Photoemission of semiconductors
J. van Laar and J. J. Scheer

The phenomenon of photoemission has played an important role in the history of fundamental physics. Einstein took the empirical laws underlying photoemission as his starting point for postulating, as an extension of Planck's quantum hypothesis, that light consists of photons. Photoemission also has a considerable practical significance; photocathodes are used in many radiation detectors and, in particular, in most image intensifiers. Present photocathodes which are reasonably sensitive to visible light, were nearly all evolved more or less empirically. The article below shows that it is now possible to arrive at a good photocathode for visible light with the aid of more sophisticated methods.

Introduction

Consider a circuit (fig. 1) consisting of a vacuum tube with two electrodes, cathode and anode, connected to a battery and a sensitive ammeter. The cathode is cold; there is no thermionic emission and therefore no current flows in the circuit. If the cathode is now illuminated, the result — under favourable conditions — is a measurable current: the light releases electrons absorbing a light quantum \( \hbar \nu \), an electron is excited to a state of higher energy. If the energy \( \hbar \nu \) of the absorbed light quantum is sufficiently high the excited electron is able to surmount the potential barrier at the surface.

This picture immediately leads to the rules found by experiment. 1) No photoemission occurs for photon energies below a certain value \( E_D \), called the photoelectric work function or long wavelength threshold. 2) The number of electrons emitted per second is proportional to the number of photons incident per second on the cathode; in other words, the photoelectric saturation current is proportional to the intensity of the incident beam of light. 3) The maximum \( E_{\text{max}} \) of the energy of the emitted electrons is linearly related to the photon energy:

\[
E_{\text{max}} = h \nu - E_D.
\]

It is important in what follows that the emitted electrons originate from a thin layer at the surface of the cathode. Electrons excited at greater depths lose too much energy on their way to the surface, by interaction with other electrons and with the atomic lattice, to be able to reach the vacuum. We assume that of the electrons excited at a distance \( x \) from the surface, only a fraction proportional to \( \exp(-x/d) \) are emitted, where \( d \) is the "escape depth". Roughly speaking, only the photoelectrons from a surface layer of thickness \( d \) can escape.

In this article we are concerned with photoemission of semiconductors, and in particular with the research on this subject which has been done in recent years at the Philips laboratories in Eindhoven. There are two aspects of this research: a) The photoelectric effect can be used as a tool for studying the solid state, in our case semiconductor materials. b) As photoemission finds wide application in light detectors, an attempt can be made to design a good light detector using the knowledge obtained from research under (a). Before entering
on a detailed exposition of the subject, we should like to say a little more about these two aspects of the research, and also quote a few of the important results.

a) In research on semiconductors, photoemission provides information on the energy levels which have a significant electron population. The photoelectric work function gives directly the distance from the upper of these levels to the vacuum level; and because of the small escape depth, information is obtained on the situation at the surface. These are the main points of interest in our research. Other investigators [2] have studied the relative density of states in the occupied levels, i.e. the energy band structure, by analysing the wavelength-dependence of the photoemission. Additional information can be obtained along these lines by measuring the energy distribution of the photoelectrons. One might also try to learn something about the escape mechanism of the excited electrons, i.e. about the transfer of energy to the lattice and possible reflections of electrons at the surface. This is a subject which has so far received relatively little attention.

In addition to the above-mentioned threshold energy for photoemission, \( E_d \), the thermionic work function \( \phi \) is a quantity which is directly accessible by experiment, for example by contact potential measurements; \( \phi \) is the difference between the vacuum level and the Fermi level in the semiconductor.

According to the band theory of semiconductors a zone of forbidden energies exists for the electrons in the material. In general, however, electronic states with energies in this forbidden zone will occur at the surface (because of impurities, lattice irregularities or other reasons). These surface states have a considerable influence on the properties of the semiconductor, in particular on \( \phi \) and \( E_d \) as functions of the doping content of the semiconductor. As will be shown, the band model leads to the following results for two extreme cases:

1) If there are many surface states, all at roughly the same energy, then \( \phi \) is independent of the doping content and \( E_d \) does depend on it (fig. 2a).

2) If there are no surface states, then \( \phi \) is dependent upon the doping content and \( E_d \) independent of it (fig. 2b).

In the present article we shall discuss the results of our work on silicon and gallium arsenide. Our measurements show that Si is a typical representative of the first case. This situation is so common that the relevant model has been assumed to possess general validity. The results of our measurements make it clear, however, that GaAs definitely does not conform to this model, but on the contrary shows fairly good agreement with the second case.

b) If we now attempt to make a good photocathode from a conventional semiconductor, and in particular, a photocathode which is sensitive to visible light, we require in the first place that the threshold wavelength should lie in the infra-red. In other words, the photoelectric threshold energy must be sufficiently low. Conventional semiconductors do not meet this requirement. There is, however, an empirical method by which the photoelectric threshold energy can be shifted to a lower energy — the adsorption of metal atoms on the surface. The most effective metal appears to be caesium, which, given the right conditions, makes it possible to reduce the threshold energy to 1.4 eV (which is the ionization energy of a caesium atom in the adsorbed state; 1.4 eV corresponds to 0.90 \( \mu \)m wavelength). We shall discuss this method, again on the basis of the energy band model.

Another requirement of a good photocathode is a high quantum yield. To achieve this, a substantial fraction of the photons has to be absorbed in the escape layer. Heavily-doped GaAs, coated with caesium, looks particularly promising in this respect. In this system the energy of an electron in vacuo lies roughly at the same height as the bottom of the conduction band. This means that an electron, once it has been excited to the conduction band, needs hardly any kinetic energy to escape from the semiconductor. The escape depth is then of the order of the diffusion-recombination length, that is to say many times greater than the escape depths normally encountered. These considera-

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[2] It may be assumed in general that an electron absorbs at the most one light quantum. Excitation processes in which an electron absorbs two quanta are also known, but they call for very special conditions. See H. Sonnenberg, H. Heffner and W. Spicer, Appl. Phys. Letters 5, 95, 1964. The threshold energy for photoemission is then lower by a factor of 2 and the relation between the numbers of incident photons and emitted electrons is parabolic.
tions prompted us to make a photocathode of caesium-coated GaAs. We found that it gave the quite remarkable yield of about 0.30 electrons per incident photon on the blue side of the visible spectrum.

The first photoemission research on semiconductors, reported twenty years ago, was done with films deposited by vacuum evaporation\[41.\] In order to obtain well-defined materials and surfaces, we confined our experiments to vacuum-cleaved single crystals. We shall not go further into experimental detail here.

\[ \therefore \quad \text{thermionic work function } \varphi \text{ is equal to the threshold energy } E_d. \] There are other methods of determining \( \varphi \), for example contact potential measurements, and the results can be compared.

Let us now consider an analogous simple model of a semiconductor, shown in fig. 3b. Here, the Fermi level lies in the forbidden zone. The energy band below it (the valence band, with upper edge \( E_V \)) is completely occupied by electrons, and the band above it (the conduction band, with lower edge \( E_C \)) is empty. In addi-

\[ \text{Description of photoemission in terms of the band theory of solids} \]

Using the band theory of solids\[5\] we shall now consider what may be expected in various cases for the photoemissive threshold energy \( E_d \) and the thermionic work function \( \varphi \).

We consider first the situation in a metal (fig. 3a). The conduction band — at least at low temperature — is filled with electrons up to the Fermi level \( E_F \). All the higher energy levels are practically empty. At the surface between metal and vacuum there is a potential barrier: the potential energy of an electron in vacuo \( (E_{\text{vac}}) \) lies above the Fermi level by an amount \( \varphi \). Photoemission may be expected from the metal if for the incident light, \( h\nu \gg \varphi \). In a metal, therefore, the

\[ \text{atom to the work function } \varphi = E_{\text{vac}} - E_F \text{ we introduce the electron affinity } E_A = E_{\text{vac}} - E_C, \] the energy gap \( E_g = E_C - E_V \) and the quantity \( \delta = E_F - E_V \), which defines the position of the Fermi level in relation to the bands. In photoemission, the electrons originate from the valence band\[8\]; we may therefore expect for the threshold energy \( E_d = E_A + E_g = \varphi + \delta \).

Let us now consider the effect on \( E_d \) and \( \varphi \) of variation of the bulk doping. To a first approximation bulk doping leaves the position of the energy bands unaffected, but it does affect the occupation of the levels and hence the position of the Fermi level; in this way the quantity \( \delta \) can be varied between 0 and \( E_g \). From fig. 3b it can then be seen at once that \( \varphi \) can be varied between \( E_A \) and \( E_A + E_g \) by bulk doping, whereas
\[ E_d = E_A + E_g \] is independent of bulk doping. For any bulk doping the value of \( \delta \) can be determined from the bulk properties of the semiconductor (conductivity, Hall coefficient). Thus, although not so directly as in the case of a metal, the thermionic work function \( \varphi = E_A - \delta \) can again be derived from photoemission measurements.

In the model outlined above it was assumed that the surface causes no complications, in other words that the energy levels are not dependent upon location with respect to the surface. Let us consider an energy band diagram in which the horizontal co-ordinate represents the spatial co-ordinate perpendicular to the surface. The assumption which we have just mentioned implies that in such a diagram the energy bands are represented by straight horizontal lines. It is known, however, that at the surface of a semiconductor there is nearly always some bending of the energy bands owing to the presence of additional donors or acceptors with energy levels in the forbidden zone \([7]\). Suppose, for example, that there exists at the surface of a P-type semiconductor a large concentration of donor levels situated in relation to the bands in such a position that they would be above the Fermi level if the bands were straight. Now this is not a state of equilibrium; the donors at the surface will give up electrons to the acceptors in the bulk of the material, giving rise to a negative space charge region near the surface combined with a positive surface charge. As a result the potential at the surface drops and the bands at the surface are bent downwards (fig. 3c).

The potential distribution at the surface can be calculated by making the assumption that the acceptor levels in a layer of a given thickness are all filled, and that the acceptor levels outside that layer are all empty \([8]\). In this layer, the "Schottky layer", there is thus a constant and finite space charge density, and outside it a space charge density equal to zero. Solving Poisson's equation for this charge distribution (in a rationalized system) one finds that the potential \( V \) in the layer is parabolically related to the distance \( x \) from the surface:

\[
V = N\varepsilon(x - x_0)^2/2\varepsilon, \quad \ldots \quad (1)
\]

where \( N \) is the concentration of the acceptors, \( \varepsilon \) the elementary charge, \( \varepsilon \) the dielectric constant and \( x_0 \) the thickness of the space charge layer. The total band bending \( \Delta V \) (the potential difference between surface and bulk) is thus

\[
\Delta V = N\varepsilon x_0^2/2\varepsilon, \quad \ldots \quad (2)
\]

In other words, for a given total band bending, the space charge layer is thicker, and the band bending therefore more gradual, the lower the bulk doping. This is of great importance in what follows.

If the number of surface donors per unit area of surface is very large, and if they all lie at roughly the same energy, then they will give up electrons to the acceptors in the bulk material only until the Fermi level at the surface just coincides with this donor level (fig. 3d). The Fermi level at the surface, and hence the thermionic work function \( \varphi \), is therefore independent of the doping; in this case we speak of a stabilized Fermi level. The band bending is now determined by the position of this donor level at the surface and by the position of the bands in the bulk of the material in relation to the Fermi level; the latter position is in turn determined by the doping.

We now consider the effect of variation of bulk doping on the threshold for photoemission \( E_d \) in the case of a stabilized Fermi level. Figure 4 shows the valence band at a stabilized Fermi level for P-type doping of various concentrations and for one kind of N-type doping (the conduction band is shown for only one case).

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\[ (4) \quad \text{L. Apker, E. Taft and J. Dickey, Phys. Rev. 74, 1462, 1948.} \]
\[ (5) \quad \text{For further details of this model, see L. Heijne, Philips tech. Rev. 25, 120, 1963/64.} \]
\[ (6) \quad \text{This applies to P-type semiconductors and to fairly weakly doped N-type semiconductors. With very strong N-type doping some emission from the conduction band is to be expected. This has never been established with certainty, however.} \]
\[ (7) \quad \text{J. Bardeen, Phys. Rev. 71, 717, 1947.} \]
\[ (8) \quad \text{See W. Schottky, Z. Physik 118, 539, 1941/42.} \]
As we have seen, the bending occurs in a thinner layer the greater the doping concentration. If the doping is very weak (fig. 4, curve 1) the part of the band bending taking place inside the escape depth \( d \) is negligible. In that case the threshold \( E_d \) is equal to \( E_g + E_A \), as it was with the straight bands in fig. 3b. Stronger P-type doping lowers the threshold energy \( E_d \), the bands in the bulk of the material being raised with respect to the energy of an electron \( \text{in vacuo} \). The resulting effect on emission becomes more noticeable as the band bending occurs to a greater extent within the escape depth (fig. 4, curves 2 and 3). With very strong P-type doping, \( E_d \) is independent of doping, since the Fermi level in the volume then coincides approximately with the upper edge of the valence band and the thickness of the space charge region is smaller than the escape depth.

Fig. 4, curve 4, shows the valence band for strong N-type doping, with stabilized Fermi level. In this case the same threshold is to be expected as with straight bands, but the yield will be lower for photon energies close to the threshold.

Table I summarizes the behaviour of \( \varphi \) and \( E_d \) in both models when the doping is varied (see also fig. 2).

<table>
<thead>
<tr>
<th>Model</th>
<th>( \varphi = )</th>
<th>( E_d = )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Straight bands</td>
<td>( E_A ) for strong N-type doping; ( E_A + E_g ) for strong P-type doping</td>
<td>( E_A + E_g ), independent of doping</td>
</tr>
<tr>
<td>Stabilized Fermi level</td>
<td>( E_A + E_g - \delta ), independent of doping</td>
<td>( E_A + E_g ) for N-type to weak P-type doping; ( E_A + E_g - \delta ), thus ( \varphi ) for strong P-type doping</td>
</tr>
</tbody>
</table>

In reality, of course, intermediate cases can occur where \( \delta \) at the surface is neither equal to the value in the bulk material, as it is in the case of straight bands, nor independent of doping, as it is with a stabilized Fermi level.

When analysing the results of the measurements one should bear in mind that the surface levels themselves can emit photoelectrons, which may mask in particular the weak beginning of the valence band emission. For this reason N-type material is generally less suitable for research on valence band emission, since the emission is exceptionally low near the threshold in this material.

Experimental results for silicon

With reference to the foregoing model, we shall now discuss the results of our measurements on single crystals of silicon \( [9] \). We begin with the spectral distribution of the emission in the case of weakly doped materials, i.e. both P-type and N-type containing \( 10^{16} \) charge carriers per \( \text{cm}^3 \) (fig. 5). We see in the first place that the spectral distribution is the same for both P-type and N-type material, indicating that the doping in each case must be weak enough to allow us to consider the bands as straight (the space charge layer being very much greater than the escape depth for photoelectrons).

![Fig. 5](image_url)

Fig. 5. Yield \( y \) of the photoemission for P-type and N-type silicon \( (1 \times 10^{16} \text{ charge carriers/cm}^3) \) as a function of photon energy \( h\nu \). The solid curve represents the relation \( y = 42(h\nu - 5.4)^{3/2} \). The scale for \( y \) is arbitrary.

Secondly, we see that the curve consists of two parts, i.e. a "tail" with a very low yield followed by a steeply rising part beginning at 5.4 eV. We interpret the tail as emission from surface levels. In the following we shall put forward two arguments in support of this. The steep section of the curve is attributed to the valence band emission. The threshold energy for this emission is thus 5.4 eV. This part of the curve appears to


[11] The values of \( \varphi = 4.85 \) eV for weakly doped and 4.90 eV for strongly doped P-type material — indicate that the stabilization of the Fermi level is not complete.
be well described by the purely empirical expression
\[ y \propto (h\nu - 5.4)^{3/2}, \]
where \( h\nu \) is the energy of the photons in electron volts.

Let us now consider the emission from more strongly
doped \( P \)-type material (\( 1 \times 10^{19}, 6 \times 10^{19} \) and \( 1 \times 10^{20} \)
charge carriers per \( \text{cm}^3 \)). The theory predicts that the
stronger the doping the lower the energy at which
emission will begin, owing to the above-mentioned band
bending caused by the presence of surface levels (fig. 4,
curves 2 and 3). This is in fact clearly evident from the
spectral distributions measured (fig. 6). The influence
of doping can be quantitatively predicted if we assume
that the Fermi level at the surface of silicon is stabil-
ized and that the band emission for straight bands is
given by \( y = C(h\nu - 5.4)^{3/2} \). This calculation is given
in the appendix of this article. The fixed position of
the Fermi level in relation to the energy of an electron
in vacuo (given by \( \varphi \)) and the escape depth \( d \) can be
fitted to the experimental results. For \( d = 2.0 \text{ nm} \) and
\( \varphi = 4.90 \text{ eV} \) a reasonable agreement is found between
calculation and experiment (fig. 7a, b, c). The value
found here, \( \varphi = 4.90 \text{ eV} \), is consistent with the value
derived by other authors from contact potential meas-
urements [10].

This brings us to the first argument for the above-
mentioned interpretation of the tail emission of weakly
doped material as being emission from surface levels.
Turning to fig. 7, we see that the curves for strong dop-
ing no longer exhibit any extra tail in the emission.
This is precisely what we would expect for emission
from surface levels: as it does not follow the shift to
lower energy with stronger \( P \)-type doping, it disappears
entirely in the stronger band emission.

The second argument in support of our interpreta-
tion is that highly accurate measurements on weakly
doped material show that the starting point of the tail
emission lies at 4.85 eV (fig. 8), and this, according
to the above-mentioned contact potential measure-
ments by Gobeli and Allen [10], is precisely the position
of the Fermi level [11]. (These authors, however, give
energy region of 0.1 eV, as follows from the accuracy with which the stabilization of the Fermi level was determined.

The 5/2 power law found for the emission from surface levels proves to be quite common, also in cases where the surface levels are due to impurities. The 5/2 exponent was found, for example, for the tail emission of cadmium telluride surfaces with impurities due to cleavage in air or baking in vacuo. The tail emission here must definitely be attributed to the impurities, because a clean surface, obtained by vacuum cleavage does not give this emission.

**Experimental results for gallium arsenide**

In the case of silicon we found a very nearly stabilized Fermi level at the surface. Our results for gallium arsenide clearly show that the Fermi level here is not stabilized and that the situation in fact conforms fairly well to the simple straight-band model (see fig. 3b).

The first indication of the lack of surface levels is the spectral distribution of the photoemission from weakly doped P-type material (fig. 9). The greater part of this distribution can be described by the empirical relation $y \propto (hv - 5.57)^{3/2}$, and only a small additional tail occurs at low photon energies. In the case of silicon the 3/2 power was characteristic of valence-band emission. If this applies to gallium arsenide too, the small tail emission means that the surface levels are present only in a low concentration, so that there may well be no stabilization of the Fermi level here. This is in fact clearly evident from the very limited influence of bulk doping on the photoemission (fig. 10).

For a stabilized Fermi level this influence can be calculated as in the case of silicon. Assuming that the escape depth in GaAs is also 2 nm, we have made the calculation for two positions of the Fermi level, given respectively by $\delta = 0.1$ eV and $\delta = 0.7$ eV at the surface. From figs. 11 and 12 it appears that the first choice gives only a poor fit with the experimental results and that the second does not fit at all. We conclude therefore that the Fermi level is not stabilized.

This conclusion is confirmed by the results of measurements of the effect of bulk doping on the thermionic work function $\varphi$. To obtain information on this point, contact potential measurements were carried out to determine the difference in $\varphi$ between $N$-type and $P$-type material. The results of these experiments showed that, even in the case of weakly doped material, the difference in $\varphi$ roughly corresponded to the difference

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ence in the position of the Fermi level in the volume. This ties up with the assumption that the bands run more or less straight at the surface.

**Photocathodes for visible light; lowering of the work function by adsorption**

We shall now deal at somewhat greater length with the problem, mentioned in the introduction, of making a satisfactory photocathode for visible light. First, it should be stated that good photocathodes in use at the present time can have a very high maximum yield, with values up to 0.30 (expressed in electrons per incident photon). A yield as high as this can scarcely be improved upon. The Na$_2$KSb-Cs photocathode [15] has its threshold wavelength at 0.85 $\mu$m; this is a sufficiently long wavelength for the detection of visible light. Existing cathodes therefore meet the requirements for visible-light detectors reasonably well.

All the good photocathodes were evolved more or less empirically. Later it turned out that all efficient cathodes were P-type semiconductors. The question that now arises is whether more scientific methods could be applied to the development of photocathodes, using known semiconductors.

A high yield can only be obtained with valence band emission. In the example of silicon given above, the threshold for photoemission with strong P-type doping

![Fig. 9. Photoemission of GaAs with weak P-type doping (2.5 x 10$^{17}$ acceptors/cm$^3$). The 2/3 power of the yield $y$ is given as a function of photon energy $h\nu$. The tail emission is of little significance.](image)

**Fig. 10. Influence of volume doping on the photoemission of GaAs.** The yield $y$ is given as a function of photon energy $h\nu$ for P-type material, 4.0 x 10$^{19}$ acceptors/cm$^3$ and 2.5 x 10$^{17}$ acceptors/cm$^3$ and for N-type, 1.0 x 10$^{18}$ donors/cm$^3$. The curves have been reduced to the same $y$-value at $h\nu = 6.35$ eV.

**Fig. 11. The yield $y$ as a function of $h\nu$ for N-GaAs, $1 \times 10^{19}$ donors/cm$^3$, as found theoretically for two values of $\delta$ and an escape depth $d$ of 2.0 nm. The experimental points (squares) are the same as in fig. 10. The curves have again been reduced to the same $y$-value at $h\nu = 6.35$ eV.**

**Fig. 12. As fig. 11, but now for P-GaAs, $4 \times 10^{19}$ acceptors/cm$^3$. Only a few of the corresponding experimental points of fig. 10 are shown (the circles). The zero point of the theoretical curve (i.e. the threshold energy $E_0$) for $\delta = 0.7$ eV is at $E_A + E_g - \delta = 5.37 - 0.7 = 4.87$ eV.**
was 4.9 eV, that is to say in the far ultraviolet (0.25 \( \mu \text{m} \)). In the case of GaAs it is not possible to shift the emission to lower energy by means of band bending, and \( E_d \) here is even higher (5.6 eV). Values as high as this are found with most semiconductors.

As we mentioned in the introduction, however, a method does exist by which the threshold for photoemission can be shifted to a lower energy, i.e. by the adsorption of electropositive metal atoms on the surface of the semiconductor. We shall now consider this method.

Suppose we have a \( P \)-type semiconductor whose Fermi level at the surface is not stabilized (see fig. 13). Metal atoms are now adsorbed on this surface (fig. 13a). Let the ionization energy of these atoms in the adsorbed state be \( I_{\text{ads}} \) (this need not be equal to the ionization energy of the free atom). If \( I_{\text{ads}} \) is smaller than the thermionic work function \( \phi \) of the semiconductor, the metal atoms will give up an electron to the acceptors in the bulk of the semiconductor. As a result, a negative space charge arises in the semiconductor, and the metal ions form an opposite surface charge. The negative space charge causes band bending: the potential inside the semiconductor rises in relation to the vacuum level. Upon the further adsorption of atoms the band bending increases. This process continues until the Fermi level has risen to a level slightly above the bottom of the conduction band at the surface (fig. 13b). As soon as this has happened, the electrons of the adsorbed atoms enter the conduction band, in which the number of available states is very large; there is no further increase of the space charge and therefore no further band bending. The metal ions, to-

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**Fig. 13.** Lowering of the threshold energy for photoemission by the adsorption of metal atoms. 

a) If the ionization energy \( I_{\text{ads}} \) of an adsorbed metal atom is lower than the work function of the clean surface of \( P \)-type material, the metal atoms give up electrons to the acceptors in the bulk. This gives rise to band bending, which continues until the Fermi level coincides with the bottom of the conduction band at the surface (b). Upon further adsorption the donated electrons enter the conduction band. They form together with the positive metal ions a dipole layer, as a result of which the levels in the semiconductor are raised with respect to the vacuum level. This continues until the optimum situation (c) is reached, where \( \phi = I_{\text{ads}} \). In \( N \)-type material (d) there is virtually no band bending; almost right from the beginning a dipole layer is formed in this material by the positive metal atoms and the donated electrons in the conduction band.

Since the electrons are able to tunnel through the
potential barrier of the dipole layer, the threshold energy for photoemission \( E_d \) finally falls to \( I_{\text{ads}} \) in strongly \( P \)-type doped material. In material with weak \( P \)-type doping, after adsorption of metal atoms, ("straight bands") the threshold energy is \( E_d = I_{\text{ads}} + E_g \), as in \( N \)-type material, in which hardly any band bending occurs (fig. 13d).

We shall now examine what happens when metal atoms are adsorbed on a semiconductor surface with a stabilized Fermi level (fig. 14). If \( I_{\text{ads}} \) is sufficiently low, the metal atoms will give up their electron to the surface states at the Fermi level (fig. 14a). The adsorbed ions now form together with the resultant negative surface charge a dipole layer which causes the potential in the semiconductor to rise with respect to vacuum. As adsorption continues a maximum lowering of the threshold is reached when the Fermi level has risen to \( I_{\text{ads}} \) below vacuum level (fig. 14b). Thereafter the adsorbed atoms have no further reason to give up an electron. In this situation the thermionic work function is again \( \psi = I_{\text{ads}} \). For weakly doped material the long wavelength threshold is now \( E_d = I_{\text{ads}} + \delta \). For strong \( P \)-type doping we again find \( E_d \approx I_{\text{ads}} \).

The behaviour of some semiconductors is not entirely in accordance with this model. If the surface of these materials is clean, the Fermi level is not stabilized, but the surface, upon adsorbing metal atoms, behaves as if the Fermi level were in fact stabilized. In this case the adsorption of foreign atoms evidently gives rise to excess surface levels. Gallium arsenide is a typical example of such a semiconductor\(^{(16)}\). No satisfactory explanation has yet been found for this phenomenon.

If one is looking for a photocathode with a low threshold energy, the above considerations show that one should take a strongly \( P \)-type doped semiconductor and cover it with metal atoms for which \( I_{\text{ads}} \) is small; whether or not the Fermi level is stabilized is then immaterial as far as the threshold energy is concerned, this being equal to \( I_{\text{ads}} \).

The lowest value of \( I_{\text{ads}} \) is found for caesium, at about 1.4 eV (0.90 \( \mu \)m wavelength), virtually independent of the substrate.

For \( P \)-type silicon coated with Cs this value has in fact been found as the threshold for valence band emission\(^{(9)}\). By varying the volume doping it is possible to estimate the escape depth for electrons in the relevant energy region. The result is \( d \approx 20 \) nm, a value also found for practical photocathodes\(^{(15)}\).

The yield of \( P \)-type silicon with Cs is very low, however (<1%). This is due to the fact that the electron transitions in silicon, caused by light with a photon energy equal to or slightly higher than 1.4 eV, are indirect transitions. These are transitions between states of different momentum, the electron exchanging momentum with the lattice vibrations. In a diagram giving the energy \( E \) against momentum \( k \) (see fig. 15) these are represented by an oblique arrow. The yield is low with indirect transitions for two reasons:

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1) The transition probability is very small for an indirect transition. This is the opposite to the case of a direct transition, where the momentum is preserved, so that no lattice vibrations are needed to maintain the balance of momentum. Because of this the absorption of the relevant light is weak and only a small fraction of the light is absorbed in the escape layer. In silicon the penetration depth is roughly 1 μm, which is very much greater than the escape depth found of 20 nm. Thus, the majority of the electrons excited do not reach the surface, and therefore do not contribute to the photoemission.

2) Even the light that is absorbed in the escape layer is to a great extent ineffective, for in principle, at a given \( h\nu \), an electron can go from any state in the valence band to any state in the conduction band, provided the energy difference agrees. In a large percentage of these transitions the final state of the electron is a state in the conduction band below \( E_{\text{vac}} \) (see fig. 16). These are known as competing transitions.

![Fig. 16. Indirect transitions in silicon with strong P-type doping (\( E_F \) lies at the top of the valence band), coated with Cs (\( \varphi = E_{\text{vac}} - E_F = 1.4 \text{ eV} \)). a is a transition where the electron receives an energy higher than \( E_{\text{vac}} \); this electron may be emitted; b and c, competing transitions where the excited electron cannot be emitted. The energy difference -\( h\nu \) for a; b and c is the same, and greater than \( E_d = 1.4 \text{ eV} \).](image)

This being said, it is obviously of interest to consider semiconductors in which the relevant transitions are direct ones. The disadvantage mentioned under item (2) is then not encountered, for at a given \( h\nu \) there is generally only one set of states in the valence and conduction bands possessing the same momentum; there are no competing (direct) transitions. As far as item (1) is concerned, with direct transitions stronger light absorption is usually found, because the probability of a direct transition is so much greater than for an indirect transition. On the other hand it could well be that the number of possible indirect transitions is much greater than the number of possible direct ones.

Let us confine ourselves to the simple situation in which the extremes of the two bands lie at the same \( k \) value. We again consider semiconductors with strong P-type doping, so that \( E_F \) coincides with the top of the valence band, and which are coated with Cs, so that \( E_{\text{vac}} - E_F = \varphi = 1.4 \text{ eV} \). Fig. 17 shows three cases: a) \( E_g > \varphi \), b) \( E_g = \varphi \), c) \( E_g < \varphi \). Case (a) is unfavourable since the electron must first enter the conduction band before it can be emitted; the threshold for photoemission is thus \( E_g = E_g > \varphi \). Again, in case (c) the threshold for direct transitions is shifted towards the blue, because the point where \( E_{\text{vac}} \) intersects the conduction band corresponds to a valence band level below \( E_F \). Only in case (b) is \( E_d \) not greater than but equal to \( \varphi \). It follows, then, that we should choose semiconductors in which the energy gap relevant to direct transitions, i.e. the optical energy gap, is roughly equal to 1.4 eV. (It may also be deduced from fig. 17c that, at a given \( E_g < \varphi \), the value of \( E_d \) approaches closer to \( \varphi \) as the valence band becomes flatter and the conduction band sharper, in other words as the effective mass of the holes in the valence band becomes greater and that of the electrons in the conduction band smaller.)

Semiconductors whose energy gap does not differ too widely from 1.4 eV are CdTe (\( E_g = 1.5 \text{ eV} \)), GaAs (\( E_g = 1.35 \text{ eV} \)) and InP (\( E_g = 1.29 \text{ eV} \)). CdTe is immediately ruled out because it cannot be given the necessary high P-type doping content. The hope that the absorption of the light might be stronger than for silicon, since direct transitions are involved, is not fulfilled by the other two materials; the penetration depth for light with \( h\nu \) values greater than \( E_g \) is of the order of 1 μm, as in silicon.

This penetration depth is much too great as long as we are concerned with escape depths of 20 nm. This does not however apply to the cases of fig. 17a and b. In these cases the bottom of the conduction band in the bulk is above the vacuum level (fig. 17a) or coincides with it (fig. 17b). This means that electrons in the conduction band possessing thermal energy are already capable of escaping into the vacuum. In other words, excited electrons can still be emitted after they have entirely lost their kinetic energy by collisions in the conduction band. Here, then, the escape depth is no longer determined by the mean free path of high-energy electrons but by the diffusion-recombination length. This lies roughly between 0.1 and 1 μm. In these cases, therefore, a penetration depth of 1 μm for light is very reasonable. GaAs is a material that closely approximates to the situation in fig. 17b.

These considerations led us to make an experimental
photocathode of GaAs, coated with Cs, which gave surprisingly good results. Single crystals of GaAs were used, with $3 \times 10^{19}$ acceptors/cm$^2$, cleaved in vacuo. The measured spectral distribution (Fig. 18) shows that the threshold for photoemission is 1.35 eV (0.90 µm), which is near the expected value. On the blue side of the visible spectrum (0.4 µm) the yield is about 0.30 electrons per incident photon; at 3.5 eV (0.35 µm) it rises to as much as 0.35. After correction for reflected light, a yield is found of roughly 0.50 electrons per absorbed quantum, which is the maximum that can be expected (since half the excited electrons go away from the surface and into the bulk of the material). The sensitivity to light with a colour temperature of 2850 K is 500 µA/lm. This photocathode is therefore even better than the Na$_2$KSb-Cs cathode, which has a long wavelength threshold of 0.82 µm and a sensitivity of 300 µA/lm.

Appendix: Calculation of the effect of bulk doping on the photoemission of silicon

We take a P-type semiconductor and choose a co-ordinate system in which the x-axis is perpendicular to the surface of the semiconductor; $x = 0$ at the surface, and $x > 0$ in the bulk.

We make the following assumptions:

1) The escape probability of an electron excited at a distance $x$ from the surface has the form $\exp(-xfd)$, the escape depth $d$ being independent of the energy of the excited electron.

2) The intensity of the light at a distance $x$ from the surface is given by $I_0 \exp(-x/fm)$, the penetration depth $m$ being independent of the photon energy.

3) The photoemission of a crystal with straight bands is given by $y = C(hv - E_0)^{3/2}$, as we found empirically.

The contribution $\Delta y$ to the photoemission originating from a layer of thickness $\Delta x$ at a distance $x$ from the surface is given for straight bands by:

$$\Delta y(x) = A(hv - E_0)^{3/2} e^{-x/f} \Delta x,$$

where $L^{-1} = d^{-1} + m$ and $A$ is an arbitrary constant.

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Suppose now, that as a result of band bending the valence band at position \( x \) is shifted to higher energy by an amount \( \delta E(x) \) with respect to its position at the surface. We now make the additional assumption that the contribution to the photoemission is independent of the state in the conduction band occupied by the excited electron. We then have for bent bands:

\[
\Delta y(x) = A \left( hv + \delta E(x) - E_0 \right)^{3/2} e^{-\alpha x/L} \Delta x . \quad (3)
\]

According to eqs. (1) and (2), for a Schottky layer:

\[
\delta E(x) = e(V(x_0) - V(x)) = \Delta E \left( 1 - \left( \frac{x - x_0}{x_0} \right) \right), \quad (4)
\]

The last term in this equation originates from the part of the crystal outside the space charge region.

The value of the integral for a given \( x_0 \), \( \Delta E \) and \( L \) has to be determined numerically.

Summary. The article discusses a study made of the surface properties of semiconductors by investigating their photoemission. The spectral distribution of the photoemission was measured on vacuum-cleaved single crystals of silicon and gallium arsenide with various amounts of P-type and N-type doping. The results are interpreted in terms of the band theory of solids, where the bands can be bent at the surface by a space charge due to surface states and where, in the presence of excess surface states, the Fermi level may be stabilized in the surface levels. The emitted electrons come from a surface layer of thickness \( d \), the escape depth. In weakly doped silicon the main emission comes from the valence band and "tail emission" from the surface states. In Si the Fermi level is stabilized; with increasing impurity content, the layer where band bending occurs finally becomes thinner than the escape depth; this explains the observed change in the spectral distribution of the emission. In the case of GaAs it is concluded that there are virtually no surface levels, no band bending and no stabilization of the Fermi level. For photoemission in the visible region the threshold energy of nearly all semiconductors is too high (~ 5 eV); it can be lowered by the adsorption of metal atoms, e.g. of Cs (to 1.4 eV). The yield of P-Si coated with Cs is small due to a too small absorption coefficient and b) "competing transitions" that do not result in emission. Strongly P-doped GaAs coated with Cs may be expected to be a good photocathode in the visible region since the competing transitions are of little significance and the escape depth is unusually large owing to the vacuum level and the bottom of the conduction band being coincident. This has been confirmed by experiment. An experimental photocathode of this composition has a long wavelength threshold at 0.9 \( \mu \)m and an outstanding photoemission: the yield is 0.35 electrons per incident photon at 0.35 \( \mu \)m.
Recent scientific publications

These publications are contributed by staff of laboratories and plants which form part of or co-operate with enterprises of the Philips group of companies, particularly by staff of the following research laboratories:

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Reprints of most of these publications will be available in the near future. Requests for reprints should be addressed to the respective laboratories (see the code letter) or to Philips Research Laboratories, Eindhoven, Netherlands.

G. A. Acket: Determination of the Hall mobility of hot electrons in gallium arsenide using 8 mm microwaves.  

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The rate of the reaction between 2-methoxybenzenediazonium and sulfite ions;  


G. Blasse & A. Bril: Structure and Eu³⁺-fluorescence of lithium and sodium lanthanide silicates and germanates.  
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