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CONVENTIONAL AND NEGATIVE ELECTRON AFFINITY PHOTOEMITTERS

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Abstract. — This talk will be divided into three parts. The first will be a brief survey of the «conventional» photocathodes with useful quantum yield in the visible and the near infrared spectral region. These cathodes include those represented by the chemical formulae Ag-O-Cs (S-1), Cs3Sb (S-11), Bi-Ag-O-Cs (S-10), Na2KSb, K2CsSb, and (Cs)Na2KSb (S-20). Second, the essential features of the negative electron affinity (NEA) concept will be discussed and the basic advantages of NEA materials for photoemission, as well as for secondary electron emission, will be summarized. In the third part, the present status of the practical use of NEA electron emitters will be presented. These include GaP, GaAs, Si, and the ternary III-V compounds. The technological problems encountered in working with these materials will be discussed. A few concluding remarks will deal with the prospects of future developments.

1. Introduction. — The development of the negative electron affinity (NEA) electron emitters during recent years represents a considerable scientific advance over the previously known cathode materials. Whereas conventional cathodes were the result of essentially empirical methods, the concept of NEA made it possible to synthesize photoemissive materials with predetermined properties, especially with regard to long wavelength threshold.

The NEA cathodes differ from the conventional cathodes not only by their improved long wavelength performance in devices such as photomultipliers and image tubes, but also by the new technological problems that are encountered in the formation of the cathodes. The emphasis in this paper will be on these practical considerations and the scope will therefore be limited in two respects. First, the paper will deal only with materials that have usefully high quantum efficiency, thus eliminating many materials that have yielded interesting scientific results. Second, the discussion will be confined to materials that are sensitive to wavelengths above approximately 4 000 Å. This eliminates the large number of materials that have high quantum efficiency in the ultraviolet region of the spectrum, particularly below 2 000 Å.

2. Conventional photocathodes. — 2.1 Properties of cathodes. — During a period of about 35 years, beginning in 1930, a total of no more than six photoemissive materials were developed that have useful sensitivity to visible and near infrared radiation. These cathode materials have been studied and described [1] in considerable detail, therefore only a brief summary will be given for the purposes of this paper.

Figure 1 shows typical spectral response curves for four of these cathodes. (The curves for Cs3Sb and Na2KSb have been omitted because their proximity to the K2CsSb curve would cause confusion.) While the quantum efficiency at different wavelengths tends to vary for individual cathodes of the same type, the threshold wavelength is generally fairly well defined. An exception is the (Cs)Na2KSb cathode whose threshold, as indicated in figure 1, may vary over a range of about 1 000 Å. This feature of the S-20 cathode will be touched upon in section IV.

The characteristics of the six cathodes that are most important for their use in devices can be summed up as follows (see also Table I).

2.1.1 The Ag-O-Cs cathode has the longest threshold wavelength (close to 2 μm) of all known cathodes, including the NEA cathodes available at this time. However, the general usefulness of the cathode is limited because it has high thermionic emission at room temperature and quantum efficiencies at visible wavelengths that are an order of magnitude lower than those of the other five cathodes. Hence, the predominant use of this material is for infrared detectors.
A. H. SOMMER

Conventional photocathodes

<table>
<thead>
<tr>
<th>Photocathode</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Specific Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag-O-Cs (S-1)</td>
<td>IR response</td>
<td>Low QE</td>
<td>IR detection</td>
</tr>
<tr>
<td>Cs$_3$Sb (S-11)</td>
<td>Inexpensive</td>
<td>Large thermionic emission</td>
<td></td>
</tr>
<tr>
<td>Bi-Ag-O-Cs (S-10)</td>
<td>Close to eye response</td>
<td>Inferior to alternative cathodes</td>
<td>General use</td>
</tr>
<tr>
<td>K$_2$CsSb</td>
<td>High QE</td>
<td>No red response</td>
<td>Scintillation counters</td>
</tr>
<tr>
<td>Na$_2$KSb</td>
<td>High temperature stability</td>
<td>No red response</td>
<td>High temperature</td>
</tr>
<tr>
<td>(Cs)Na$_2$KSb (S-20)</td>
<td>High QE, High red response</td>
<td>Expensive</td>
<td>Low light level</td>
</tr>
</tbody>
</table>

2.1.2 The Cs$_3$Sb cathode was the first high quantum efficiency (QE) material to be developed. It has been surpassed by later materials not only in QE but also in threshold wavelength and in low thermionic emission. From the technical point of view, it can therefore be considered obsolete. However because of the simplicity of the manufacturing process, it is still widely used for applications where optimum performance is not required.

2.1.3 The Bi-Ag-O-Cs cathode was developed specifically for obtaining a spectral response approaching that of the eye for use in photo-emissive camera tubes for color television such as the image orthicon. For other applications, it is inferior to alternative cathodes because of relatively high thermionic emission and low peak QE.

2.1.4 The K$_2$CsSb cathode is characterized by very high QE in the 4 000 Å region, combined with extremely low thermionic dark current. This makes the cathode ideal for detection of very low light levels (photon counting), particularly in scintillation counters where the radiation to be detected is in the 4 000 Å region.

2.1.5 The Na$_2$KSb cathode has a response curve similar to that of K$_2$CsSb with a somewhat longer threshold wavelength. This cathode is the only one known, including the NEA cathodes, where response throughout the visible range is obtained without the presence of Cs or Rb. This absence of Cs probably accounts for the most valuable property of this cathode, viz., its stability at ambient temperatures of above 100 °C.

2.1.6 The (Cs)Na$_2$KSb cathode is the only conventional cathode that has both high QE throughout the visible range and useful response in the near infrared. The main reason why it has not replaced most of the other conventional cathodes is the complexity of the manufacturing process. It has somewhat higher thermionic emission than the K$_2$CsSb cathode and is inferior to the Ag-O-Cs cathode above 9 000 Å.

2.2 TECHNOLOGY OF CATHODE FORMATION. — Despite their differences in chemical composition,
the methods for making the conventional cathodes have many features in common. These methods will be described briefly (see also Table II) with emphasis on those aspects which differ most markedly from the processes used in making NEA cathodes.

### Table II

**Common features of conventional photocathodes**

1) Polycrystalline material is adequate and permits choice of substrate.
2) Evaporation of the low vapor pressure component; hence
   a) (Usually) no exposure to air.
   b) Large area.
   c) Curved surface.
   d) Semitransparent cathode.
3) Reaction with alkali metal(s) at elevated temperature produces:
   a) Low work function surface film which is an integral part of homogeneous bulk material.
   b) Good stability at room temperature.

(see section 3). According to the most commonly used procedure, the low vapor pressure component of the cathode material, i.e., Ag, Sb, or Bi, is evaporated onto a substrate consisting either of a metal or, for semitransparent cathodes, of glass or quartz. This evaporation is usually done in the final vacuum of the device. In the second processing step, in some cases after surface oxidation, the photoemissive compound is formed by exposing the evaporated metal film to alkali metal vapor at an elevated temperature in the region of 150°-200°C.

The deposition of the base material by evaporation has several advantages. First, by performing all processing steps in a high vacuum environment, the formation of contaminating surface films can be avoided. Second, large-area cathodes can be made without difficulty. Third, the substrate geometry can be either flat or curved. Finally, the most important feature of the evaporation method is that, provided the metal is evaporated to optimum thickness, cathodes can be made to operate in the semitransparent mode equally as well as in the reflecting mode.

The high processing temperature of 150 to 200°C appears to produce a homogeneous bulk material of several hundred Angstrom thickness. It is believed [2] that the high processing temperature has a beneficial effect on the performance of photocathodes in devices because a material that is formed at 150°C is likely to be chemically stable at room temperature.

The cathodes made by the conventional processes are always polycrystalline. As will be discussed below, there is no reason to expect a significant improvement from the use of single crystals.

### 3. Negative electron affinity photocathodes

#### 3.1 The concept of negative electron affinity (NEA)

The concept of NEA has been discussed in many recent publications (see, for instance, references [3] and [4]); therefore, a brief review of the basic difference between conventional and NEA cathodes will suffice for the purposes of this paper.

There is good evidence [5], [6] that conventional cathodes with high QE in the visible range are strongly p-type doped semiconductors with an n-type surface layer, represented schematically by the energy band model of figure 2a. The Fermi level is close to the valence band maximum in the bulk, and the bands bend downward near the surface, thereby lowering the vacuum level with respect to the bulk conduction band minimum. This results in an «effective» electron affinity \( E_A \). Photoemission from the valence band occurs for photons having a minimum energy \( (E_G + E_A) \), but the «hot» electrons excited to levels above the vacuum level lose energy quickly \( (\sim 10^{-12} \text{ s}) \) through interaction with phonons until they have been «thermalized» at the bottom of the conduction band. As a result, only those electrons can escape into vacuum that have been produced so close to the surface (a few hundred Angstroms) that their energy still exceeds the value \( (E_G + E_A) \).

![Fig. 2. Energy band models of conventional and NEA photocathodes.](image)

By contrast, in NEA materials (Fig. 2b), the bands are bent such an extent that the vacuum level lies below the bottom of the conduction band minimum in the bulk material, i.e., the effective electron affinity is negative. In this case, the thermalized electrons have sufficient energy to escape, and, since they have a long lifetimes \( (\sim 10^{-9} \text{ s}) \), they can diffuse from a considerable distance to the surface and still be emitted. Thus, the essential difference between the conventional (positive electron affinity) and the NEA emitters is that the latter have an escape depth that is several orders of magnitude greater.

Figure 3 shows schematically the effect of NEA, i.e., of enhanced escape depth, on the spectral response curves of photoemitters. Curve (a) represents...
the response of a conventional emitter (positive electron affinity) and curve \((b)\) that of an NEA emitter. Equal values of \(E_G\) are assumed for both cases to emphasize the basic difference. Comparison of the curves shows that:

3.1.1 At short wavelengths, where the photon energy is much larger than \(E_G\), so that the light absorption is high, the QE is substantially the same for both materials. The reason is that most of the light is absorbed within the short escape depth (a few hundred Angstroms) associated with positive electron affinity materials.

\[
\text{FIG. 3. — Basic difference between spectral response curves of conventional and NEA photocathodes.}
\]

\[
\text{Fig. 4. — Basic difference between conventional and NEA secondary emitters.}
\]

3.1.2 The threshold wavelength of \((b)\) is longer than that of \((a)\) because, for equal \(E_G\), the threshold photon energy of \((a)\) is greater than that of \((b)\) by the energy corresponding to the effective electron affinity \(E_A\).

3.1.3 The most important difference between \((a)\) and \((b)\) is that, with increasing wavelength, the QE of the NEA cathode remains much higher close to the threshold. The reason is that, if the cathode is used in the reflection mode, an ever-increasing fraction of the photoelectrons is produced beyond the escape depth of positive electron affinity emitters but within the escape depth of the NEA material.

Although the main subject of this paper is photoemission, a brief diversion concerning the effect of NEA on secondary electron emission is appropriate. In secondary emission, hot electrons are produced by the impact of energetic primary electrons rather than by photons. The number of secondary electrons per primary electron increases with the primary energy \(E_p\), but the secondaries are also produced at an increasing distance from the vacuum interface, hence the number of emitted electrons depends on the escape depth.

To illustrate the effect of NEA on secondary electron emission, typical \(\delta\) versus \(E_p\) curves for conventional \((a)\) and NEA \((b)\) materials are shown in figure 4. To emphasize the basic difference, it is assumed that both materials have the same «intrinsic» gain factor i. e., that they require the same energy for the production of one secondary electron. Because NEA materials have a longer escape depth, curve \((b)\) increases linearly with \(E_p\) up to high values of \(E_p\) whereas the gain of conventional materials \((a)\) begins to drop at values where too many electrons are produced beyond the much shorter escape depth.

It is important to note that, at low primary energies, up to about 300 eV, NEA materials have no advantage over conventional secondary emitters for the same reason that NEA photocathodes have no advantage at short wavelengths. In both types of emitter, the superiority of the NEA material manifests itself only when the electrons are produced beyond the limited escape depth associated with positive electron affinity.

In concluding the remarks on secondary emission, it is worth noting that the first NEA material to find practical use was a secondary emitter, viz., GaP(Cs) [7], [8], [9], [10], [11]. This has proven very successful as a dynode material in photomultipliers because the gains obtained are an order of magnitude greater than those obtained with conventional secondary emitters.

3.2 TECHNOLOGY OF NEA CATHODE FORMATION. — Since the first experimental verification of the NEA concept by Scheer and van Laar in 1965 [12], a large number of NEA cathodes has been produced and investigated. These comprise two basic materials: first, III-V semi-conductors of various composition, including ternary and quaternary compounds, and, second, elemental silicon. In order to obtain NEA, these basic materials are «activated» with Cs and — in most cases — oxygen [13] or fluorine [14] to obtain a low work function surface. The technological problems associated with making these cathodes are basically the same for all of the materials and will be discussed before the individual cathodes are described.

The outstanding difference between NEA and conventional electron emitters is that for NEA emitters single crystals of great perfection and well-controlled doping must be used as a base material. Imperfections in the crystal can reduce the diffusion length of the electrons and thus reduce the large escape depth which is the reason for the high efficiency of NEA emitters. (Polycrystalline NEA materials have found practical use in some special cases (see section 3.3.2.1)). By contrast, for conventional emitters, polycrystalline materials are quite adequate because the escape depth is small compared with the size of the microcrystals, i. e., the material is effectively a single crystal for the electrons produced within a few hundred Angstroms from the surface. The need for single crystals imposes the following limitations on the formation of NEA cathodes (see Table III).

3.2.1 To date, the only successful method of producing single crystal III-V cathode materials has been the epitaxial growth of suitably \(p\)-doped...
TABLE III

Common features of NEA photocathodes

1) Single crystal is (usually) required and limits choice of substrate.
2) Bulk material is grown epitaxially. Hence,
   a) Exposure to air unavoidable and therefore heat cleaning in vacuum necessary.
   b) Limited area.
   c) Flat surface.
   d) Difficulty in forming semitransparent cathode.
3) Reaction with alkali metal (usually) at low temperature produces,
   a) Low work function surface film deposited on homogeneous bulk material.
   b) Limited stability at room temperature.

material by either the vapor-phase [15] or the liquid-phase [16] method on a single-crystal substrate with similar lattice constant. Si single crystals are usually grown in the bulk. Attempts to produce single-crystal films of III-V compounds by simpler techniques, such as simultaneous evaporation of the components or sputtering of the compounds [17], have, at the time of writing, not produced crystals of satisfactory quality.

3.2.2 It is virtually impossible to avoid exposing the single-crystal base material to air between removal from the growth equipment and mounting in the device. The exposure to air contaminates the surface, hence an additional process is required to clean the crystal in the final vacuum before surface activation with Cs. In the early work [12], this was accomplished by cleaving the crystal in vacuum, but by this method only very small area surfaces can be obtained and the procedure is not practical in complex tubes. Cleaning is now usually accomplished by the simpler method of heating the crystal to a temperature close to that where the material decomposes (III-V compounds) or melts (Si). The heating is done by radiation, by electron bombardment, or by resistance heating. In all three cases, difficulties arise in achieving uniform heating over the whole area which is required because the optimum temperature is very critical. Moreover, it is difficult to measure the temperature accurately. An optical thermometer is generally used, but, to obtain reliable results, the emissivity of the material must be known or, at least, must be reproducible from crystal to crystal.

3.2.3 The requirement for a single crystal substrate limits the area that is practically feasible. At present, III-V compounds are used only for cathodes having areas in the 1 to 3 cm² range. In the case of Si, the simpler and more advanced technology makes somewhat larger areas possible.

3.2.4 Unless sophisticated grinding techniques are used, single crystals have a plane surface and are therefore not suitable for devices where the electron optics requires a curved geometry.

3.2.5 Probably the greatest obstacle to the general use of NEA emitters up to the present has been the difficulty of making semitransparent cathodes which can be used with light incident from the substrate side. This requirement is almost essential for image tubes and television camera tubes. The most desirable solution for making semitransparent cathodes would be epitaxial growth on a transparent substrate, such as quartz or sapphire. Attempts in this direction, however, have so far been unsuccessful [18]. At present, best results for III-V NEA cathodes are obtained by epitaxially growing a thin cathode layer on a relatively thick single-crystal III-V substrate that has a lattice constant similar to that of the cathode layer. In addition, the substrate has a larger band gap than the cathode. Hence it acts as a «window» in that it absorbs only short wavelength light while permitting longer wavelength light to be absorbed in the NEA material.

3.2.6 In contrast to the conventional cathodes where the alkali metal forms a homogeneous chemical compound with the base material, the Cs (or Cs-O or Cs-F) activation of the NEA emitters is a much more critical process because, as has been established for GaAs [19], (In, Ga)As [20], [21], and Si [22] [23], surface layers of monomolecular dimension are required. The details of this surface activation are only partially understood (except for Si, see below). With some materials, best performance is obtained if the activation takes place at temperatures close to room temperature. Low temperature activation may lead to operational instability, but there are indications that this instability can be improved or eliminated by more carefully controlled conditions. In conclusion, the most important differences between conventional and NEA photocathodes are summarized in Table IV.

TABLE IV

Comparison of conventional and NEA photocathodes

<table>
<thead>
<tr>
<th></th>
<th>Conventional</th>
<th>NEA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystallinity :</td>
<td>Polycrystalline</td>
<td>Single crystal</td>
</tr>
<tr>
<td>Substrate :</td>
<td>Arbitrary</td>
<td>Single crystal</td>
</tr>
<tr>
<td>Exposure to air :</td>
<td>Avoidable</td>
<td>Unavoidable</td>
</tr>
<tr>
<td>Area :</td>
<td>Arbitrary</td>
<td>Small</td>
</tr>
<tr>
<td>Geometry :</td>
<td>Flat or curved</td>
<td>Flat</td>
</tr>
<tr>
<td>Semitransparent cathode :</td>
<td>Easy</td>
<td>Difficult</td>
</tr>
<tr>
<td>Surface film :</td>
<td>Integral part of bulk material</td>
<td>Deposited on bulk material</td>
</tr>
<tr>
<td>Stability :</td>
<td>Satisfactory</td>
<td>Requires improvement</td>
</tr>
</tbody>
</table>

3.3 NEA CATHODE MATERIALS. — 3.3.1 General considerations. — The NEA cathode technology is still in an early stage of development, but one specific
relationship between spectral response curves and energy band gaps of various materials has been consistently observed. While curves similar to curve (b) in figure 3 have been obtained under optimum conditions, for instance with GaAs, there is a general trend for the QE to decrease with decreasing band gap energy $E_G$. Qualitatively, this observation agrees with expectation [21] because, if one assumes that the work function (difference between Fermi level and vacuum level) does not vary substantially from compound to compound, the magnitude of the effective negative electron affinity, and thereby the escape probability of the electrons, will decrease with decreasing $E_G$ (see Fig. 2). The ultimate limit to the reduction of $E_G$ is, of course, set by the fact that $E_G$ must be greater than the work function to make NEA possible.

The lower escape probability at smaller $E_G$ values means, in practical terms, that increased threshold wavelength (lower $E_G$) of photoemission is generally obtained at the expense of reduced QE. For any specific application, the most useful NEA cathode, therefore, is one that has the largest band gap compatible with the desired threshold wavelength. This is the reason why NEA cathodes with different $E_G$ values have been developed rather than using the materials with smallest band gap for all applications. However, since work function values much below 1 eV are difficult to obtain, NEA cathodes that respond to the whole visible spectrum are generally limited to semiconductors with band gaps in the 1 to 1.7 eV range.

3.3.2 Cathodes used in devices. — Of the materials that have been studied to date, only a few have been developed to a stage where they can be incorporated into devices such as photomultipliers or image tubes. Compared with the six conventional cathodes discussed in section 2, at the time of writing only three NEA cathodes have found practical application. These are:

1. GaAs. — GaAs is the most widely used NEA photocathode because it has higher response above 7000 Å, as well as a flatter response throughout the spectrum, than any other cathode. Figure 5 shows typical response curves (*). Curve (a) represents the best performance that has been obtained in simple experimental tubes (about 1 500 $\mu$A/lm white-light response). In photomultipliers, the sensitivity is usually lower, but sensitivities above 800 $\mu$A/lm, corresponding to curve (b), and up to 1 200 $\mu$A/lm are now frequently achieved. The threshold, in accordance with the GaAs band gap of 1.35 eV, is at about 9 200 Å.

In addition to higher quantum efficiency and longer threshold wavelength, GaAs, as well as the other

(*) All response curves shown refer to cathodes in sealed-off tubes. Higher QE’s have been obtained in ultra-high vacuum demountable systems.

NEA III-V compounds, has the great practical advantage that the thermionic emission (dark current) at room temperature is much lower than that of conventional cathodes with long wavelength response. The factors determining the thermionic emission of III-V compounds have been discussed by Bell [24]. The low thermionic emission cannot be an inherent characteristic of NEA cathodes because the dark current of Si NEA cathodes is much higher (see below) than that of the III-V compounds.

The superiority of the GaAs cathode over previously used materials is apparent from figure 6 and is illustrated by the following examples. In many spectroscopic instruments, response over the whole visible and near-infrared region is required. In the past, two photomultipliers with conventional cathodes had to be used, one for the blue and one for the red and infrared regions. The use of a single GaAs tube greatly simplifies operation. Additional advantages in this application are the flat response throughout the spectral range and the very low dark current. The high infrared response of GaAs, combined, again, with the low dark current, has been found to be particularly useful for Raman spectroscopy [25]. Research in astronomy has also benefited from the use of GaAs tubes, a typical example being the study of the oxygen content of the Mars atmosphere [26].

For the above-mentioned applications, photomultipliers with cathodes operating in the reflection
mode are quite adequate. Semitransparent cathodes, which are required for image and television camera tubes, are still in the developmental stage, but promising results have been reported with thin GaAs films grown epitaxially on single crystals of wider band gap III-V compounds, as described earlier. Examples are GaAs on GaP [27], GaAs on Ga(As, P) on GaP [28] and GaAs on (Ga, Al)As grown on GaP [29].

2. \(\text{GaAs},_0\text{P},_x\text{As} \) — Ga(AsP) compounds have larger band gaps and correspondingly shorter threshold wavelengths than GaAs, and the band gap increases with increasing P content. If the threshold wavelength is not critical, such a material is preferable because a larger effective NEA results in high quantum efficiency, as was pointed out before, and also in a simpler activation process. The compound \(\text{GaAs},_0\text{.73P},_x\text{As} \) [30] has a band gap of 1.7 eV, corresponding to a threshold wavelength near 7 700 Å. Because it has high quantum efficiency over the whole visible spectrum, combined with extremely low thermionic emission at room temperature (\(10^{-16} \text{ A/cm}^2\)), it is used in photodiodes and photomultipliers for applications that do not require infrared response.

The GaAs\(_{0.73}\)P\(_{0.25}\) cathode is used in both single-crystal and polycrystalline forms. The polycrystalline material is usually deposited on a thick metal substrate. It has, of course, a shorter escape depth than do single crystals and, hence, lower sensitivity at long wavelengths (see Fig. 7), but, in many cases, this loss is more than balanced by the simpler fabrication process and by the possibility of making cathodes of larger area and of curved geometry. This latter consideration is particularly important for the use of NEA materials as dynodes in photomultipliers. Therefore the previously mentioned GaP dynode is generally made of polycrystalline GaP deposited on curved molybdenum electrodes.

3. \(\text{In}_x\text{Ga}_{1-x}\text{As} \) — (In, Ga)As compounds have smaller band gaps and, hence, longer threshold wavelengths than GaAs, and the band gap decreases with increasing In content. These compounds are more difficult to make than binary compounds such as GaAs because the In : Ga ratio is very critical; moreover, as discussed earlier, the effective NEA decreases with decreasing band gap energy, resulting in more critical surface activation and lower quantum efficiency. However, for many purposes, the longer wavelengths of the ternary materials are essential. Two specific examples are (1) the detection of the wavelengths emitted by the GaAs laser, which are just beyond the threshold of the GaAs cathode, and (2) the detection of the Nd-YAG laser radiation at 1.06 \(\mu\)m. For the former, an indium content of approximately 6 % (\(E_G = 1.28 \text{ eV}\)) is adequate, and photomultipliers with \(\text{In}_{0.08}\text{Ga}_{0.92}\text{As} \) cathodes have been successfully fabricated. For useful response at 1.06 \(\mu\)m, an indium content of about 18 % (\(E_G = 1.15 \text{ eV}\)) is required. Under optimum experimental conditions, quantum efficiencies up to 2 % at 1.06 \(\mu\)m have been obtained with \(\text{In}_{0.18}\text{Ga}_{0.82}\text{As} \) [20] but, up to the present, sensitivities in photomultipliers are lower. Thus, this cathode, although successfully used for special applications, represents a border-
line case between «practical» and «developmental» materials. It should be noted, however, that even a quantum efficiency of only 0.1% at 1.06 μm is higher than that of the only available alternative, the Ag-O-Cs (S-1) cathode, and that the thermionic dark current of the (In, Ga)As compound is several orders of magnitude lower than that of Ag-O-Cs.

In figure 8, typical curves are shown for compounds with 6% and 18% indium content in comparison with a GaAs curve. It is evident that, as expected, the smaller band gap increases the threshold wavelength, but, at the same time, the associated lower escape probability, for the reasons discussed earlier, reduces the efficiency, especially in the region adjacent to the threshold.

![Figure 8: Spectral response curves of InₓGa_{1-x}As(Cs, O) photocathodes.](image)

3.3.3 Developmental cathodes. — 1. III-V materials. — There are two main requirements for enhancing the usefulness of NEA III-V emitters. (1) In order to obtain higher infrared response, crystal growth and processing of ternary compounds with band gaps smaller than that of GaAs must be further improved. (2) Better methods must be developed for growing and activating semitransparent cathodes of GaAs as well as of ternary compounds.

With regard to crystal growth, good results for ternary III-V compounds of varying qualitative and quantitative composition have been obtained by using epitaxial growth from either the vapor [15] or the liquid phase [16]. Most of the work on (In, Ga)As has been done with crystals grown from the vapor phase [31] whereas In(As, P) has been made predominantly by liquid-phase growth [32]. A more recent development is the use of the quaternary compound (In, Ga)(As, P), also grown from the liquid phase [33]. One of the major problems with all these materials is that, while there are activation methods that work well under optimized experimental conditions in demountable ultra-high vacuum systems, it is difficult to adapt these methods to devices.

As for semitransparent cathodes, the need for crystallographically matching substrates has been mentioned earlier. An additional problem arises because the thickness of both substrate and cathode film must be carefully controlled to obtain optimum sensitivity and good uniformity. This difficulty does not exist with reflecting cathodes because, above a minimum thickness, sensitivity and uniformity are independent of thickness.

2. Silicon. — The NEA Si(Cs, O) cathode [34] differs from the III-V cathodes in both basic properties and practical problems. To start with the former, NEA is obtained with Si only on the (100) crystal face [35] whereas NEA photoemission is obtained with the III-V cathodes for all faces that have been investigated. Second, Leed and Auger studies [22] show that the Cs and O atoms are located on well-defined sites on the Si crystal, and the mechanism of emission has been satisfactorily explained in theoretical terms [23]. By contrast, the Cs-O layer on the III-V compounds is amorphous, and its structure is not understood in detail.

The spectral response curve of an NEA Si cathode is shown in figure 9. In accordance with the band gap energy of 1.15 eV, the threshold wavelength is near 1.1 μm. Figure 10 shows that the long wavelength response compares favorably with In₀.₁₈Ga₀.₈₂As.

For practical use, Si has several outstanding advantages. First, the semiconductor technology is much further advanced than that of the III-V materials. Second, an elemental material is inherently simpler to make than binary, not to mention ternary and quaternary, compounds. Third, larger area crystals are available. Fourth, the escape depth is larger than in III-V compounds, and, therefore, semitransparent cathodes can be made in the form of self-supporting thin films of sufficient thickness to have reasonable mechanical strength. Unfortunately, all these advantages are nullified by one unwanted property of the Si cathode, viz., a very high thermionic dark current at room temperature (> 10⁻¹¹ A/cm²) [36]. This high dark current makes NEA Si unsuitable for both photocathodes and dynodes operating at room temperature, but cooling to − 50 °C substantially eliminates the dark current. The only promising application of NEA Si(Cs, O)
to date has been in tubes where the material is used as an electron source in the «cold» cathode [37].

4. Future developments. — It is hazardous to predict future technical developments, but it is an interesting challenge. In the following, the prospects for improved conventional and NEA cathodes will be considered separately.

4.1 CONVENTIONAL CATHODES. — Over the last 40 years, a great amount of effort has been spent on producing new photocathode materials; therefore, the discovery of completely novel compounds is not very likely. However, there appear to be fruitful possibilities in basic improvements of some existing cathodes. Two examples deserve mention.

4.1.1 The Ag-O-Cs (S-1) cathode is unique in having a long wavelength threshold which exceeds even that of presently available NEA cathodes. On the other hand, the quantum efficiency does not increase appreciably for photon energies up to 3 eV as it does in all other cathodes. Thus, the quantum efficiency in the visible region is more than 10 times lower than that of the other cathodes. Since the mechanism of the Ag-O-Cs cathode is still not understood in detail [1], research may well lead to a modified material that has higher response at short wavelengths without an attendant loss in the threshold region.

4.1.2 The (Cs)Na$_2$KSb cathode is characterized by large fluctuations in threshold wavelength (see Fig. 11) as a function of processing technique. There is reason to believe that the bulk material, and hence the band gap energy, is the same for cathodes having different long wavelength thresholds. The most likely explanation for the variations in spectral response is that the degree of band bending varies, thereby changing the magnitude of the effective
electron affinity. Assuming a band gap of approximately 1 eV [38], the longest observed threshold wavelength (see Fig. 11) corresponds to an effective electron affinity of only a few tenths of one eV. If this could be further reduced, it might be possible to reach NEA, resulting not only in a longer threshold but also in greatly increased escape depth and hence quantum efficiency. (Of course, the escape depth would still be limited by the polycrystalline nature of the cathode material.) As to the practical approach to these improvements, experiments with different doping materials and/or surface activation seem indicated. If NEA should be obtained, the next step would be to develop methods of making single crystals of alkali antimonides.

4.2 NEA cathodes. — In contrast to the conventional cathodes, the NEA materials are of such recent origin that there is a greater probability of novel compounds being developed in the future. For instance, methods may be found to activate Ge to NEA. This would combine the advantages of extended infrared response ($E_G = 0.7$ eV) with those associated with the use of an elemental semiconductor. In the meantime, there are still many problems with the available NEA materials that have a good chance of being solved by further research. The following are a few examples.

4.2.1 Modification of the activation process for NEA Si may lead to a reduction of thermionic dark current. This would make Si a very desirable material for infrared detectors and particularly for semitransparent cathodes (and dynodes).

4.2.2 Further improvement in the infrared response of III-V compounds can be expected. Quite recently, progress has been made both in quantum efficiency and in threshold wavelength. At low temperatures, a QE as high as 7.5 % at 1.06 μm has been measured with the quaternary compound (In, Ga) (As, P) [34]. On the other hand, a threshold wavelength as high as 1.58 μm has been obtained with (In, Ga)As [21].

4.2.3 Improvements are most urgently needed in the technology for making semitransparent single-crystal cathodes because the use of reflection-type cathodes is limited essentially to photomultipliers as distinct from imaging devices. There is still no prospect of a simple evaporation technique, but it would be a desirable first step if the presently used substrates, which absorb a considerable portion of the visible light (see p. 55), could be replaced by materials having a sufficiently large band gap to transmit light through the whole range of the visible spectrum. The most promising approach at this time appears to be the heteroepitaxial vapor-phase growth of III-V compounds from organometallic compounds on such light-transmitting substrates as spinel or sapphire [39].

References