体的固态电子材料和器件被认为是值得大力研究的对象。其中的关键人物之一就是Bell Lab的第三任总裁 --- **Mervin Kelly**。

"inventing ways to invent things."

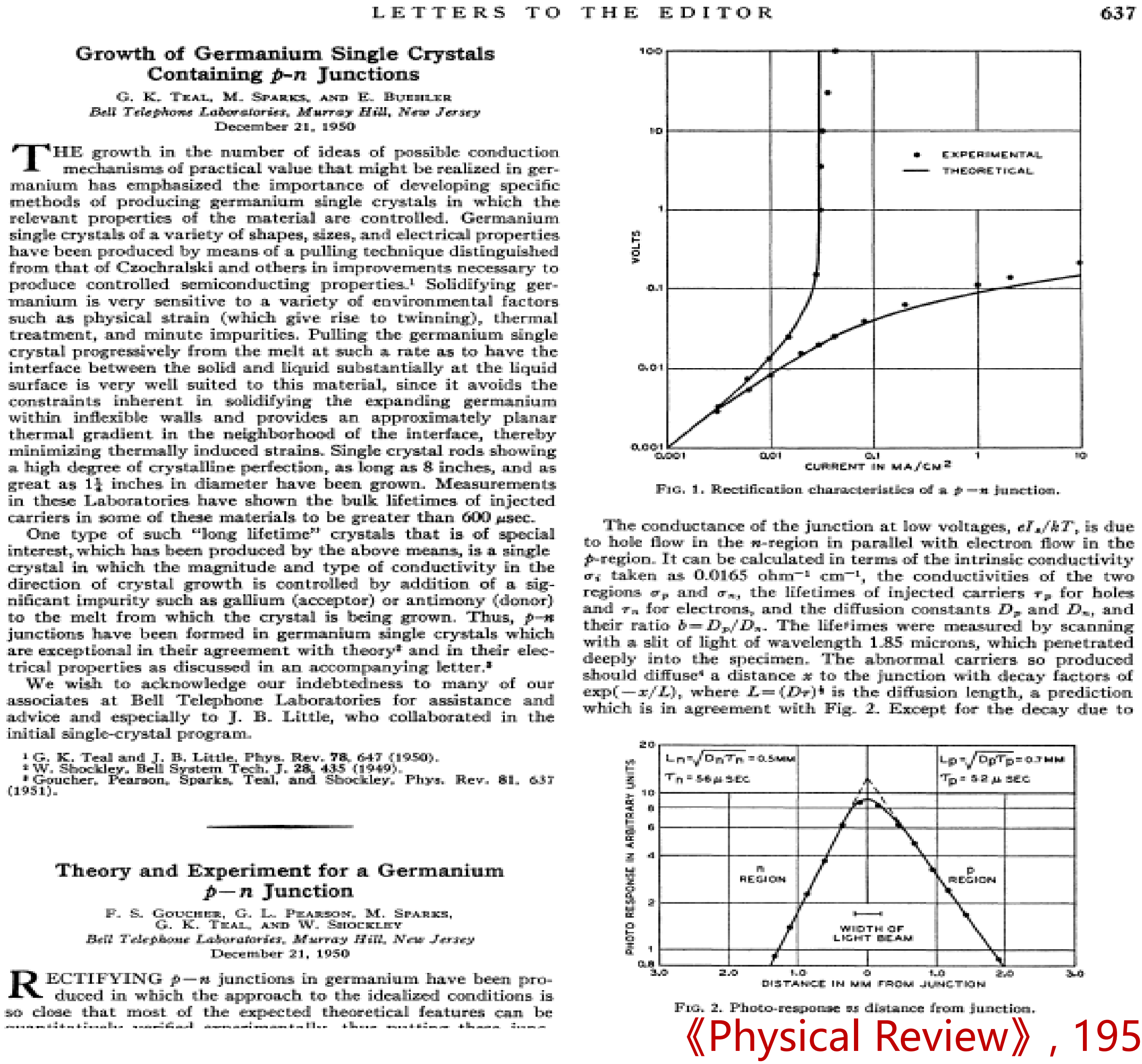
一、 Bell实验室

在Kelly和 Shockley等人的努力下， Bell Lab对半导体理论有了很大进展。肖克莱在1941年就提出了半导体pn结理论。但随后战争的需要，Bell Lab的研究科学家都纷纷转到各处未战争服务。如肖克莱就到华盛顿进行监测潜艇的工作。

但在战争基本胜负已定但尚未结束的时候，Kelly就建议招肖克莱回来继续半导体的研究。1945年，固体物理组分成了半导体研究组和冶金组，前者研究半导体理论和器件，后者研究半导体材料和相关材料工艺。

正是在这样的安排为以后Bell Lab 发明晶体管和相关的工艺技术奠定了基础。

一、 Bell实验室



Growth of Germanium Single Crystals Containing p-n Junctions

G. K. Teal, M. Sparks, and E. Buehler
Bell Telephone Laboratories, Murray Hill, New Jersey
December 21, 1950

THE growth in the number of ideas of possible conduction mechanisms of practical value that might be realized in germanium has emphasized the importance of developing specific methods of producing germanium single crystals in which the relevant properties of the material are controlled. Germanium single crystals of a variety of shapes, sizes, and electrical properties have been produced by means of a pulling technique distinguished from that of Czochralski and others in improvements necessary to produce controlled semiconducting properties.[1] Solidifying germanium is very sensitive to a variety of environmental factors such as physical strain (which give rise to twinning), thermal treatment, and minute impurities. Pulling the germanium single crystal progressively from the melt at such a rate as to have the interface between the solid and liquid substantially at the liquid surface is very well suited to this material, since it avoids the constraints inherent in solidifying the expanding germanium within inflexible walls and provides an approximately planar thermal gradient in the neighborhood of the interface, thereby minimizing thermally induced strains. Single crystal rods showing a high degree of crystalline perfection, as long as 8 inches, and as great as $1\frac{1}{4}$ inches in diameter have been grown. Measurements in these Laboratories have shown the bulk lifetimes of injected carriers in some of these materials to be greater than 600 μsec.

One type of such "long lifetime" crystals that is of special interest, which has been produced by the above means, is a single crystal in which the magnitude and type of conductivity in the direction of crystal growth is controlled by addition of a significant impurity such as gallium (acceptor) or antimony (donor) to the melt from which the crystal is being grown. Thus, p-n junctions have been formed in germanium single crystals which are exceptional in their agreement with theory[2] and in their electrical properties as discussed in an accompanying letter.[3]

We wish to acknowledge our indebtedness to many of our associates at Bell Telephone Laboratories for assistance and advice and especially to J. B. Little, who collaborated in the initial single-crystal program.

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[1] G. K. Teal and J. B. Little, Phys. Rev. **78**, 647 (1950).
[2] W. Shockley, Bell System Tech. J. **28**, 435 (1949).
[3] Goucher, Pearson, Sparks, Teal, and Shockley, Phys. Rev. **81**, 637 (1951).

Theory and Experiment for a Germanium $p-n$ Junction

F. S. Goucher, G. L. Pearson, M. Sparks, G. K. Teal, and W. Shockley
Bell Telephone Laboratories, Murray Hill, New Jersey
December 21, 1950

RECTIFYING $p-n$ junctions in germanium have been produced in which the approach to the idealized conditions is so close that most of the expected theoretical features can be

Fig. 1. Rectification characteristics of a $p-n$ junction.

The conductance of the junction at low voltages, eI_s/kT, is due to hole flow in the n-region in parallel with electron flow in the p-region. It can be calculated in terms of the intrinsic conductivity σ_i taken as 0.0165 ohm^{-1} cm^{-1}, the conductivities of the two regions σ_p and σ_n, the lifetimes of injected carriers τ_p for holes and τ_n for electrons, and the diffusion constants D_p and D_n, and their ratio $b=D_p/D_n$. The lifetimes were measured by scanning with a slit of light of wavelength 1.85 microns, which penetrated deeply into the specimen. The abnormal carriers so produced should diffuse[4] a distance x to the junction with decay factors of $\exp(-x/L)$, where $L=(D\tau)^{\frac{1}{2}}$ is the diffusion length, a prediction which is in agreement with Fig. 2. Except for the decay due to

Fig. 2. Photo-response *vs* distance from junction.

《Physical Review》, 1951, 81(4):637

一、 Bell实验室

1984年以后，按照美国政府分拆AT&T的协议，从贝尔实验室中分割成立了Bellcore；

1996年，贝尔实验室以及AT&T的设备制造部门脱离AT&T成为朗讯科技。AT&T保留了少数研究人员成为其研究机构——AT&T实验室。贝尔实验室是朗讯科技公司的研究开发部门；

现在Bell Lab在Nokia旗下；

https://www.bell-labs.com/

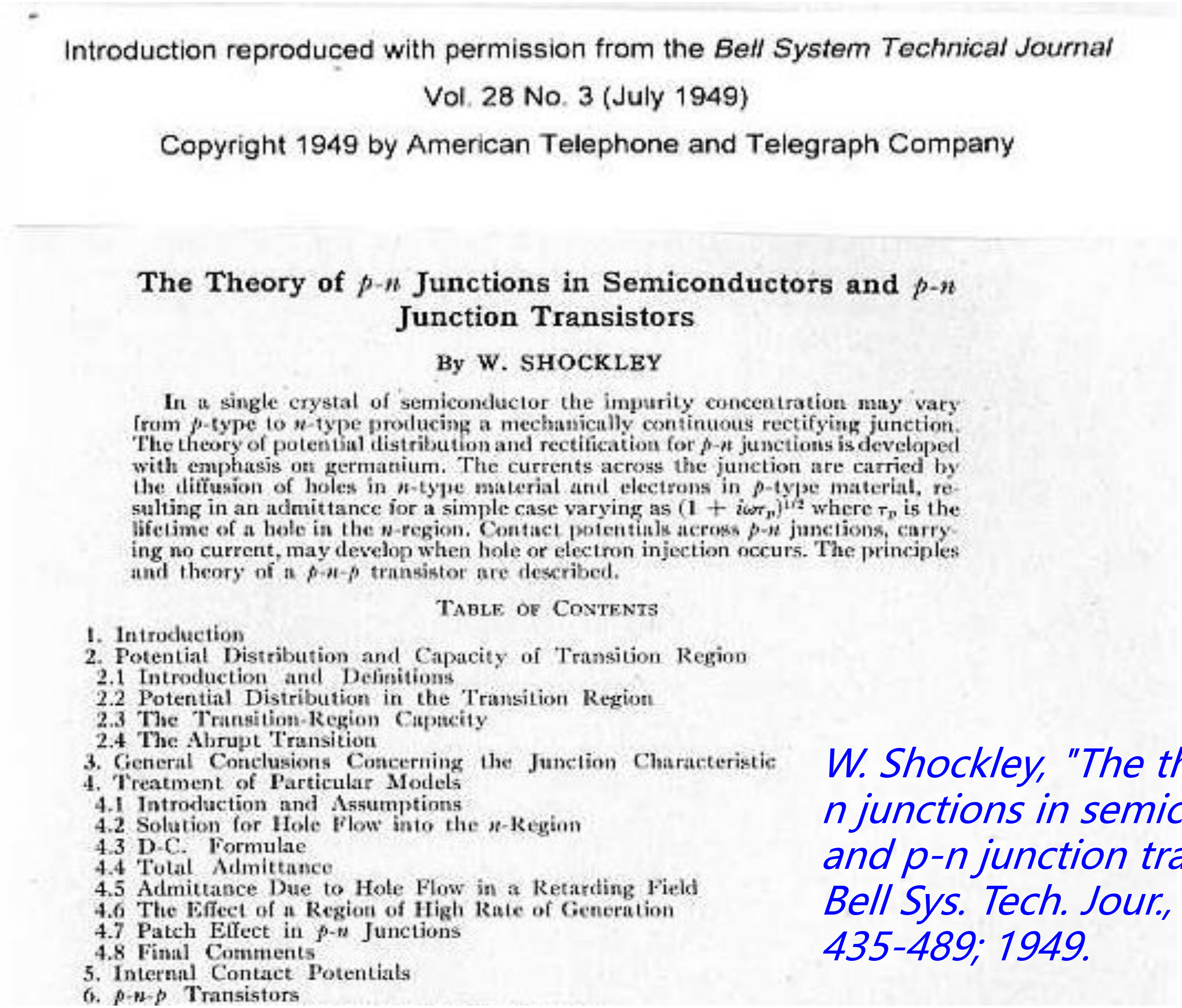
一、 Bell实验室

Bell实验室自此以后在半导体器件、材料和工艺等方面做出了杰出的贡献，可以说，没有 Bell Lab，就不会有今天的信息时代的诞生，至少不会那么快的诞生。Bell Lab也被称为 ***“The Idea Factory”*** 。

详细可参见： “The Idea Factory: Bell Labs and the Great Age of American Innovation” by Jon Gertner

Bell Lab自成立起，一直注重基础性研究，至今已获得8项Nobel奖。 *(据说如果单独拿出来和所有国家一起排队的话，Bell Lab一个实验室可以排第4位。）*

二、Shockley的pn结理论



Introduction reproduced with permission from the *Bell System Technical Journal*
Vol. 28 No. 3 (July 1949)

The Theory of *p-n* Junctions in Semiconductors and *p-n* Junction Transistors

By W. SHOCKLEY

In a single crystal of semiconductor the impurity concentration may vary from *p*-type to *n*-type producing a mechanically continuous rectifying junction. The theory of potential distribution and rectification for *p-n* junctions is developed with emphasis on germanium. The currents across the junction are carried by the diffusion of holes in *n*-type material and electrons in *p*-type material, resulting in an admittance for a simple case varying as $(1 + i\omega\tau_p)^{1/2}$ where τ_p is the lifetime of a hole in the *n*-region. Contact potentials across *p-n* junctions, carrying no current, may develop when hole or electron injection occurs. The principles and theory of a *p-n-p* transistor are described.

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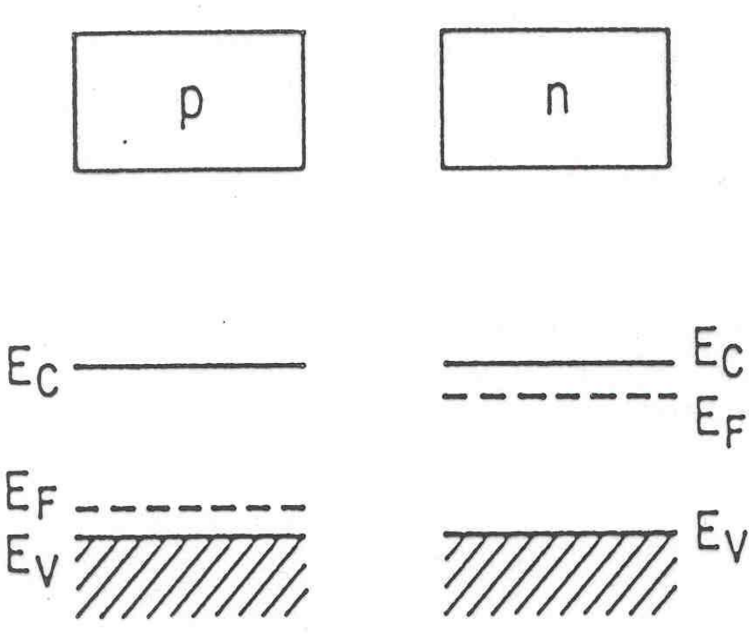
W. Shockley, "The theory of p-n junctions in semiconductors and p-n junction transistors," Bell Sys. Tech. Jour., vol. 28, pp. 435-489; 1949.

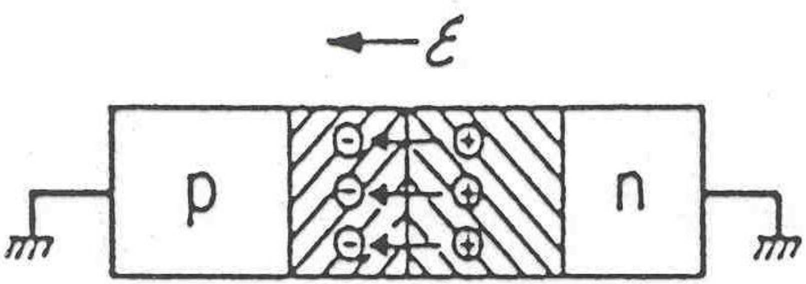
二、Shockley的pn结理论

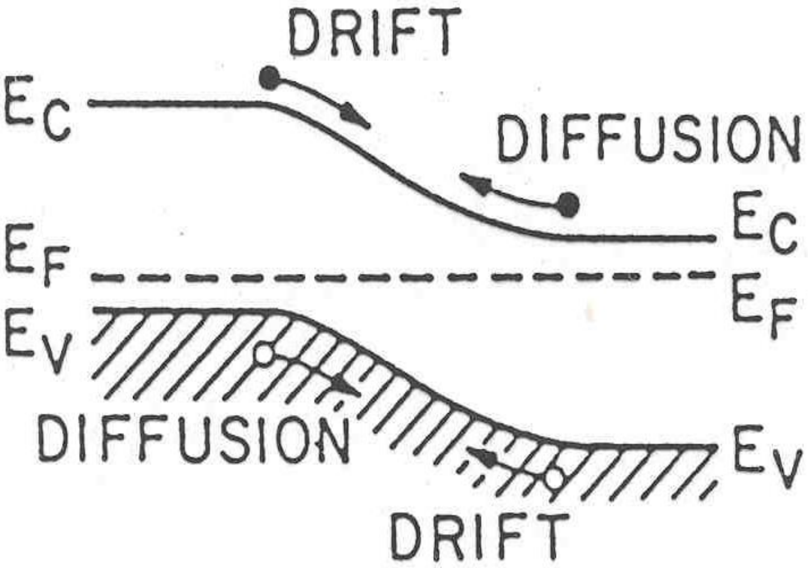


考虑两块半导体，一块是 n型，一块是p型。在n型半导体中电子很多而空穴很少，在p型半导体中空穴很多而电子很少。左图是n型和p型半导体的能带图。

由于p型半导体中空穴浓度高，n型半导体中电子浓度高，在pn结结面附近存在着空穴和电子的浓度梯度，导致电子和空穴的互扩散 --- **扩散运动**。

二、Shockley的pn结理论





内建电场的产生

pn结结面附近的载流子还要参与**漂移运动**。

阻碍电子和空穴继续扩散的作用。

在无外加电压的情况下，载流子的扩散和漂移最终将达到动态平衡。

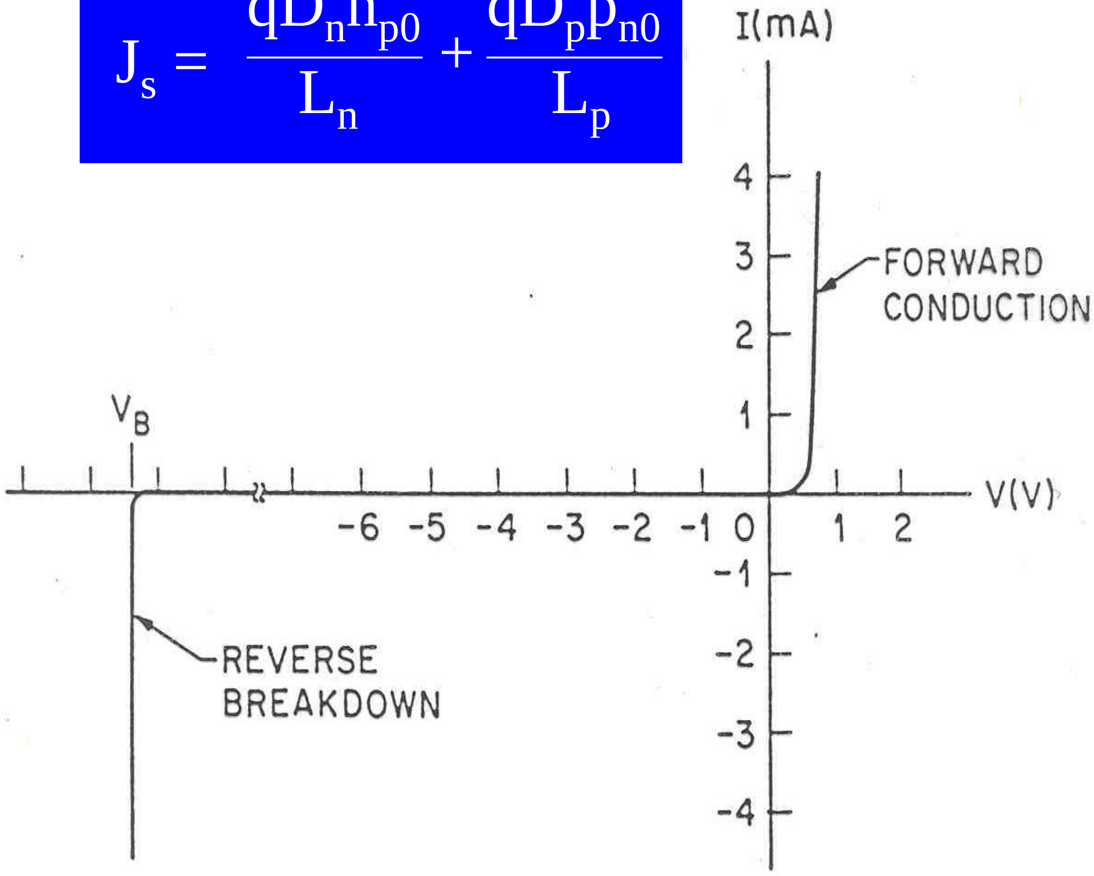
→ **净电流为零**

二、Shockley的pn结理论

理想p-n结的电流电压方程（肖克莱方程）

$$J = J_s[\exp(qV/kT)-1]$$

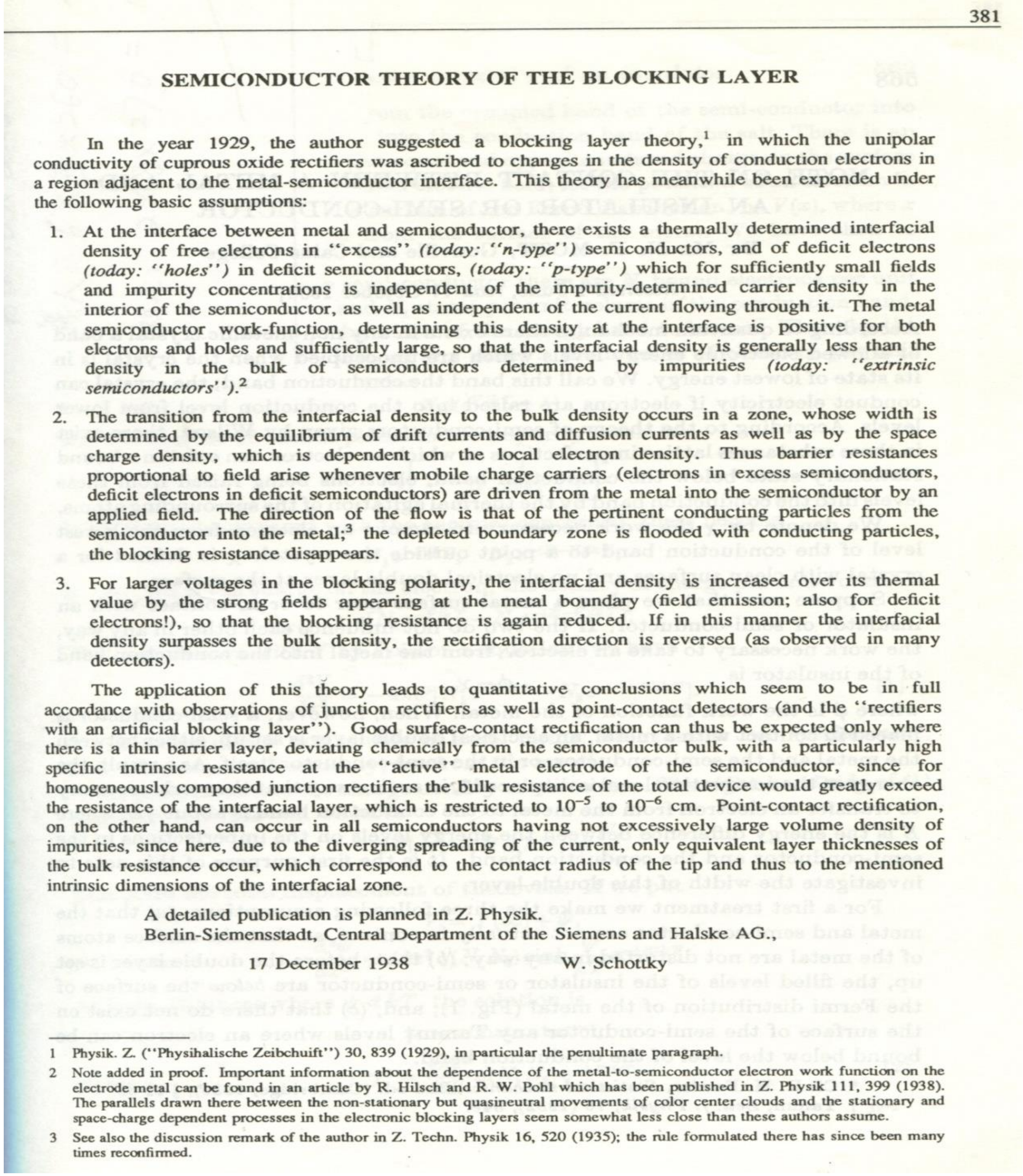
$$J_s = \frac{qD_n n_{p0}}{L_n} + \frac{qD_p p_{n0}}{L_p}$$



p-n结**具有单向导电性或整流效应**。在正向偏压下，正向电流密度随着正向偏压呈指数关系迅速增大。在反向偏压下，$J=-J_s$，即反向电流密度是常量，与外加电压无关。故称J_s为反向饱和电流密度。

三、金属-半导体接触与整流

虽然对整流效应的实验观测很早就已得到，但对其的物理认识是在1930年左右才完成的。其中肖特基等人做出了突出贡献。提出了在金属和半导体表面存在**势垒区（阻挡层）**的概念。



SEMICONDUCTOR THEORY OF THE BLOCKING LAYER

In the year 1929, the author suggested a blocking layer theory,[1] in which the unipolar conductivity of cuprous oxide rectifiers was ascribed to changes in the density of conduction electrons in a region adjacent to the metal-semiconductor interface. This theory has meanwhile been expanded under the following basic assumptions:

1. At the interface between metal and semiconductor, there exists a thermally determined interfacial density of free electrons in "excess" *(today: "n-type")* semiconductors, and of deficit electrons *(today: "holes")* in deficit semiconductors, *(today: "p-type")* which for sufficiently small fields and impurity concentrations is independent of the impurity-determined carrier density in the interior of the semiconductor, as well as independent of the current flowing through it. The metal semiconductor work-function, determining this density at the interface is positive for both electrons and holes and sufficiently large, so that the interfacial density is generally less than the density in the bulk of semiconductors determined by impurities *(today: "extrinsic semiconductors")*.[2]
2. The transition from the interfacial density to the bulk density occurs in a zone, whose width is determined by the equilibrium of drift currents and diffusion currents as well as by the space charge density, which is dependent on the local electron density. Thus barrier resistances proportional to field arise whenever mobile charge carriers (electrons in excess semiconductors, deficit electrons in deficit semiconductors) are driven from the metal into the semiconductor by an applied field. The direction of the flow is that of the pertinent conducting particles from the semiconductor into the metal;[3] the depleted boundary zone is flooded with conducting particles, the blocking resistance disappears.
3. For larger voltages in the blocking polarity, the interfacial density is increased over its thermal value by the strong fields appearing at the metal boundary (field emission; also for deficit electrons!), so that the blocking resistance is again reduced. If in this manner the interfacial density surpasses the bulk density, the rectification direction is reversed (as observed in many detectors).

The application of this theory leads to quantitative conclusions which seem to be in full accordance with observations of junction rectifiers as well as point-contact detectors (and the "rectifiers with an artificial blocking layer"). Good surface-contact rectification can thus be expected only where there is a thin barrier layer, deviating chemically from the semiconductor bulk, with a particularly high specific intrinsic resistance at the "active" metal electrode of the semiconductor, since for homogeneously composed junction rectifiers the bulk resistance of the total device would greatly exceed the resistance of the interfacial layer, which is restricted to 10^{-5} to 10^{-6} cm. Point-contact rectification, on the other hand, can occur in all semiconductors having not excessively large volume density of impurities, since here, due to the diverging spreading of the current, only equivalent layer thicknesses of the bulk resistance occur, which correspond to the contact radius of the tip and thus to the mentioned intrinsic dimensions of the interfacial zone.

A detailed publication is planned in Z. Physik.
Berlin-Siemensstadt, Central Department of the Siemens and Halske AG.,
17 December 1938 W. Schottky

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[1] Physik. Z. ("Physihalische Zeibchuift") 30, 839 (1929), in particular the penultimate paragraph.

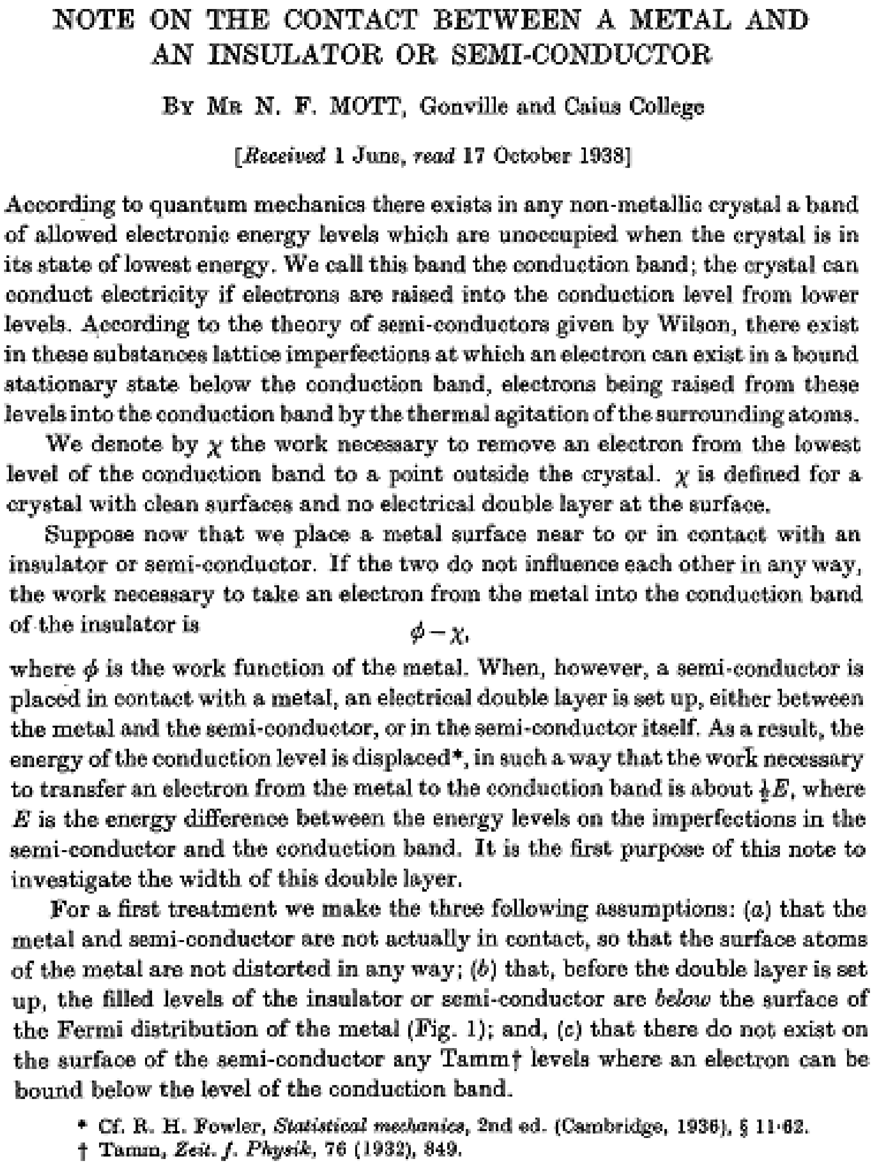
[2] Note added in proof. Important information about the dependence of the metal-to-semiconductor electron work function on the electrode metal can be found in an article by R. Hilsch and R. W. Pohl which has been published in Z. Physik 111, 399 (1938). The parallels drawn there between the non-stationary but quasineutral movements of color center clouds and the stationary and space-charge dependent processes in the electronic blocking layers seem somewhat less close than these authors assume.

[3] See also the discussion remark of the author in Z. Techn. Physik 16, 520 (1935); the rule formulated there has since been many times reconfirmed.

三、金属-半导体接触与整流

随着量子力学的发展，人们接受了电子可以隧穿过势垒层进行传输的观点，并建立起金属和半导体功函数和亲和势的概念。

到 1939 年，苏联的B . Davidov，英国N Mott和德国的肖特基(W Schottley)分别给出了金属 - 半导体接触整流理论。



NOTE ON THE CONTACT BETWEEN A METAL AND AN INSULATOR OR SEMI-CONDUCTOR

BY MR N. F. MOTT, Gonville and Caius College

[*Received* 1 June, *read* 17 October 1938]

According to quantum mechanics there exists in any non-metallic crystal a band of allowed electronic energy levels which are unoccupied when the crystal is in its state of lowest energy. We call this band the conduction band; the crystal can conduct electricity if electrons are raised into the conduction level from lower levels. According to the theory of semi-conductors given by Wilson, there exist in these substances lattice imperfections at which an electron can exist in a bound stationary state below the conduction band, electrons being raised from these levels into the conduction band by the thermal agitation of the surrounding atoms.

We denote by χ the work necessary to remove an electron from the lowest level of the conduction band to a point outside the crystal. χ is defined for a crystal with clean surfaces and no electrical double layer at the surface.

Suppose now that we place a metal surface near to or in contact with an insulator or semi-conductor. If the two do not influence each other in any way, the work necessary to take an electron from the metal into the conduction band of the insulator is

$$\phi - \chi,$$

where ϕ is the work function of the metal. When, however, a semi-conductor is placed in contact with a metal, an electrical double layer is set up, either between the metal and the semi-conductor, or in the semi-conductor itself. As a result, the energy of the conduction level is displaced*, in such a way that the work necessary to transfer an electron from the metal to the conduction band is about $\frac{1}{2}E$, where E is the energy difference between the energy levels on the imperfections in the semi-conductor and the conduction band. It is the first purpose of this note to investigate the width of this double layer.

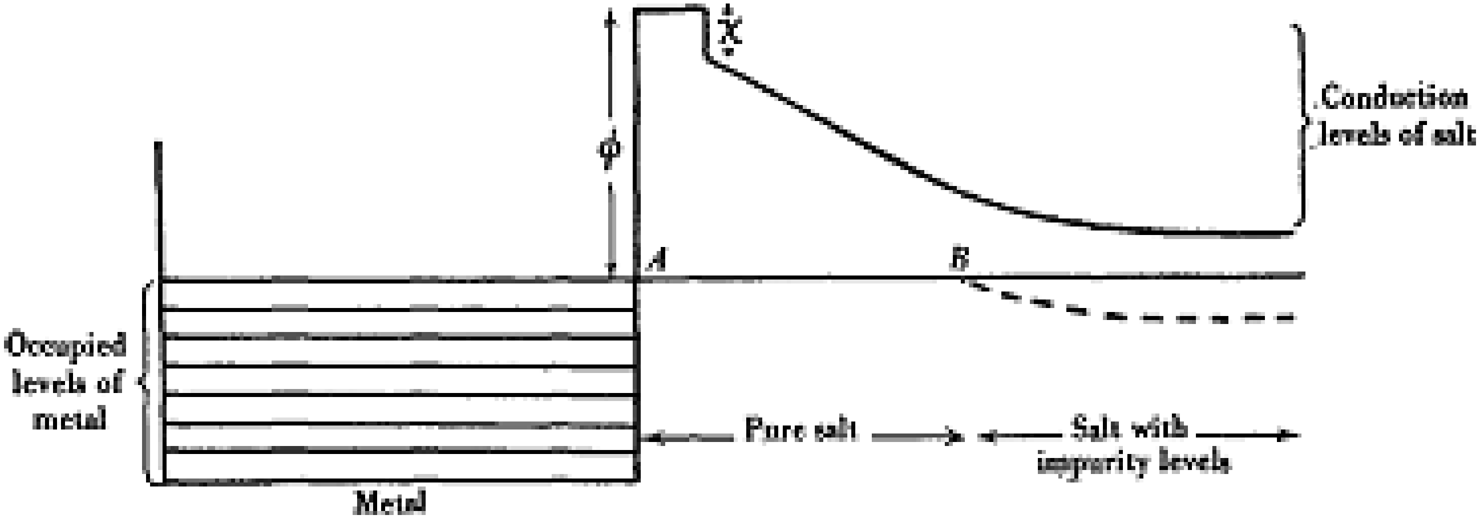
For a first treatment we make the three following assumptions: (*a*) that the metal and semi-conductor are not actually in contact, so that the surface atoms of the metal are not distorted in any way; (*b*) that, before the double layer is set up, the filled levels of the insulator or semi-conductor are *below* the surface of the Fermi distribution of the metal (Fig. 1); and, (*c*) that there do not exist on the surface of the semi-conductor any Tamm† levels where an electron can be bound below the level of the conduction band.

* Cf. R. H. Fowler, *Statistical mechanics*, 2nd ed. (Cambridge, 1936), § 11·62.

† Tamm, *Zeit. f. Physik*, 76 (1932), 849.

图是Mott关于金属-半导体接触的经典论文，发表于1938年。

三、金属-半导体接触与整流



Mott文章中给出了清晰的金属-半导体接触能带图。

金属和半导体接触时，由于两者功函数的不同，如果$W_m > W_s$，则电子将从半导体流入金属，半导体的电子的费米能级也将会下降直至两者的费米能级完全处在同一水平上。半导体内因存在正电荷分布，会在半导体的一侧表面内形成能带的弯曲。这样半导体表面和内部间将存在电势差。

下面我们来简单介绍一下他们所建立的金-半接触机制和整流效应的来源。

三、金属-半导体接触与整流

1、金属和半导体的功函数

概念：

电子受原子核束缚，要成为自由电子，
必须克服正电荷引力。

离化能： 当电子从原子或分子热运动中吸取能量，
脱离束缚所需能量；

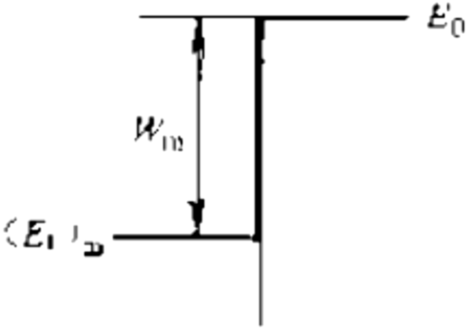
功函数： 电子从液体或固体中逸出所需能量；

真空能级E_0
电子能级

三、金属-半导体接触与整流

金属中电子：

1、绝对零度时，排列在E_F之下；
2、T，则有一小部分电子由E_F之下到E_F之上；
3、功函数，是E_F能级附近电子到真空中去所需能量；
4、功函数的大小标志着电子在金属中束缚的强弱；



金属中的电子势阱

金属功函数的定义是E_o与E_F能量之差：

$$W_m = W_{金} = E_o - (E_{Fm})$$
$$= q\phi_m$$

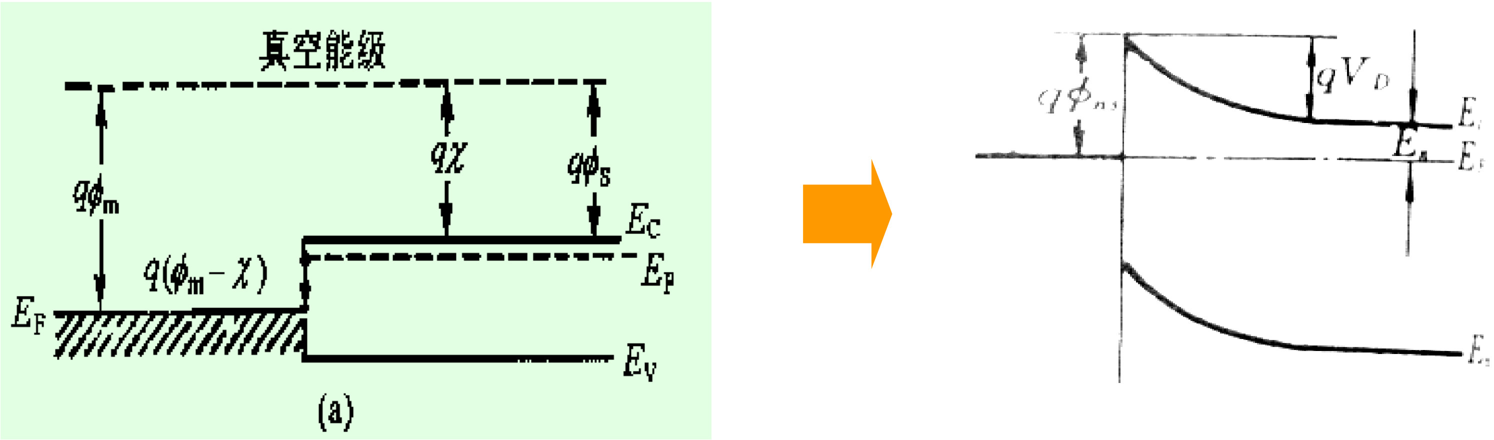
三、金属-半导体接触与整流

2、肖特基势垒的形成与势垒高度---接触电势差

金属-n型半导体

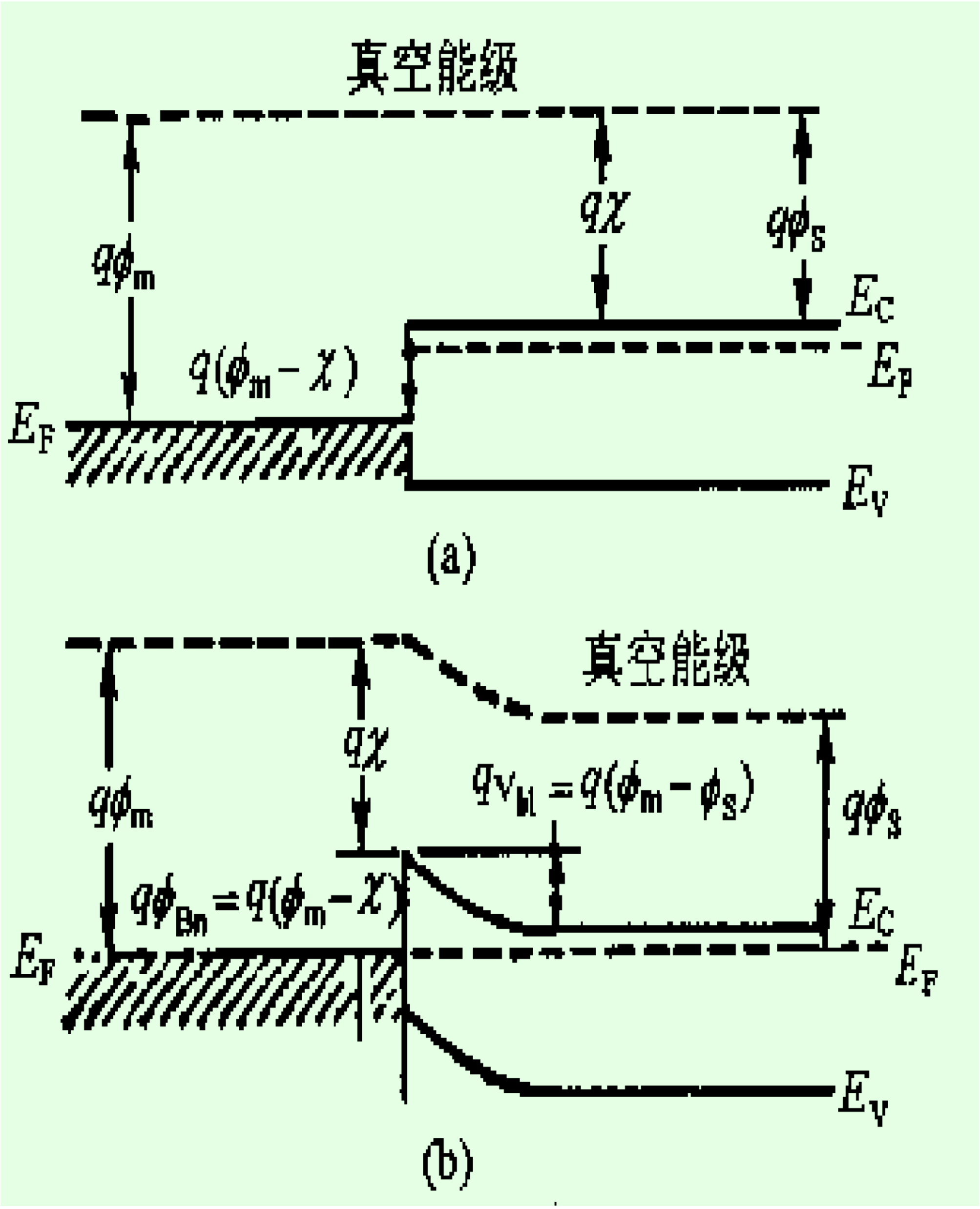
1、$W_m > W_n$，

2、电子由能量高的n 区流向能量低的金属，



1、电场将阻止电子进一步流动，平衡时电流为零;
2、金属面电荷，几个原子间距;
3、是p^+n结;

三、金属-半导体接触与整流



势垒的形成

对金属中的电子来说

$$q\phi_{ms} = q(\phi_m - \chi)$$

对半导体中的电子来说

$$\begin{aligned} qV_b &= W_m - W_s \\ &= q\phi_m - q(\chi + \phi_n) \\ &= (E_F)_n - (E_F)_m \end{aligned}$$

三、金属-半导体接触与整流

金属与n型半导体接触
($W_m < W_s$)

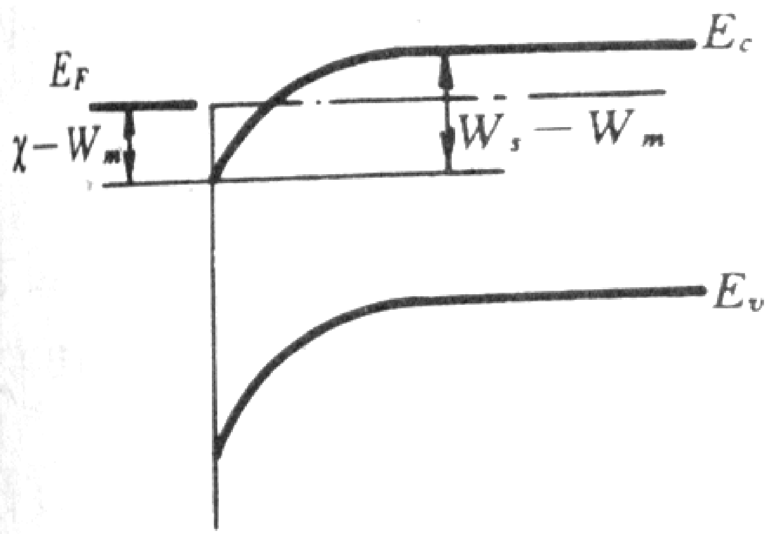


图 7-5　金属和 n 型半导体接触能带图($W_m < W_s$)

金属与n型半导体接触：

1、$W_m > W_s$

形成阻挡层

2、$W_m < W_s$

形成反阻挡层

三、金属-半导体接触与整流

金属与p型半导体接触

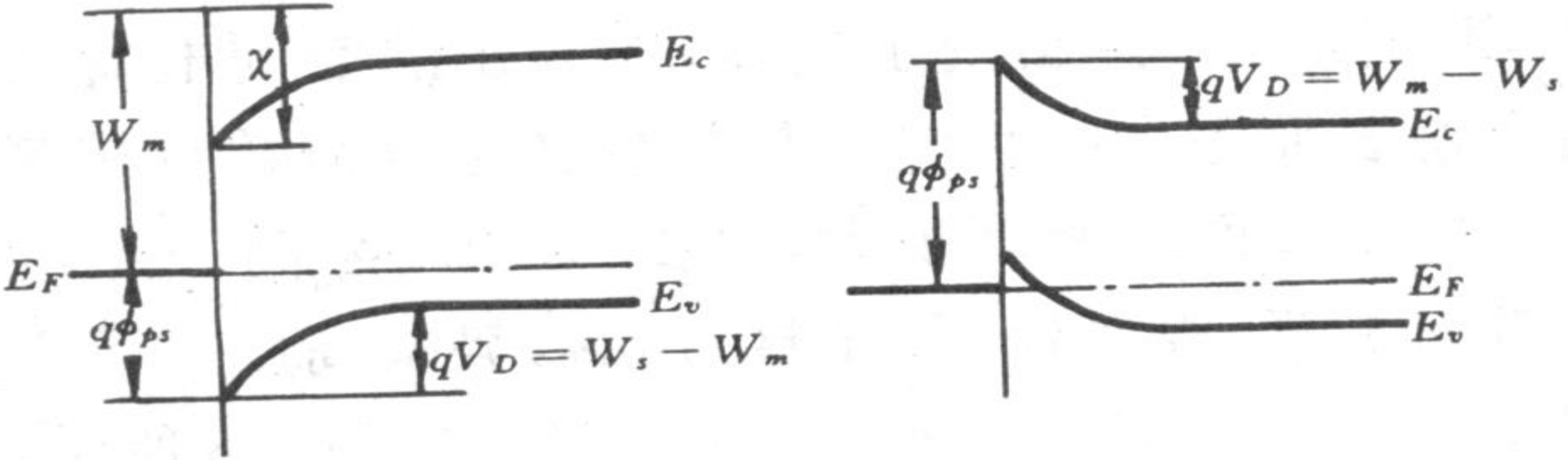


图 7-6　金属和 p 型半导体接触能带图

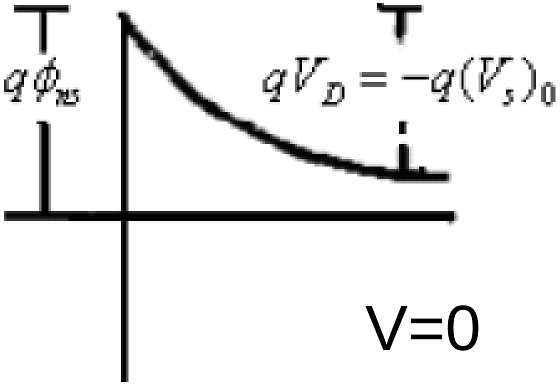
(a)p 型阻挡层($W_m < W_s$)；(b)p 型反阻挡层($W_m > W_s$)。

三、金属-半导体接触与整流

3、金属半导体接触的整流效应

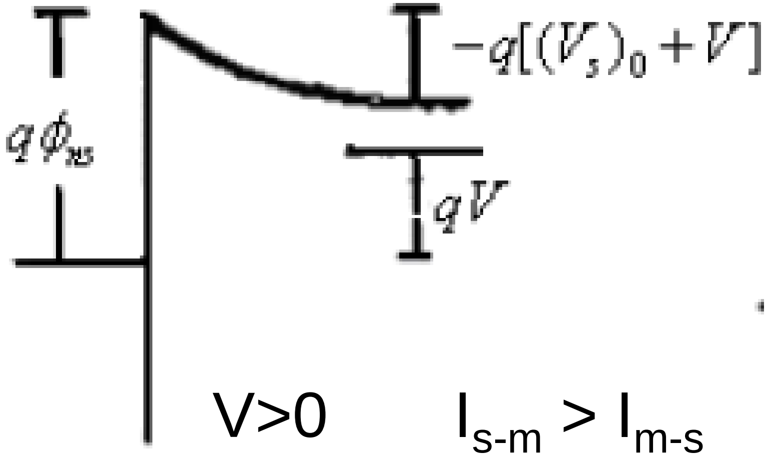
在金属和半导体接触形成阻挡层后，在平衡态时，阻挡层中是没有净电流流过的。

当在紧密接触的金属和半导体之间加上电压V时，电压主要降在阻挡层上（高阻区），因此，表面势将变为$(V_s)_o+V$。



V=0

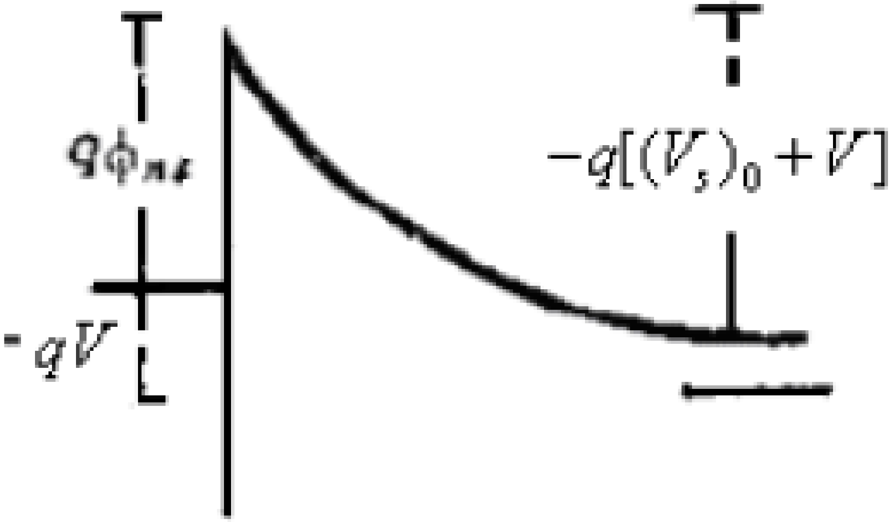
$I_{s\text{-}m} = I_{m\text{-}s}$ **动态平衡**



V>0 $I_{s\text{-}m} > I_{m\text{-}s}$

正向电压时：形成一股从金属到半导体的正向电流，它是由多数载流子构成的，外加电压越高，势垒下降越多，正向电流越大；

三、金属-半导体接触与整流



$V<0$

$I_{s-m} < I_{m-s}$

反向电压时，形成一股从半导体到金属的反向电流，由于金属中的电子要越过相当高的势垒才能到达半导体中，且金属一边的势垒不随外加电压变化而变化，所以，此电流很小且随反向电压增大趋于饱和。

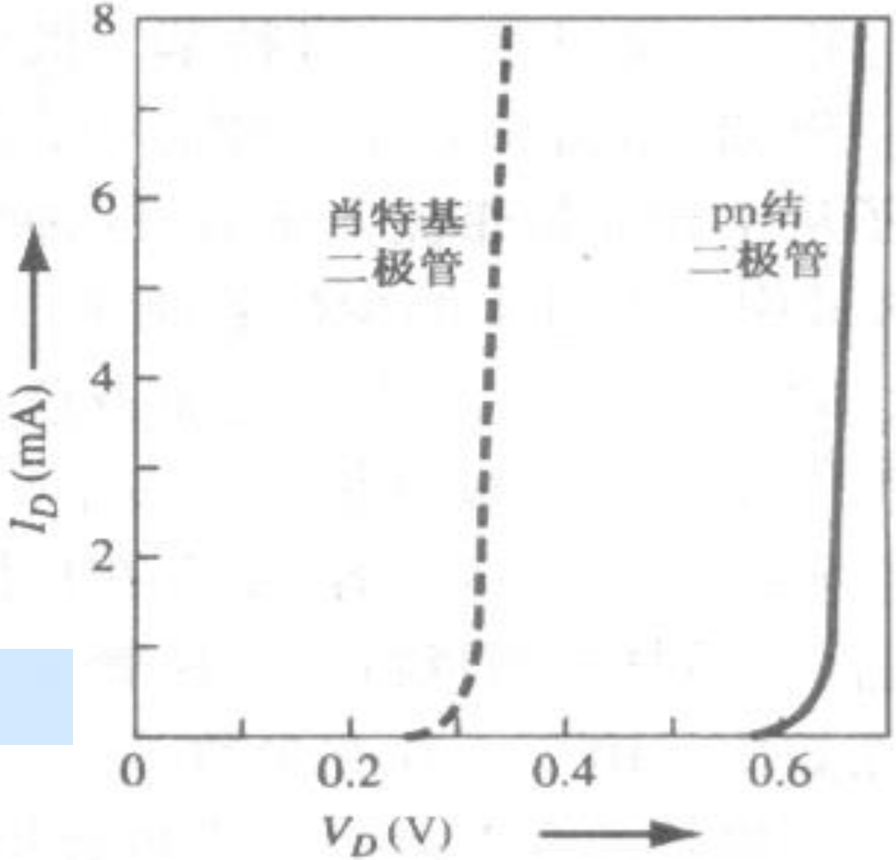
整流效应

三、金属-半导体接触与整流

利用金属 - 半导体整流接触特性制成的二极管称为肖特基势垒二极管（Schottky Barrier Diode –SBD)，它和后面将要提及的pn结二极管具有类似的电流 - 电压关系，即都具有**单向导电性**。

$I_f = ART^2 \exp[-q(\phi_{ms} - V)/k_o T]$

肖特基势垒二极管



这就是Braun为什么发现金属和半导体接触时电流电压特性不满足欧姆定律的原因，也是一种整流效应。

第六讲　结语

THE MANIPULATION OF NEUTRAL PARTICLES

Nobel Lecture, December 8, 1997

by

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The written version
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chose to present a
path of research.

I joined Bell Lab
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I joined Bell Laboratories in the fall of 1978 after working with Eugene Commins as a graduate student and post-doc at Berkeley on a parity non-conservation experiment in atomic physics.[1] Bell Labs was a researcher's paradise. Our management supplied us with funding, shielded us from bureaucracy, and urged us to do the best science possible. The cramped labs and office cubicles forced us to rub shoulders with each other. Animated discussions frequently interrupted seminars and casual conversations in the cafeteria would sometimes mark the beginning of a new collaboration.

In my first years a
x-ray microscopy and worked on an experiment investigating energy transfer in ruby with Hyatt Gibbs and Sam McCall as a means of studying Anderson Localization.[2, 3] This work led us to consider the possibility of Mott or Anderson transitions in other exciton systems such as GaP:N with picosecond laser techniques.[4] During this work, I accidentally discovered that picosecond pulses propagate with the group velocity, even when the velocity exceeds the speed of light or becomes negative.[5]

While I was learning about excitons and how to build picosecond lasers, I began to work with Allan Mills, the world's expert on positrons and positronium. We began to discuss the possibility of working together while I was still at Berkeley, but did not actually begin the experiment until 1979. After three long and sometimes frustrating years, a long time by Bell Labs standards, we finally succeeded in exciting and measuring the 1S–2S energy interval in positronium.[6]

--- Steven Chu
(朱棣文)