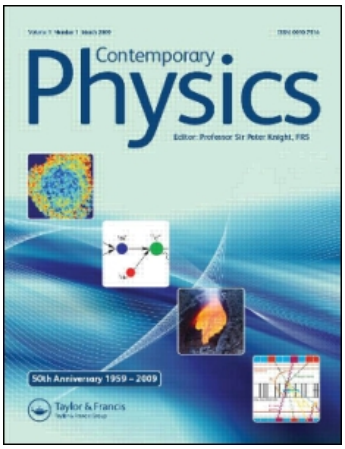


Contemporary Physics
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713394025

Photocathodes—past performance and future potential

Peter D. Townsend

Online Publication Date: 01 January 2003

To cite this Article Townsend, Peter D.(2003)'Photocathodes—past performance and future potential',Contemporary Physics,44:1,17 — 34
To link to this Article: DOI: 10.1080/00107510302717
URL: http://dx.doi.org/10.1080/00107510302717

Contemporary Physics, 2003, volume 44, number 1, pages 17–34

Taylor & Francis
Taylor & Francis Group

Photocathodes—past performance and future potential

PETER D. TOWNSEND

Light detection and imaging at very low intensities, even down to individual photon detection, has been made possible by the development of photomultiplier and imaging tubes. They have two main components: a photocathode detector and an electron multiplication section, but throughout their long history their performance has been limited by the response of the photocathodes. Reappraisal of the underlying science of cathode preparation emphasizes that they are still performing well below their full potential. The reasons for this are discussed and some indications of how improvements could be made are suggested. Since many of the potential advances are within the scope of current technology it is certainly feasible to achieve enhancements in performance by factors of two to ten across the blue to near-infrared spectral range. Higher improvement factors are implied but will be difficult to realize in the normal spectral range for wavelengths below 1 μm. Significant gains in sensitivity, and perhaps in response speed, will open many new opportunities for low light level sensors and the prediction is that they will be an enabling technology for developments in biological and medical applications, among others.

1. Introduction

The concept of making a light detector by using photon absorption to liberate an electron is scarcely a new idea. Indeed, the first demonstration of electron emission was by Hertz in 1885 [1] and the explanation of the photoelectric effect, in terms of quantization of photon energy, was made by Einstein in 1905 [2], for which he won the 1921 Nobel prize. Thus even a century ago, using bright optical signals, it was possible to measure a small current of emitted electrons. The exciting prospect offered by those very modest first experiments was that, by the same basic process, the sensitivity could be increased to detect light at very low intensity, down to the level of individual photons. In parallel with this power measurement is the opportunity to record images. Lower intensities required a means of amplification to turn the single electron into a usefully large burst of charge. In photomultipliers (PM) this is achieved via a cascade of secondary electron emission stages, called dynodes. Discussion of photomultipliers, their uses and future opportunities can be approached in terms of the advantages and/or limitations of the initial photocathode and of the amplification stage. The two aspects are in stark contrast. The theory and design of the secondary amplification stages are well understood. There are design variants according to needs of response speed and amplification gain but, although these can benefit from further refinements, they do not limit current usage. Cathode development is very different. The choice of materials, the methods of deposition and reasons for variability, as well as the physics of the process are far from clear, despite a large literature (as in reviews [3–8] and manufacturers documentation [9,10]). Consequently, the progress with cathode performance has been spasmodic and often empirical, with many conflicting views on the ideal composition of the cathode materials and how to implement improvements.

For completeness this review will briefly indicate a few of the many applications of photomultipliers and imaging detectors and present the current performance in terms of sensitivity, gain, response speed and wavelength coverage. This survey will also highlight some of the future uses that could be considered if the cathode performance can be increased. Since there are other types of detector, such as the CCD or semiconductor diode devices, the performance and advantages, or not, of these alternatives relative to photocathode detectors need to be considered for each application. In some situations, for example at high light levels, or for very long signal integration experiments, as in

Author's address: Engineering and Information Technology, University of Sussex, Brighton BN1 9QH, UK. E-mail: P.D.Townsend@sussex.ac.uk

Contemporary Physics ISSN 0010-7514 print/ISSN 1366-5812 online © 2003 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/0010751021000029606

astronomy, semiconductor items may be preferable. However, photocathode detectors are intrinsically far more sensitive at very low light levels for high energy photons (UV and visible light) and in some cases are used as image intensifiers before signal handling via CCD systems. Their inherent gain factor of towards 10^7, coupled with nanosecond response times, good linearity and a very large dynamic range guarantees that photocathode devices will be pre-eminent at low light levels for at least the next decade.

2. Current performance of photocathode detectors

The list of typical applications of commercially available photomultipliers and photocathode-based imaging detectors given in section 3 will underline the importance of this technology in an extremely diverse set of scientific disciplines. However, the prerequisite is the performance of the photocathode, and the key factors which determine it, both positive and negative, include the following. Cathode compositions have varied over the years and some examples of nominal composition are included in table 1, on which further discussions will be made in later sections.

(1) Spectral coverage within the range 200 to 900 nm is widely available from many manufacturers. Shorter wavelengths can be detected directly via UV-transparent windows to reach wavelengths down to $\sim$110 nm. Alternatively, photon energy conversion from UV to visible via a surface phosphor can be $\sim$30% efficient and this offers a lower price detector as a compromise against sensitivity loss.

(2) Sensitivity to light beyond $\sim$800 nm is poor. S1 type cathodes nominally operate to $\sim$1100 nm but are problematic in terms of reproducibility and sensitivity and need cooling. Very recently some detectors have been marketed with sensitivity in the near-infrared to wavelengths as long as $\sim$1.6 μm. These are likely to be improved as at present they have very low efficiency of less than one photoelectron per 100 photons, require cooling and are extremely expensive.

(3) A key factor is the quantum efficiency (QE) at the cathode. This monitors the photon-to-charge conversion, and is normally 20 to 30% at say 400nm, but it falls to a few per cent by $\sim$850 nm. The absolute values claimed from different manufacturers may differ but the broad pattern of behaviour is consistently as shown in figure 1. Note, however, that research papers indicate that values as high as 70% have been achieved.

It is not totally correct to compare cathode QE of *extracted* electrons with the higher QE values for *excitation* of electrons of semiconductor CCD type detectors (the latter values are much higher, particularly at long wavelengths). Instead it is necessary to consider total performance (i.e QE times amplification) and CCD devices suffer from minimal internal gain, whereas the cathode devices routinely have amplification from 10^6 to 10^7 within the detector, prior to any external electronic amplification. As a guideline the cathodes have the advantage for device output currents below about 1 μA. For a PM tube with a gain of 10^7 an anode current of $\sim 10^{-6}$ A represents a cathode output of $\sim 10^{-13}$ A, hence an input photon flux of $\sim 10^6$ photons/s. PM tubes are clearly preferable at lower fluxes but either type of detector is useful with higher light intensity.

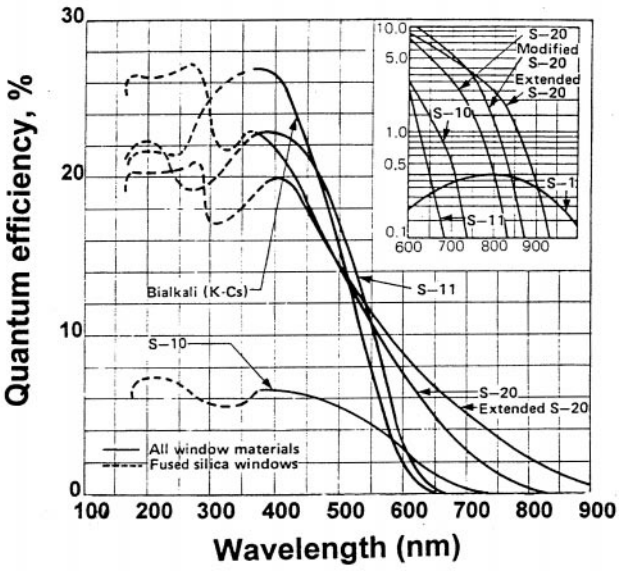


Figure 1. Examples of quantum efficiency for various types of commercially available cathode. Note that these are intended to show generic performance rather than precise detail. Research values can be higher but may be accompanied by relatively higher dark currents. See table I for compositional details.

(4) Cathode systems have a dynamic intensity range of almost 10^6 with only limited deviations from linearity (i.e. a few per cent). The direct current responses can operate quite linearly from the lowest light levels, which are set by the background dark current at values of nanoamps or less, and extend upwards for intense light signals, which can generate 100 μA. Continuous operation at the highest values may be more limited in some detectors. In the pulse counting mode the lower threshold range is more impressive since it is at the individual photon level. At the highest rates there will be limitations set by pulse pile up in the electronics of the counters, which require corrections to be applied. In more sophisti-

cated applications some experience is required to allow for minor variations in linearity and sensitivity related to variations in sensitivity depending on history of exposure to light, changes in temperature or electrical instability of the power supplies. Long-term stability of response and tube ageing are also factors which may need to be considered in specialized experiments, but in normal practice such variations tend to be ignored. Indeed the factors listed here compare extremely well with any competitive type of detector.

(5) In scintillation detectors the phosphor emission spectral characteristics can be matched by selection of the photomultiplier type. Standard response speeds for pulse detection from the 10 to 90% signal levels have time resolutions of 1 or 2 ns and specialized devices achieve times as brief as ~ 600 ps.

(6) Imaging detectors offer all the preceding performance but with the benefit of spatial information. They are designed to be gated on the nanosecond time-scale to provide imaging of fast events, as for streak cameras, or to record spectral data that change during chemical reactions or explosions.

(7) Modern detectors operate with in-built high voltage power supplies which now require only a low voltage power source. Tube sizes and geometries are very varied and standard catalogue options range from 12 mm (½ inch) to 300 mm (12 inch) diameter. Square or hexagonal designs exist for close packing. The perception of photomultipliers as large devices with high voltage power supplies is thus somewhat dated. Even larger area coverage can be achieved with an assembly of detectors. An extreme example was the assembly of the Kamiokande neutrino experiment with an assembly of 11 000 photomultiplier tubes of 500 mm diameter. At $3000 per tube this is expensive, and the investment cost was underlined by an accident in 2001 which destroyed some 7000 tubes. Nevertheless, the scientific importance of such a detector array is indicated by the continued confidence for a planned Super-Kamiokande detector, with 20 times the capacity of the original.

(8) Imaging detectors include comparable cathode materials and sensitivity found in PM tubes but they retain image information. The ability to gate the recording gives freeze frames of very fast events (i.e. ns resolution). The spectral range can be confined to UV visible, near-infrared or broad band, but the details are lost in the signal processing, so there are not yet photocathode-based equivalents of colour CCD cameras. Since neither detector directly offers wavelength information similar filter patterning could be employed. The intensified image can be directly viewable by a phosphor screen, as in night vision devices, or processed by electronic or CCD routes to give quantitative spatial information. In some uses imaging tubes are used in luminescence spectroscopy and offer wavelength multiplexing of transient signals with high sensitivity by spreading the spectrum across the face of the input plane. A further high sensitivity luminescence example is with X-ray imaging from very low dose irradiation of patients. The potential uses for cathode-based imaging tubes far exceed current applications, in part because they have been overlooked since CCD systems are so familiar and are produced at low cost, as well as being compact. However, higher sensitivities by factors of 50 to 100 are easily obtainable with current imaging tubes, plus higher speed response. The negative factors are size and cost which reduce mass-market usage, but not necessarily state of the art or specialized applications.

There are also a number of designs which give limited spatial information. These are not adequate for picture type imaging, as they may only contain say 4 to 100 discrete detection areas, but obviously are beneficial in many types of photon detection.

3. Current applications of photocathode detectors

The performance descriptions indicate applications that exploit photocathode characteristics. In addition to academic research in spectroscopy, radiation physics, particle and high energy physics, the detectors are embedded in a host of commercial systems. Related spectroscopy of fluorescence offers detection of contaminants, including items as diverse as detection of plankton and water quality, assays for immunology, enzymes identification, biological and chemical tracers, isotopic ratios, and signals related to tagged cells as in cancer detection or biological studies. Direct emission during chemiluminescence and bioluminescence offer useful data even when the signal levels represent only a few hundred photons per second. Luminescence techniques provide powerful methods for archaeological and geological age determinations, as well as for detection of fake artefacts. To fully exploit the levels of discrimination the detectors can offer spectral and time resolution. The ability to go down to photon counting levels means the analyses may even be performed when the impurities or trace molecules providing the source signals are at the parts per billion level within a carrier target system. Equally there are many uses in forensics, chemistry and materials science.

Additional information is even more readily interpreted when it is combined with imaging techniques and examples includes robotic, military and high speed photography as well as variants of the simple power detection from PM tubes. Less obvious is that by using solar-blind cathodes (i.e those which respond only to UV light and are insensitive to

sunlight), one can view the world with extreme sensitivity for UV light sources. Examples here are detection of forest fires, electrical discharges from high tension power lines and clear imaging of the exhaust plumes from aircraft. Radar difficulties in sensing Stealth design aircraft can become irrelevant with solar blind detection. These examples demonstrate the value of a further role, which is the conversion of non-visible signals into visible ones in which UV, near-infrared or very low light level signals are intensified for direct observation on a phosphor screen. More quantitative data processing either from the CCD read out of the phosphor or, with a larger dynamic range, from position sensitive encoded detection of the charge arriving at the anode plane. The images are then displayed on a computer screen after data processing. In addition to images, the display can display wavelength multiplexed spectroscopic signals with inherent sensitive advantages for weak or transient signals.

Although many PM tubes have been in constant use for decades this extremely attractive operating life is not universal and not all PM systems are designed for a long and useful life. The shortest life expectancy is where they are incorporated in briefly operating missile detection vehicles. At the hundred hour life expectancy level are those PM tubes designed for oil well logging. Here the PM tubes are used as throw-away items. In this case a gamma ray source is included within the drill head and shielded from direct interaction with a PM tube and scintillator. Gamma emission into the surroundings cause backscattered Compton signals providing information on the surrounding rock and bore hole, which is detected via the scintillator plus PM tube. The changing signal intensities are used to monitor variations in geological strata and assist the directionality of drilling. The PM tube is specially designed to operate at high temperature ($\sim 150^{\circ}$C).

Improvement in the detection technologies will benefit all the existing applications with spectroscopic and luminescence uses in physics, chemistry and engineering, but one suspects the really major expansion will come in the fields of biology and medicine. For example there is a rapidly increasing literature which demonstrates examples of cancer detection by differences in intensity of emission from normal and malignant cells. Signals can be excited optically and measurements made *in vivo*. Skin and lung examples are obvious since they are directly accessible, or via optical fibres, but even sub-surface signals can be sufficiently strong to offer useful information. *In vivo* luminescence through the skull is possible at long wavelengths and differences between normal and Parkinson disease modified cells have been cited. The former examples imply cancer detection is possible at a very early stage: for example when it is at the millimetre size scale and when treatment is most effective. The brain luminescence signals offer a means of monitoring drug treatments. The weakness of these techniques at present is that many of the signals require not just total intensity measurements, but detailed resolution of emission spectra to highlight the cellular differences. Crucially the signals are often at the long wavelength end of the detector sensitivity. There is thus a far more major incentive to improve red and near-infrared detectors than those in the blue or green region. To place this in perspective a broad wavelength coverage photocathode will already absorb some 40% of the incident blue light, but less than 1 or 2% of the longest wavelengths in the working range. Therefore blue detector absorption can only be improved by a factor of ~ 2.5, whereas at long wavelengths the improvements are potentially of a factor of 50. Further gains are feasible in the efficiency of electron extraction. It is clear that with such a huge commercial market available, and a very large room for improvement, higher performance will follow in the relatively near future.

An alternative optical route for cancer detection is to use very short laser pulse excitation and pulse delay measurements. If the light is scattered from a buried tumour site then the time resolution offers positional information for the site, and with increasingly faster detection methods in the sub-nanosecond range there is the potential to identify tumours, e.g. in the breast, at a very early stage. Further, the method should be applicable to younger high density tissue and so extend the age range of screening methods.

Cathode development is a live activity since the photocathode detection is often the enabling stage for progress and market expansion. The alternative semiconductor imaging devices and detectors are attractive for stronger signals for reasons of cost, size, ease of operation, or particularly for longer wavelengths, superior performance. However, the combination of technologies can also be fruitful and for example there are considerable benefits in preceding a CCD detector with a photocathode intensifier stage.

Many of the applications and the design criteria needed for selection of the optimal PM tubes or imaging systems are discussed in the various manufacturers catalogues [9,10]. Indeed some of the literature is excellent and offered in great detail. There is no need to replicate here many of the discussions of topics such as the choice of materials for selection of window transparency, or alternative designs of dynode structure and their influence on pulse length and gain. Comments on changes in characteristics with variables such as temperature or light intensity are also mentioned in most cases. Perhaps, because this is a topic with a long technological tradition, the catalogues almost always offer considerable scientific insights while guiding the choice of detector selection. Of particular note are the books that were produced by Burle and Philips (the latter is now available from Photonis) [9]. Some examples of photomultiplier tubes and an image intensifier are shown in figure 2(*a*).

Figure 2. Some examples of photomultiplier tubes and an image intensifier. Larger or different shape tubes also exist. Ability to see into the tubes emphasizes the lack of cathode absorption.

4. Methods of electron multiplication

Figure 3 sketches two classic types of photomultiplier structure. Figure 3(*a*) is a head-on detector in which the light arrives through a window and is partially absorbed in the cathode layer. When photoemission occurs, the extracted electron is accelerated across to a set of secondary electron emitters, termed dynodes. The photoelectron gains $\sim$100 V in energy on crossing to the first dynode, at which point the impact liberates several secondary electrons. In the sketch shown here the grids are in the so-called 'linear focus' geometry. This is a construction that is ideal for fast pulse detection or very large detector areas. In other cases different geometries of 'box and grid' or 'Venetian blind' are preferred. With careful geometric design, and some ten or twelve repeat stages each amplifying by $\sim$2 to 10 times per stage, the charge pulse at the end of the amplification stage contains around 10^7 electrons resulting from the initial single photon event. Figure 3(*b*) shows a variant of this system for a reflective cathode where the light enters the vacuum chamber to impinge on a cathode within the tube. The amplification process is then as before. Advantages in this case can be lower construction cost and thicker cathodes, which are in a reflective mode that boosts long wavelength performance.

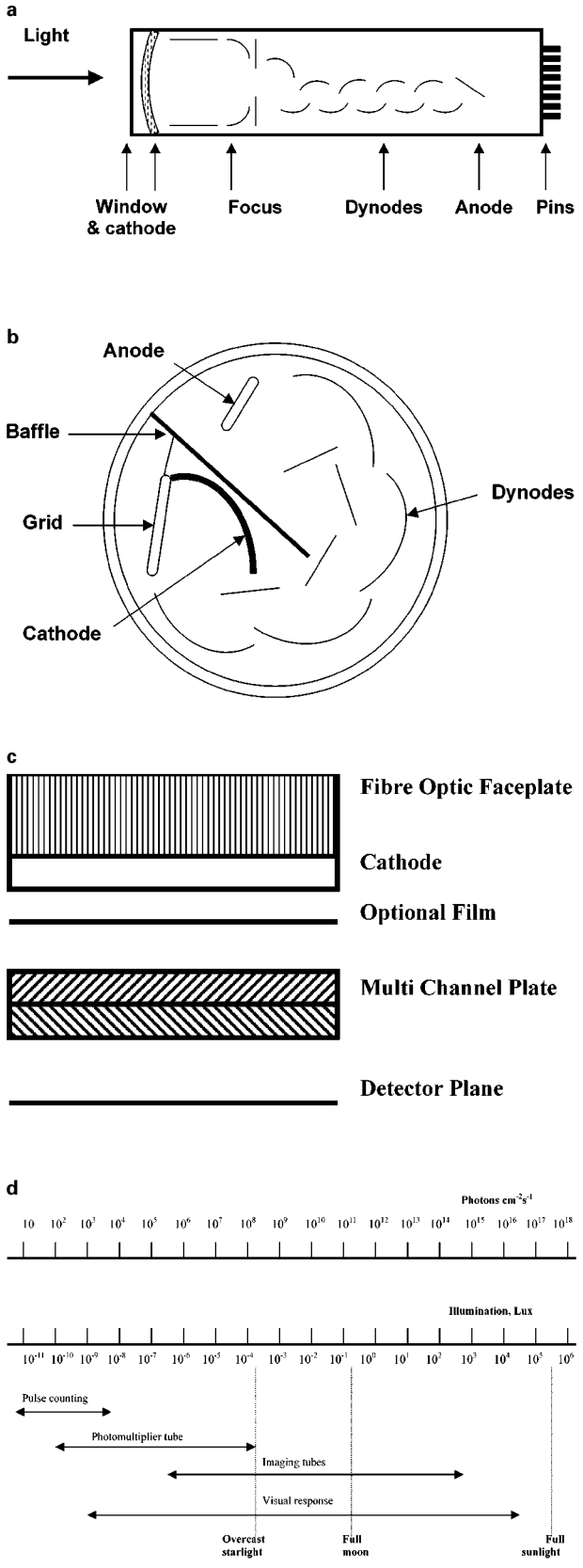
The design of the geometries must include efficient secondary electron transport and a tight time resolution of the output pulse. Transit times within the dynode stack are normally sub-nanosecond and the pulse width for a single event is on the order of a nanosecond. Because the gain arises from repetitive random secondary electron events there is always a range of pulse heights of the charge pulse corresponding to a single input event. Statistics of this are well documented and designs can optimize single electron events (SER). This is crucial for particle detectors since different energy particles generate different quantities of light in the scintillator in front of the cathode. The varying numbers of simultaneously generated photons thus give characteristic pulse heights and the method is routinely used in energy discrimination.

Less obvious features of the design of the dynode stack are the need to minimise gas desorption which can be accelerated back to the cathode and give an afterpulse signal. Particularly with large charge pulses there can be light generated within the dynode stack and again this must be blocked from reaching the cathode. Further design considerations include the use of materials which do not have radioactive elements that trigger false signals (e.g. no ^{40}K in the glass), and reduction of static charges on the glass or insulating sections of the tube. Magnetic screening is equally important since the electron trajectories are readily distorted. Basically, however these problems are well recognized and dynode designs have been engineered to cause minimal problems.

There are equivalent difficulties in detail in microchannel plates (MCP) in imaging tubes. Imaging tubes, e.g. figure 3(*c*), include replacement of the dynode stack by microchannel plates where the inner surface of each microchannel is coated with photoemissive material and the electron cascade emerges from the end of the channel. One major advantage of this feature is that the electric field between cathode and microchannel plate is so strong that any photon image information of the cathode can be maintained in the electron pathways through the channel plate. Signals may be extracted either as a viewable image on a phosphor detector, or as positional information on patterned, or resistive multi-anode structures. Image information is obviously valuable in many uses and is available with highly sensitive imaging performance. To gain a perspective on this, we need to recognize that light levels of overcast night are too bright for such detectors and images are obtainable with input light levels of as few as 10^4 photons/s. For visible light this is at a power level of $<10^{-14}$ W, (i.e. some 10^{10} times less than full sunlight). Figure 3(*d*) includes a reference scale to offer some conception of photon density, power and visual sensitivity. The scale is a guide for visible light levels.

In the MCP there is a further problem that charge depletion of an individual tube during a pulse causes a recovery delay time which decreases the channel response. In normal imaging this is unimportant but in spectroscopy, where a spectrum is spread across the image plane, sharp line features on a weak background may be distorted in intensity if they saturate individual channels.

Progress with imaging tubes contains several contradictions. Since they are considerably more expensive than PM tubes they have a more limited range of markets. Also they were initially developed some time after the advent of PM cathode devices. Nevertheless, their value in low light level imaging has obvious military and surveillance



implications. In about 1965 the value of their sales was comparable with that of PM tubes and has continued to rise rapidly to be three or four times greater at £150 to £200m per year worldwide. The impetus came successively via rifle night sights, tank driver devices and currently with night goggles for all infantry. Despite this immense market government research funding mostly stopped in the mid-1980s. Hence the best commercial imaging tubes currently available have sensitivities which differ little from the research claims of the 1960s. In non-military applications improvements in sensitivity and wavelength coverage, as well as response speeds down towards tens of picoseconds, are being developed. There are also improvements with tubes now having a longer operational life at high performance. Such devices have a firm niche market which will probably expand, not least via medical usage.

5. Historical development of photocathodes

Photocathodes benefit from a 70-year development, but do so from a research base with only a broad understanding of the subtleties that define high cathode performance, or indeed the choice of cathode materials [3–8]. There has been progress in selection of cathode composition but this has been stepwise by introduction of new compositions, followed by refinements, rather than a continuous steady progress. In this respect cathode development differs significantly from optical detectors using semiconductor technology (e.g. CCD cameras) where there is a far greater understanding of the processes, partly because the semiconductor field involves enormously more people, companies and commercial markets. Semiconductor developments have recognized, backed by investment, the essential need for intensive purification of materials, whereas for cathodes this is less appreciated although probably equally important. Exceptions are the III-V cathodes where the literature strongly underlines the benefits of extreme care in materials preparation. Details of different photocathodes will be mentioned later. In general there is always a conflict between the need to have cathode material which strongly absorbs light, but is

Figure 3. (*a*) Sketch of a head on, 'semi-transparent' photocathode arrangement with a curved cathode and linear focus geometry for the dynode stack. (*b*) Sketch of a reflective cathode (side window) photomultiplier (PMT) in which a thick cathode is deposited on a reflective metal backing. (*c*) Sketch of an imaging tube system with a fibre-optic faceplate and microchannel plate (MCP) current amplifiers. The method signal detection varies between direct visual read-out on a phosphor screen, alternatively via a CCD image of the phosphor, or direct electronic position information which is viewed after computer processing. (*d*) Intensity reference scales indicate the operational ranges of the detectors in terms of photons $cm^{-2}s^{-1}$ or illumination in lux.

sufficiently thin that electrons can be extracted. One factor which has not often been mentioned is that the skin depth (i.e. the penetration into a strongly absorbing medium) for light absorption in the cathode is strongly wavelength dependent. For short wavelengths, in a multialkali cathode, this is on the scale of 30nm for wavelengths below 400nm. Hence, although thicker cathodes may have value in increasing absorption for longer wavelengths, they automatically decrease the response for UV/blue light since electrons generated close to the input window may not reach the vacuum surface. An example of the theoretically estimated skin depth is given in figure 4.

Thin cathode films are inevitably resistive and this poses a problem for high light intensities over a large dynamic intensity range since there will be charge depletion and distortion of the signal intensity. There are similar problems with imaging tubes and intensifiers, particularly in the central region of the detector. Higher electrical conductivity is often achieved by metallization with a layer between the window and the cathode. However, the presence of the metal underlayer is only a partial solution as it will introduce strong reflections, and hence leave less available light.

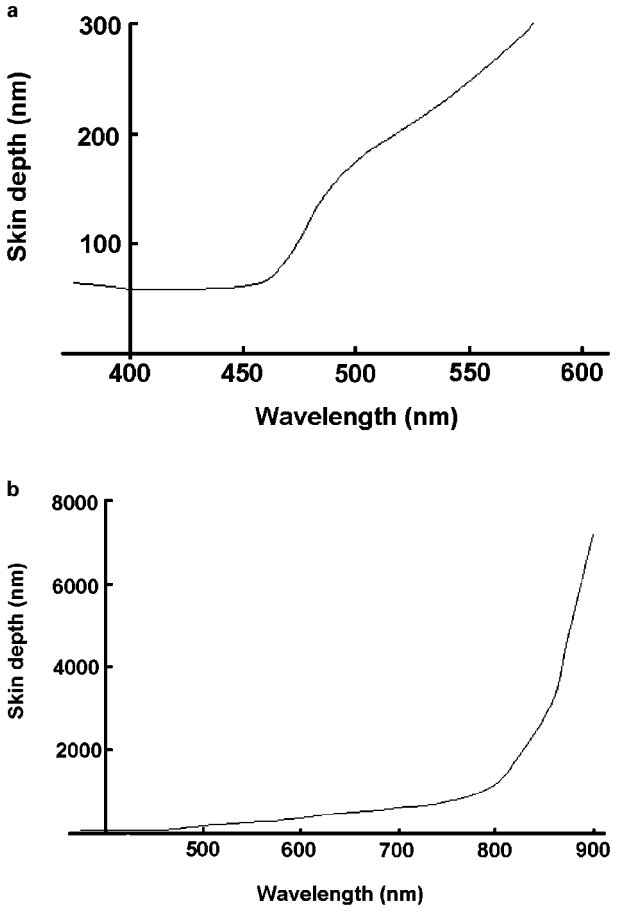


Figure 4. A calculation for a multi-alkali cathode on the skin depth for light absorption in an S20 tri-alkali cathode. (a) and (b) show different expanded ranges.

The final step of electron emission implies a low work function, and here guidelines from bulk materials characterized in ultra-high vacuum may be helpful, but definitely do not identify the real situations in detector systems. The materials which are suitable for photon absorption and electron excitation may not be ideal for electron emission. Hence either a compromise or a modified surface layer is needed. The route to the 'choice' of component materials is intriguing. In a 1993 review [7] one of the pioneers of cathode design, Alfred Sommer, wrote that in the first 40 years of cathode development there were six main cathode types found by persistence, inspiration and luck and one example based on physical concepts.

A fundamental monitor of cathode performance is the quantum efficiency (QE), which is defined as the percentage of ejected electrons per incoming photons. Pursuit of this art of cathode preparation has been likened to cookery, in that the ingredients are known, but variable, and the processing and final product is highly subjective. Similarly, mass production techniques may result in consistency but lack the quality of the best from cordon bleu kitchens. Initial cathodes started from QE values below 0.01%, but in $\sim$1930 a cathode which included silver, oxygen and caesium (called S1) could sometimes be processed to yield the unprecedented QE of $\sim$0.5%. Inclusion of caesium is sensible since it has the lowest work function of the alkali ions, whereas Ag seems a far less likely candidate since it has a much higher work function. In hindsight, the silver and oxygen may well be associated as metallic nanoparticles with an oxygen and/or caesium coating. Even after 70 years the S1 cathode is still interesting as it has an unusually long wavelength response, but the drawbacks with it are that processing is still not well understood and the performance can change dramatically after exposure to light. The erratic changes in behaviour may be linked to optically driven combination or disassociation of nanoparticles, in the same manner as silver halide particles respond in the photographic process. These S1 PM tubes are highly individual, and random response changes by a factor of 200 have been noted from the same cathode during the course of one day! It is necessary to cool the tubes towards 77K to suppress the thermal emission for PM usage. The cathodes played a crucial role in night sight imaging tubes or photographic dark rooms where a low level image, or one in the near-infrared, is intensified onto a phosphor screen. The items are still available, although no longer manufactured. In terms of understanding, S1 is a disaster, since the details of the process are still purely at the speculative level and the overall QE value has scarcely been changed. The real advances in cathode performance have instead come by introduction of alternatives.

The various manufacturers differ in detail with their cathode compositions, the precise methods of deposition, the sequence of coating steps needed to build up the final cathode, and the overall thickness of the layer. However, the net results do not differ dramatically, i.e. less than 50% between them for each generic type. Indeed, once a new cathode composition has been formulated, and proven to give consistent results with a particular spectral coverage, it appears to be very difficult to make significantly large advances in the efficiency. Comparisons between the catalogues of the late 1960s and today show only small changes for equivalent cathodes. This is not a criticism of the manufacturers, but instead reflects the complexity of the problem, and the fact that much of the deposition process is a matter of judgement and experience. With a multi-parameter process, an acceptable performance is often preferable to an optimum value (i.e. if it is marketable and reproducible). The catalogues cite typical and average photomultiplier sensitivity, with 'average' being in the upper quartile of tube quality. Minimum and typical values can differ by a factor of two, but there are always indications that with better control even higher performance cathodes can exist.

The contrast between photocathode advances and those in computing and information technology are apparent from the time dependence of the advances. Trends are often estimated on the basis that there is some inherent law (as noted by Moore) for a systematic rate of growth of signal capacity, or computer speed, etc. with time. For PM cathode QE one can also seek such a trend, albeit with less well-defined data (table 1 and figure 5). If one uses the spread of QE values from various manufacturers, then a plot of QE versus year visually confirms the impression of progress up to the present. However, the data differ significantly from those of the semiconductor progress graphs. For cathodes the advances are by the introduction, often fortuitous, of new cathode types. For each of these new generic types there are then only small improvements over the following years as the processing methods are honed. Nevertheless, over the last 25 years the performance of each type has rarely moved above the original spread of values.

Precise comparisons are difficult since there may also be changes in thickness of the cathode layer and small compositional changes are still described by the same generic name, or gains have been added by other factors. Examples include the use of curved cathodes, sand blasted, roughened or pyramidal cathode surfaces. Each of these

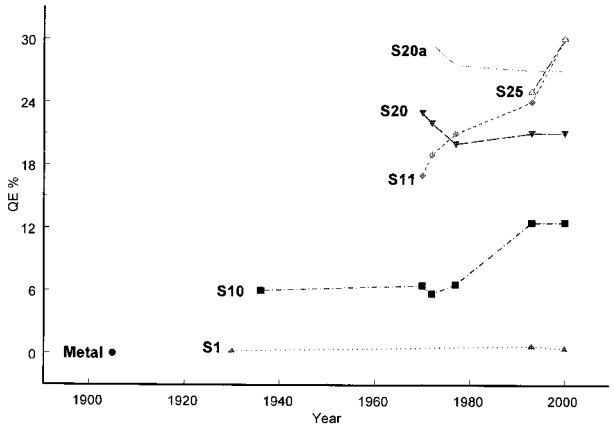


Figure 5. Published peak quantum efficiency values claimed in catalogues for different types of commercially available PM tubes as a function of time.

Table 1. Examples of compositions of photocathodes.

Cathode	Composition	Wavelength coverage, nm	Comments
S1	Ag-O-Cs	300–1100 300–1200	Low QE, but wide spectral range, noisy unless cooled to 77K, often unstable
S10	Ag-BiO-Cs	300–720	
	Na-K-Sb*	300–700 140–600	Modest QE peak ~15 to 18% but will function to 175°C
S11	Sb-Cs	300–720	An early cathode of modest performance
Bialkali	Sb-K-Cs*	300–680	Low thermionic emission. Peak ~26%; 70 μA/lumen
	Sb-Rb-Cs	300–700	110 μA/lumen
S20	Na-K-Sb-Cs	300–900	Peak ~23 to 25% near 400 nm and ~0.4 to 1% at 800 nm
S25	Extended S20	300–930	Peak <20% near 400 nm but ~1.0 to 3.5% at 800
Solar blind	KBr, CsI, RbTe, CsTe	Various limits <400 nm	All insensitive to visible light. UV peaks near 12 to 15%
III–V	GaAs, GaP, etc.		Composition defined limit into the near-infrared with alloy compositions, maximum ~1700 nm

*Indicates good scintillation detector compatibility.

features can offer small improvements. Inclusion of these ideas is helpful as it maintains the overall trend of a steady growth pattern, but the main conclusion to draw from figure 5 is that there is minimal systematic progress due to a detailed understanding of the technology. Rather, in the past it has advanced in sudden jumps resulting from persistent searches for new cathode materials.

Note that the curved cathodes improve electron collection efficiency and the non-planar features take advantage of the higher absorption for light which is incident at non-normal incidence. Merely introducing the light at non-normal incidence into a planar window does not always lead to any improvement, since a higher fraction of the light is reflected which offsets the improvements in absorption. The standard normal incidence to the window and a roughened or structured cathode design does provide greater energy transfer to the cathode. The methods used so far are certainly not optimal and the potential benefits are displayed in figure 6, which details the calculated absorption as a function of wavelength and cathode thickness for two examples. The first is for 442nm light on a bi-alkali cathode and the second is for 700nm light on a multi-alkali material. The details are highly sensitive to polarization and wavelength [11–13]. The theoretical predictions of improvement have not always been used to optimize the practical design, as for example the pyramid structures use an angle near 45 degrees which offer negligible gains for the bi-alkali example at 442nm and just a few per cent enhancement for the 700nm example. Instead, the design aims to benefit from reflected light which hits the second pyramid face before being reflected back from the cathode. Note that, except for laser beam signals and examples in high resolution spectroscopy, most light sources include a wide angular spread which decreases the structure advantage discussed here. Nevertheless, the next generation of cathodes are being designed to exploit the improved absorption rather better.

Understanding and modelling can definitely contribute to predictive progress, and this is most evident for the III-V semiconductor cathodes. Cathode composition is exploited to vary the spectral range, and by careful deposition growth and composition, to build in internal fields which aid electron movement towards the emissive surface. The methods discussed include alternative processes. The first is to vary the band gap of the III-V layers. A second approach is to have high internal fields of 10^6 V/m which lift electrons into higher valley conduction bands. Such layers are termed transferred electron (TE) cathodes. An impressive TE example derived from such deposition control [14] is the move to the newest family of cathodes [10] which were first reported some ten years ago [15] that are designed for operation out towards 1.6 μm.

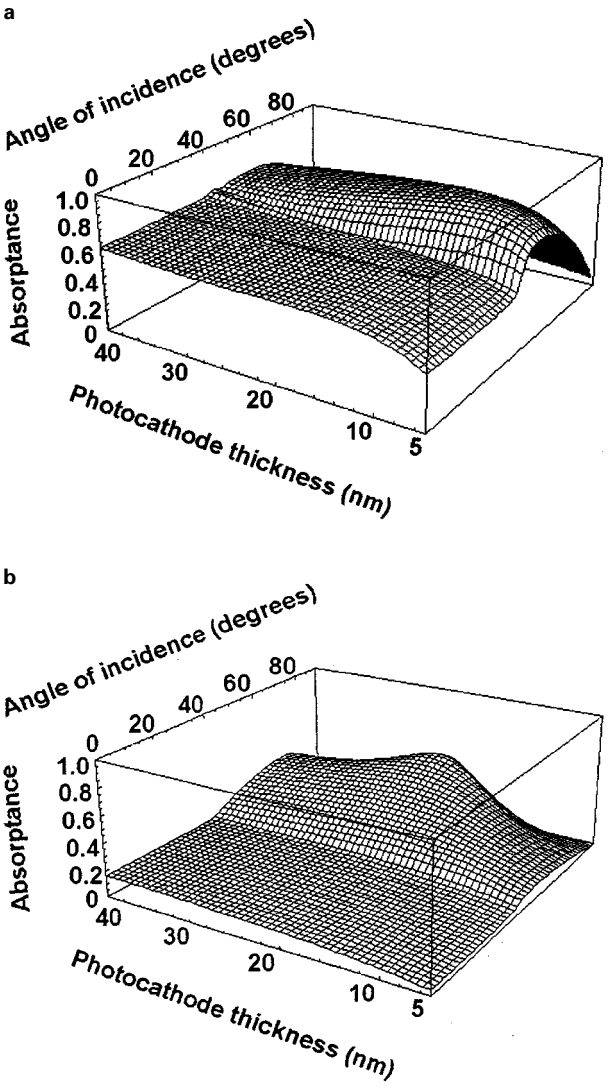


Figure 6. The absorption, averaged over polarization, as a function of angle and cathode thickness for (*a*) 442 nm light on a bi-alkali cathode and (*b*) 700 nm light on a multi-alkali layer.

6. Negative electron affinity

The final concept is to have band bending resulting from doping of the surface and this is often referred to as negative electron affinity (NEA). Details of NEA designs have been discussed in detail for 40 years [16, 17]. The increase in efficiency for electron escape does not significantly alter the form of the QE curve but there is enhancement and a consequent extension of the long wavelength response. Examples include silicon, III-V and multi-alkali cathodes. The normal situation is modelled in terms of a p type semiconductor and electron attraction at the vacuum surface. For the silicon and GaAs examples the internal fields may extend a few tens of nanometres. The key work in development of III-V cathodes is described in the patent by George Antypas [17]. An example of a

possible structure is sketched in figure 7. Note that in this example the cathodes are first grown on a high quality crystalline substrate with variations in composition, and then bonded on to the cathode window. The choice of a 7056 glass for bonding was fortuitous since it was one of the first trials and one of the few successful window substrates. Note removal of the bonded layers from the growth substrate is required. The technology is thus much more demanding than the simple evaporation methods of the alkali layers deposition. Figure 7(*b*) offers one view of how the changing compositions could cause electron transport towards the vacuum interface. It should be further noted that the layers are very thick compared with the multi-alkali examples and hence there is a need to have very long electron transport (i.e on the micron scale). Similarly, suppression of the loss of electrons at the bonded interface is crucial. Each of these factors places major demands on the fabrication in terms of grain size and purity. There is a consequent reduction in response speed which is a problem in rapid signal detection or gated and streak cameras, but not for imaging purposes.

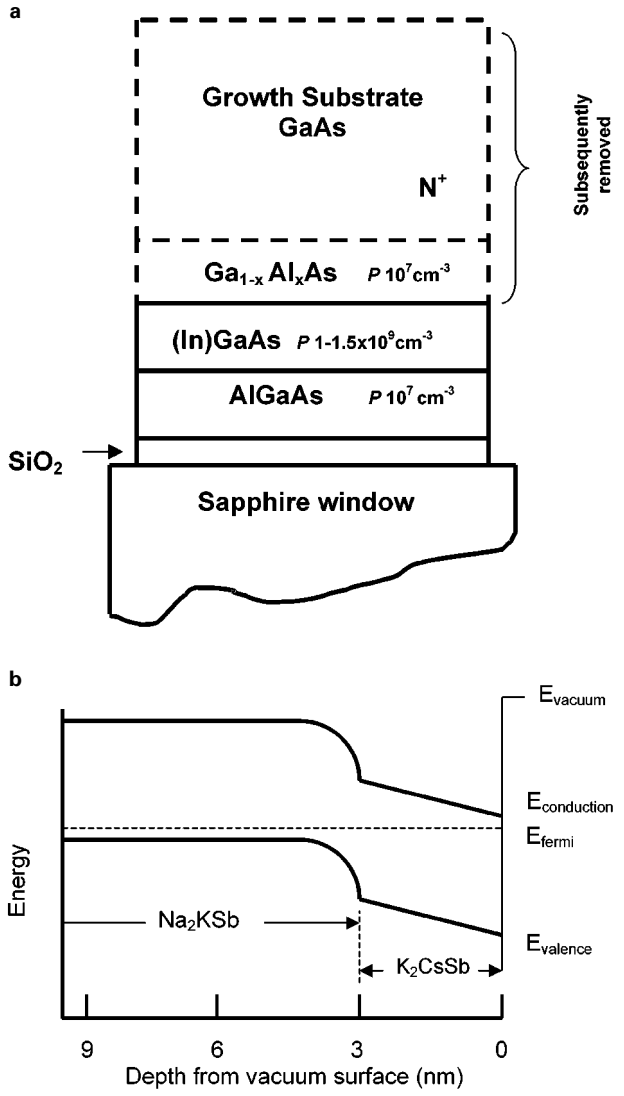


Figure 7. (*a*) Sketch of layer construction used in the development of negative electron affinity cathodes. Growth substrate is sacrificed after bonding. (*b*) Conceptual band picture for a multi-layer cathode with a thick caesiated layer near the surface.

The design of the non-commercial examples of modified cathode geometries, or those with light confined by waveguiding in the windows, will be discussed later. Mostly they have the objective of increasing the energy transfer to the cathode, either by multiple interactions or by higher angles of incidence. As indicated in table 2 the performance of these research photocathodes, or those enhanced by waveguiding, is often very impressive and of considerable value in fields such as spectroscopy and luminescence when the signals fall in the long wavelength end of the cathode response. Note in particular that the gains from the guiding are obtained without any increase in the dark current from the tube. Re-invention of the basic idea seems to have occurred in bursts from $\sim$1960 to the present [18–20] but has not been included in generally available commercial detectors.

Returning to the history, real progress came at the end of the 1930s when cathodes were made with antimony and caesium, and then with Ag, Bi, O and Cs, or later with a range of alkali combinations. These various mixtures gave peak QE values up to 20% or more. Measurement of temperature dependence of thermal emission and the position of the long wavelength response limit (figure 5) suggest that there was a work function of much more than 1 eV. Thus thermal electron emission is inhibited at room temperature and the PM tubes are functional without any special cooling. By contrast, the long wavelength devices made from multi-alkali mixtures (S20) introduced by the 1970s have a lower escape energy of $\sim$1 eV and so must be cooled below room temperature to minimize the thermal 'dark' current from the tube. A summary was given in table 1 in terms of cathode type. It must be recognized that the same type name can include a range of variants, both deliberate and fortuitous. Catalogues may imply two distinct types of cathode are specifically fabricated, but production is labour intensive, and so post-production selection is often used to define for example whether a tube is an S20 red, or an extended red, type. In fact many tubes fall between the 'typical' limits.

7. Quantum efficiency

The QE values offer a fundamental insight into the photoelectric process but for many applications a more convenient description is termed radiant sensitivity and this is defined as $E(\lambda) = \lambda\ QE/1.24$ mA/W, where λ is the

Table 2. Examples of peak quantum efficiency and wavelength limits.

Year	Wavelength limit	Maximum QE	Generic tube type
Pre 1930	UV/Blue	$<0.01\%$	Metals
$\sim$1930	1050 nm	$\sim0.1\%$	S1 Ag-O-Cs
$\sim$1936	650 nm	~5	S11 Sb-Cs
1960s	740 nm	~6	S10 Bi-Ag-O-Cs
	600 to 750 nm	~15	S11, S13 Bi-alkali
	850 nm	20–25	S20 Multi-alkali
1980s	920 nm	$\sim30-60$	III-V materials
late 1990s	1600 nm	~1 (at 1600 nm)	TE designs, operable only at very low temperature
Non-commercial examples cited in the research or patent literature, or unpublished			
1960 onwards	Improvement in blue to red from 2 to 10 times, i.e. effective QE values above 50% in the blue		Optical waveguide windows, either existing or redesigned
1960 onwards	Improvements up to 1.5 to 5 times for wavelengths from 400 to 900 nm		Modified and structured surfaces
2002	$>100\%$ in the UV if several electrons per high energy photon $>45\%$ out to 900 nm for idealized novel structures with high grade S20 cathodes		Theoretical QE performance (i.e. not necessarily realizable, but indicating there is much room for improvement)

wavelength in nm. Similarly, rather than define the QE wavelength performance for each tube the convention is to use signal output sensed for standard light sources and broadband filtering (of primarily visible light). The values are quoted in amps per lumen and they offer a useful single parameter guide to performance. For red sensitive cathodes additional filter information is needed. The performance numbers are most variable for the red tubes and a supplier may cite 'typical' cathode values as 200 μA/lumen, with second grade tubes down to 120 μA/lumen, but selected premium tubes will exist to say 280 μA/lumen. The immediate challenge is thus not to find new 'magic' cathode compositions, but to quantify and consistently form those that match the current best at all wavelengths. Reflective mode tubes can provide higher performance from some manufacturers and values of 350 to 550 are offered for S20 or III-V cathodes. Note even these values are still less than the best research examples with numbers as high as 700 μA/lumen being mentioned for multi-alkali examples [21]. Detection with III-V cathodes, particularly with NEA design, as used in both imaging and PM tubes, have frequently been cited since 1971 with values of 2000 μA/lumen in research demonstrations. The problem is to translate these performance figures into mass production commercial detectors. As will be discussed below, there are several factors which limit the overall performance, so 100% conversion efficiency from photon energy to emitted electrons is unrealistic, but research data clearly indicate improvements of cathodes are feasible. The manufacturing and economic problems must also be considered for commercial detectors.

It should also be recognized that many routine applications prefer room temperature use and this results in a compromise between QE and dark current since the cathodes which have high sensitivity generally have a much higher dark current. So at room temperature the signal to dark current is worse for the more sensitive cathodes. In research applications cooled PM tubes are more standard so availability of higher performance tubes would be welcomed.

8. Key factors in optimizing cathode efficiency

To optimize the efficiency it is necessary to satisfy at least five key conditions. The first, reflection loss, is clear cut, but discussion of the next three factors is more confused as they are not independent parameters. Hence their objectives will be listed.

(i) The first problem is to maximize the window transmission so that incident light should not be absorbed by the window material and there should be minimal reflectivity either at the outer window/air interface or at the window/cathode junction. Transparency limits are set by the band edge of the window, and at longer wavelengths by colour centres, or from impurities or defects created by UV or ionizing irradiation. References [9] indicate transmission characteristics of amorphous and crystalline materials used in the detectors. The range of materials is limited by exclusion of materials which are brittle, hygroscopic or reactive, or which cannot withstand the high vacuum, thermal bonding, or cathode chemistry of the tube formation, or those materials containing natural radioactivity (specifically potassium). For visible light silicate glasses are economic and well matched for the tube housings. In the UV silica is preferred and in principle transmits to $\sim$160 nm, but sapphire is also used. For deeper UV, to about 110 nm, then MgF_2 is chosen. In all cases there is always

a reflection loss from the dielectric to air interface defined by the refractive index (n). The reflectivity with respect to air for the non-absorbing region is $R=((n-1)/(n+1))^2$ and since the indices of silica or sapphire are near 1.5 or 1.77 in the visible region they give reflection losses of say 5 to 7% (and greater in the UV). The surface reflectivity problem is worse for fibre-optic faceplates in imaging tubes since the fibres are often variants of heavy metal fluorides with higher refractive indices as high as 1.79. For specific and limited applications these values can be reduced at selected wavelengths by addition of an anti-reflective coating layer. Broadband anti-reflective performance is more difficult although in principle it can be predicted theoretically via sub-wavelength patterning (often termed moth eye). Realization of the relevant patterning for short wavelengths is not, however, an economically simple process.

The internal interfaces are more problematic as they will either be between the glass and an absorbing dielectric coating such as the alkali or semiconductor cathode film, or a metal intermediate layer (added to give rapid response times, or high brightness linearity). For a semiconductor example with a real part of the refractive index between say 2.3 and 3.6 the reflective loss rises to 30% or more. Perfect anti-reflection coatings are no longer an option since the imaginary part of the dielectric constant induces a small residual reflection. This is a very small percentage of the incident light and the more crucial problem is that any anti-reflection design must be made at the window interface prior to cathode (or metal) deposition. The materials of the layer must equally be compatible with the tube manufacture. Consequently this option does not seem to be used, despite the high signal loss from reflection. In the past reflection losses were treated as minor with solutions which were not cost-effective, when compared to the poor QE of the cathodes. With better cathode design this is a problem which will need to be addressed, and will be worth the effort.

(ii) Ideally 100% of the photons should reach the cathode and be absorbed, and as already mentioned, this implies neither reflection nor transmission losses.

(iii) Every excited electron should be promoted to a high level in the conduction band and move unhindered through the cathode material to the vacuum surface.

(iv) All the excited conduction band electrons should arrive at the surface in energy states above the vacuum level (i.e. their energies should exceed the work function for escape from the surface).

(v) Finally, in the absence of light there should be a negligible number of thermally excited electrons in levels which can escape from the surface. For cathodes which only respond to high energy UV/blue photons this is not a problem, but for cathodes which operate out to long wavelengths this is still a serious factor, even when using cooled cathodes.

The problems of compromise between the requirements of (ii), (iii) and (iv) are obvious. Pure metals are not suitable as cathode materials since, while thin metal films offer very strong absorption they do so with high reflectivity. Also the presence of many electrons within the conduction band contributes to multiple scattering, which reduces the energy of electrons excited by photons and so minimizes the probability of escape. Even pure metals with a low work function, such as the alkalis, have QE values below 0.1%. Insulators are at the other extreme of possible materials, and as they have few conduction electrons, scatter is minimized, but absorption is only possible for energies above the bandgap. For UV responsive PM cathodes this is not a problem but it is progressively more difficult to maintain any useful QE in the visible or longer wavelength regions. The conclusion is that cathodes must be made of materials with semiconducting type properties. Surprisingly the 'semiconductor' compositions for the semi-transparent (end on) window cathodes are predominantly alkali metals and antimony. The conflict is that to satisfy condition (ii), strong absorption at long wavelengths, the cathode thickness must be increased (not needed for UV/blue light where the skin depth is small). This is achieved at the expense of fewer electrons being successfully transported to the emissive face, condition (iii). For the S20 cathodes, made of a tri-alkali mixture and sensitivity out to >800 nm, nearly 90% of the light is transmitted. Figure 8 shows the calculated absorption and transmission values determined from the dielectric constants of S20 photocathodes as a function of cathode thickness. In practice red sensitivity is bought at the price of lower blue QE since the UV/blue photons are absorbed at the window side of the layer and the excited electrons cannot reach the vacuum surface. The problem is reduced for reflective mode cathodes since the thickness can be increased and the layer deposited on a reflective metallic substrate. In these cases the S20 QE values at say 800nm rise from ~ 0.25 to $\sim 2.5\%$, but again the current loss of response in the UV has been accepted (perhaps incorrectly) as a necessary compromise.

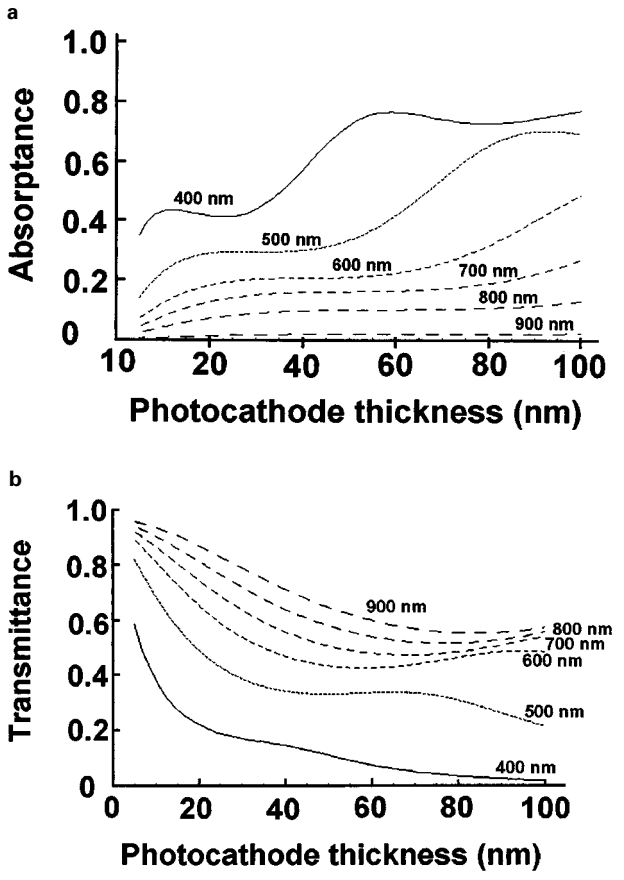


Figure 8. Calculated absorption and transmission values for S20 cathode material for selected wavelengths as a function of cathode thickness.

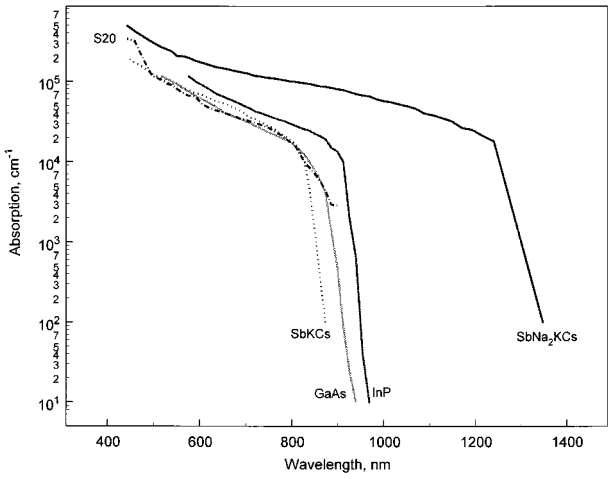


Figure 9. Examples of cited absorption coefficients for alkali and III-V type cathodes. Note the values are subject to the method of determination and are tube dependent. The data labelled S20 were derived from dielectric constants.

9. Cathode deposition

Having selected the materials of the cathode, and the thickness, there is no freedom to increase the intrinsic absorption. By using the III-V semiconductor alloys strong absorption, high electron mobility and long escape lengths can in principle all be maintained, even for long wavelength photons. Figure 9 indicates that, while there are minor differences in shape of the absorption curves as a function of wavelength, the alkali cathodes may have higher absolute absorption and possibly a more slowly falling tail beyond the effective band gap than the III-V based cathodes. Note that derivation of cathode absorption data is not unequivocal and the figure shows values from two sources for the S20 composition. Despite the higher absorption values claimed for the alkali cathodes the reality can be that the QE values for III-V compounds may still exceed those of the alkalis, and various cathodes of the same generic type have very different long wavelength cut-off values. Thus absorption is only one important factor.

The differences may be resolved by considering item (iii). Not least because this is a factor over which there is some control and which shows positive response to careful cathode production. Long-range electron transport within the cathode film implies minimal losses in energy from scattering with other electrons, interfaces or defect and impurity states. Automatically this means that the greatest mobility is to be expected within large single crystals of 'perfect' homogeneous composition which are free of stresses and grain boundaries, etc. Indeed this seems to be the case and is one reason for the use of the III-V materials. With careful control of the deposition conditions simple semiconductor compounds such as GaAs, or related III-V alloys, can be grown to give high-quality large-grain regions. These are still normally below the quality obtainable with molecular beam epitaxy in ultra-high vacuum, but they clearly demonstrate that for optimum electron transport this is an essential factor. The III-V growth control is well advanced and so it is possible to vary composition during growth and build changing band gaps which introduce internal fields that drive electrons in a preferred direction towards the vacuum interface. Such improved performance is gained by taking considerable care during slower cathode deposition, and major improvements in the quality of the vacuum systems, growth control and initial purity of the components.

By contrast the alkali/Sb-based compositions have developed from the simple evaporation techniques of the 1930s. They are rapid and involve several alkali species, as well as Sb which can be deposited in a wide range of compositions. Although there are specific crystalline phases, such as Na_2KSb, they are unlikely to be homogeneous. Indeed composition is actively changed during

deposition and some producers commence with extra Na_3Sb at the glass interface. Further, they will tend to form small grains with alkali contaminants and anti-site alkali ions etc., all of which contribute to electron scatter. The discussions are made in terms of semiconductor properties of the cathodes but, relative to normal semiconductor technology, the care taken is extremely low and the number of resultant lattice defects and electron traps is high. The weaknesses in performance are therefore not surprising. While it is conventional to discuss a photocathode layer of total thickness, say 30 nm, this disguises the fact that the material is built up in many steps of different alkali and antimony composition. Hence within the 30nm may be 20 processing steps and so 'long-range' uniformity will be on the scale of perhaps 20 monolayers. Coupled with this are problems that the source materials are not of the purity expected in the semiconductor industry, the vacuum during deposition is definitely poor, and in many cases it is deliberately altered by addition of oxygen (or other gases). The net result is a set of layers with many interfaces in the direction normal to the plane of the cathode. In solid state terms this suggests there will be considerable electron scattering and potentially a severe limitation on the density of states causing inhibited electron movement towards the vacuum interface (i.e. the layer may behave as a two-dimensional solid). Such inherent design difficulties are ignored in many of the theoretical discussions of the possible alkali compositions and the simulations of band predictions. Overall, the electron transport in the multi-alkali cathodes is unlikely to ever match that in the III-V material.

The scale of the electron mean free path in the S20 cathode is obviously not much greater than the cathode thickness since increases in the layer thickness beyond about 30 nm (i.e. to increase red absorption and QE) reduces blue performance. For the 'head on' transmission mode cathodes the drop in QE for the blue end of the spectrum is caused because the strong absorption initiates the photoelectric effect close to the input window, rather than uniformly through the layer. The implication is that a typical path length for excited electron escape is on a comparable scale to the cathode thickness. Values measured for different thickness multi-alkali cathodes as a function of wavelength [5] indicated variability by factors of greater than three times between cathodes of different thickness and short wavelengths and there was stronger wavelength dependence at long wavelengths. The thickness variations influence the grain size and might partly be related to the problem of a limited density of states for a thin cathode. The observation of lower escape lengths for long wavelengths is consistent with higher energy photons promoting electrons to high conduction band states, hence despite scatter losses the travel would be greater before the electrons sink to levels below the escape conditions. The arguments all indicate that greater cathode uniformity and larger single grain crystals could improve the transit of electrons within the cathode. Whilst transmission mode cathodes are essential for many applications (e.g. from scintillators to imaging tubes) it is surprising that there has been less interest in solving the cathode deposition problems of reflective mode cathodes for broadband detectors with long wavelength response. As already mentioned, the dark current is a factor of concern and without cooling many high QE tubes have an unacceptable high level of dark emission.

At first sight it might appear that the UV/blue quantum efficiency is already quite respectable (i.e. values of $>25\%$). However, there are several measurements from diode cells [22] or pulse height distributions [23] which indicate that many photons of high energy generate not just one, but two or more electrons per event. Energetically this is likely since, assuming a long wavelength limit of say 920 nm (1.34 eV), then for wavelengths less than $\sim$460 nm there is sufficient energy for electron pair generation, and three electrons for wavelengths below 306nm. Note that in early photoelectric data for alkali metals the number of electrons increased significantly with deep UV illumination (e.g. with QE rising from $<0.1\%$ to $>10\%$). If such multiple electron events form a significant fraction of the total excitations then there is the potential to have an apparent QE value well above 100% (i.e potentially 300% in the UV end of the spectrum). The current complacency that the cathodes are performing well in the UV may be ill founded and greater care in reducing electron scatter could give considerable improvements in performance.

10. Electron emission

The final role of the photocathode is to emit an electron. How this occurs is far from obvious. Reference to tabulated values of work functions clearly shows that alkali ions have the smallest values (all below $\sim$2.5 eV), and inclusion of surfaces such as Pd, Pt, W, Sn, Hg, etc. would be unfortunate since the values are well above 3.5 eV. The intuitive approach for 70 years has been to include Cs in the outer surface layers as this has the lowest work function for electron escape to the vacuum. There appear to be variations in the cited value. For an ultra-clean caesium surface it is near 2.4 eV, but is variously quoted near 2 eV in other determinations. As seen from the QE curves with wavelength many cathode types operate out to well beyond 620nm (i.e. 2 eV) and the S1 and some S20 cathodes perform, albeit poorly, to $\sim$1100 nm (1.12 eV) [21]. The experimental data show that the surface work function is modified. This can arise as a surface metal layer, by alloying between the Cs and

the multi-alkali cathode, and/or by further chemical interactions, most obviously from the presence of oxygen. The change in work function is not confined to alkali substrates. Data for clean cleaved GaAs and heavily p type GaAs with a monolayer of Cs show dramatic changes in photoemission limits, from $\sim$5.5 eV to $\sim$1 eV and the electron yield rose by $>$100 times, even at the high photon energies [14]. The standard model used to explain this advantageous reduction in the effective surface energy is to assume that because of the various impurities, and surface monolayers of Cs, plus the unspecified role of oxygen, the energy bands of the cathode are lowered at the surface. The net effect of the bent band model is that the difference between the top of the cathode valence band is now nearer the vacuum level. A typical sketch of the energy scheme is shown in figure 10, which suggests that the surface has to be positive relative to the cathode film and, in band model terms, the Fermi level position would best fit this for p type surfaces. This was a useful model 30 years ago to explain the low energy threshold for photoemission. It is now cited as though it has been proved, but in fact there is no clear evidence for the source of the near surface states nor even if a band model is truly appropriate. Modern views include complex thoughts on the role of grain boundary states. Caesiated GaAs, where a few Cs monolayers are thought to act as a metal, can result in specific electron emission of a single spin state. Despite the fact that there is an extensive literature on the role of caesium and oxygen for NEA, and a reduced work function on multi-alkali and GaAs substrates, there are still disagreements and uncertainties as to how the sensitization is effective. It is certain that for GaAs the emission is strongly crystal face sensitive, with the {111B} face having an escape probability as high as 50% [24, 25]. A monolayer of Cs is effective but efficiency decreases with further layers. Adding oxygen beneficially lowers the work function and, more surprisingly, subsequent removal of some Cs, followed by a further deposition of Cs and O improves the performance. For III-V materials the band bending is assumed to be confined to a few nanometres near the caesiated surface. For S20 cathodes such a depth is comparable with the cathode thickness.

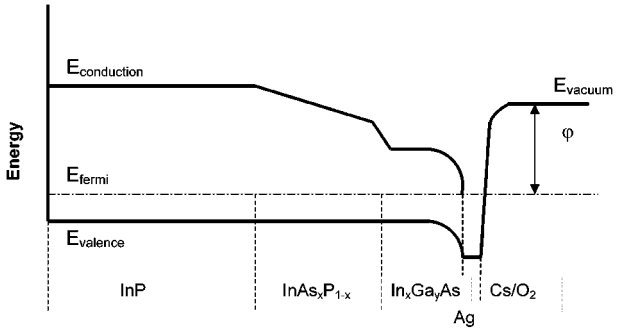


Figure 10. Early view of a band model for a transferred electron photocathode in which the energy gap is successively reduced towards the surface. There is a front face Ag contact layer and a reduced work function from Cs/O activation [4].

Instead of band bending there are alternative views in terms of interface potentials, but for monolayers of Cs this is an equally difficult concept. Indeed, the depth over which band bending occurs is unclear since, in comparisons between Cs and Cs–O–Cs mixtures containing just one or two monolayers the emission limit can be moved almost 1 eV according to some authors. Similarly, in the models as shown in figure 10 there is still a need for a dramatic potential change of $\sim$0.4 V over say 4 nm. These examples correspond to fields in the range of $\sim$1 V down to 0.1 V/nm (i.e. 10^9 V/m). Sustaining such values without causing surface breakdown on a multi-alkali or III-V surface seems slightly unrealistic. An alternative energy level scheme is needed that perhaps has a Cs metal, or one of the caesium oxide compounds, that is accessible by tunnelling or resonant energy transfer. Figure 11 contrasts the quantum efficiency and long wavelength limits from multi-alkali and III-V examples as the result of Cs, or Cs plus oxygen, to underline the effectiveness of the Cs addition.

The many literature examples do not appear to explicitly discuss the unusual property of Cs and oxygen in that both of them can form negative ions with relatively small electron affinity values. Tabulated values for Cs^-, O_2- and O^- are 0.472, 0.451 and 1.46 eV respectively. One may therefore speculate that an electron could be transported through the alkali system, associate to the Cs to form a negative surface ion, and then by a resonance energy process move to the surface bonded oxygen. The orbital rearrangements of the surface oxygen may then favour electron extraction into the vacuum. The possible merit of this type of process is supported by the observation that, for cathodes which have a few monolayers of oxygen added to the Cs, the long wavelength threshold is increased, even for the same cathode composition and an added Cs layer. Interestingly the shift can correspond to an energy difference of $\sim$0.42 eV [21] which matches the negative ion formation energies of Cs^- or O_2-. The spectroscopy literature of superoxides, and parallel data for nitrogen surface compounds, all indicate that bond rearrangement occurs after electron transfer. Although a role for negative ion formation had not been considered, it could offer reductions in the work function for electron emission and does so on precisely the energy scale that is observed. It might also help to explain the large improvements seen between merely using Cs and a few alternate monolayers of Cs–O–Cs. If oxygen were only

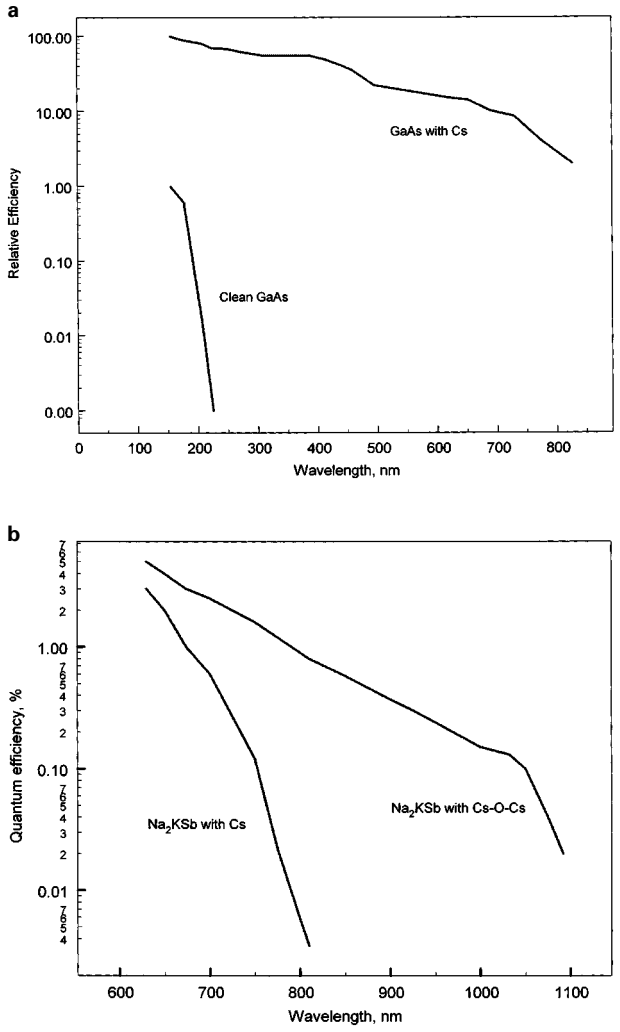


Figure 11. (*a*) Comparison of the QE for pure cleaved GaAs and material modified by addition of a monolayer of Cs [14]. (*b*) Multi-alkali comparison between cathodes with just Cs surfaces and caesium plus oxygen [21].

physically absorbed on the surface then there might be traces of negative oxygen emission in addition to the electrons.

11. Alternative routes to enhanced cathode performance

The alkali based cathodes are attractive since they require a modest technology and can be as easily used on end window as well as side window tubes. They also have fast response times and survive ion beam damage from residual gas (e.g. any positive ions formed that are accelerated back into the cathode). This latter is not a trivial problem since it is a limiting factor in photon imaging tubes which use III-V layers. For example a 1980 review of the third generation tubes is still relevant in terms of achievable performance [26]. In the imaging tubes a thin membrane is interposed between cathode and the end of the microchannel plate to allow passage of electrons but block the ions. This greatly reduces performance but offers longer operating life. For imaging tubes an advantage of a transmissive structure is that an anti-reflection layer can be interposed between the window and the cathode and this has offered some 20% more signal than for reflective GaAlAs mode systems. In terms of performance this can offer QE values of $\sim$55% (or 2000 μA/lumen) and even higher values of 70% are cited for GaAsP. However the material is virtually impossible to grow in the imaging tube system. Performance data are included in a recent perspective of photocathode values and novel applications [27].

Rather than use thick cathodes or difficult growth conditions many experimental designs have been proposed to attack the problem of poor photon absorption. Particularly for the alkali cathodes much of the long wavelength light is transmitted, and if instead this can be absorbed, then there are large potential gains in performance. Numerous examples consider routes to provide multiple reflections at the cathode, either by structuring the cathode, or by using the window as an optical waveguide. There are advantages in both cases. For the structured designs the main benefit is via an increase in absorption efficiency at non-normal incidence, as discussed earlier, where the most obvious feature is the gain achieved for the longer wavelengths. The extreme version of this design is to trap the light in a waveguide adjacent to the cathode. In principle, it will travel back and forth across the window until all the power is extracted by absorption in the cathode. Hence, in the perfect waveguide example the theoretical improvements in the trialkali response are spectacular, as shown in figure 12(*a*). In this example the effectiveness is a function of window thickness and is improved for thinner windows. In practice, published data have been confined to examples where a standard tube is externally modified, for example by addition of a surface prism so a window of $\sim$2 mm is appropriate. The reports of one such data set are given on figure 12(*b*). They show measured gains of a factor of $\sim$2 in the blue and above 10 times in the red. Hence the effective maximum QE of the tube has risen from $\sim$25 to 50%, and in some examples it is claimed to have reached $>$60% in the blue. Theoretically, higher values could be reached. The benefits are readily derived for tightly confined optical beams, as for lasers, or (as in figure 12(*b*)) from a high resolution monochromator with f/10 optics. The most useful feature of the prism addition is the benefit seen at long wavelengths, and the fact that one can upgrade existing systems, for just the price of a prism, to give a performance which is not yet commercially available.

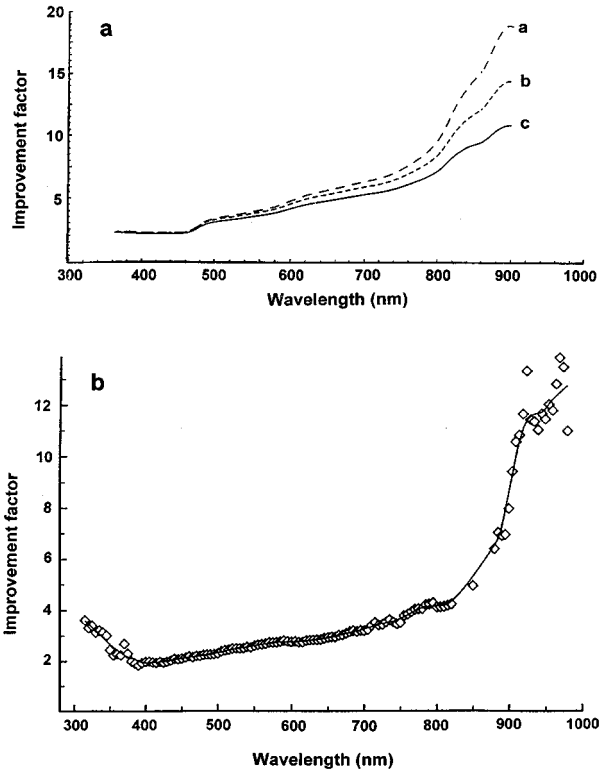


Figure 12. (*a*) Benefits in performance predicted and measured for light guided in the photomultiplier window for different window thicknesses of 1, 2 and 3 mm for *a*, *b*, *c*, respectively, and (*b*) an example of experimental data [20].

12. Future prospects

As indicated in the discussion of current and future applications, there are numerous new opportunities for photocathode-based systems, as well as all the current examples. A recent addition has been the use of high intensity picosecond laser pulses on photocathodes to produce trains of extremely high current, picosecond duration electron pulses, each containing up to a microcoulomb of charge [28]. There are therefore a diverse range of strong commercial interests to exploit and develop the new markets. Advances via the introduction of new photocathode materials cannot be discounted, but realistically these are less likely than improvements in the usage of existing materials. Quite crucially the problem of removing signal loss by reflection and transmission and thus increasing absorption will dramatically raise the QE values. Photocathode detection at longer wavelengths, for example to 1.5 μm, is still in its infancy and so major improvements are likely to ensue. For the near infra red spectral range (e.g beyond 700 nm) there is so much room for improvement that significantly higher QE devices are almost guaranteed in the very near future. Thus while photocathode detectors have been used for more than 70 years they have not yet become obsolete, and indeed have the prospect of remaining a central enabling technology for a wide variety of fields for the foreseeable future.

The imaging options are certainly far from fully exploited, not only for the imaging tubes, as briefly discussed here, but in the many variants and low resolution image acquisition concepts that have been considered [29, 30] but not yet fully commercialized. Finally, the design of colour imaging at photon counting levels is still at the level of imagination.

Acknowledgements

I am grateful to Dr Stuart Harmer for access to unpublished data and to my friends and colleagues in Sussex, Electron Tubes Ltd, Photek and IMPECABLE for encouragement and criticism, particularly Drs S Hallensleben, J Howorth and R McAlpine. I also thank both EPSRC and the Framework V IMPECABLE programme (G5RD-CT-2000-00372) for financial support.

References

[1] Hertz, H., 1887, *Ann. Physik*., **31**, 983–1000.
[2] Einstein, A., 1905, *Ann. Physik*., **17**, 132–143.
[3] Sommer, A.H. and Spicer, W.E., 1965, Photoelectric emission. In *Photoelectronic materials and devices*, edited by S. Larach (Princeton, NJ: Van Nostrand Co Inc). pp. 175–221.
[4] Jedicka, M. and P Kulhanek, 1986, *Vacuum*, **36**, 515–521.
[5] Dolizy, P., Groliere, F. and Lemonier, M., 1988, *Adv. Electron. Electron Phys*. **74**, 331–338.
[6] Bates, C.W., 1992, A survey of photocathode research. *Proceedings of Photoelectronic Image Devices*, (London: IOP Publishing Ltd). pp. 319–330.
[7] Sommer, A.H., 1993, *SPIE*, **2022**, 1–12.
[8] Beguchev, V.P, Shefova, I.A. and Musatov, A.L., 1993, *J. Phys. D*., **26**, 1499–1502.
[9] Items available from manufacturers include detailed books from: *Photomultiplier Handbook*, Burle *Photomultiplier Tubes: Principles and Applications*, Photonis Imaging Sensors (originally from Philips Export BV 1994) *Understanding Photomultipliers*, Electron Tubes Ltd, 2001 *List of suppliers*, Europhotonics April/May 28-29, 2002.
[10] Useful catalogues and performance parameters are well documented in standard catalogues from Burle; DEP; Electron Tubes Ltd, Hamamatsu; Photek Ltd; Photonis. These are often updated and details can be found on their web sites. : www.burle.com; www.dep.nl; www.electrontubes.com; www.hamamatsu.com; www.photek.co.uk; photonis.com.
[11] Moorhead, M.E. and Tanner, N.W., 1966, *Nucl. Inst. Methods*, **A378,** 162–170.
[12] Chyba, T.H. and Mandel, L., 1988, *J. Opt. Soc. Am*., **B5,** 1305–1311.
[13] Harmer, S.W., 2000, DPhil thesis, Sussex.
[14] Spicer, W.E., 1977, *Appl. Phys*., **12,** 115–130.
[15] Costello, K., Aebi, V., Davis, G., La Rue, R. and Weiss, R., 1995, *SPIE,* **2550**, 177–188.
[16] Martinelli, R.U. and Fisher, D.G., 1974, *Proc. IEEE*, **62**, 1339–1360.

[17] Antypas, G., 1976, Process for making III-V devices, US patent 3,959,045.
[18] Rambo, B.E., 1964, *Air Force Technical Report A1* **TDR** 64-19 April 1964
[19] Gunter, W.D., Grant, G.R. Shaw, S.A., 1970, *Appl. Opt*. **9**, 251–257.
[20] Hallensleben, S. and Townsend, P.D., 2000, *Opt. Lett*. **25**, 1511–1513.
[21] Guo, T. and Gao, H., 1993, *Appl. Surf. Sci*. **70/71**, 355–358.
[22] Johnson, C.S., Bonney, I. and Fioryan, R.F., 1988, *SPIE*, **932**, Ultraviolet technology II, 285–290.
[23] Current data from Sussex and Electron Tubes Ltd, to be published.
[24] Rodway, D., 1984, *Surf. Sci*., **147**, 103–114.
[25] Rodway, D.C. and Allenson, M.B., 1986, *J. Phys. D*., **19**, 1353–1371.
[26] Howorth, J.R., Holtom, R., Hawton, A., Folkes, J.R. and Palmer, I.C., 1980, *Vacuum*, **30**, 551–555.
[27] Kaufmann, K., 2000, *Laser Focus World*, **October**, 77–81.
[28] Boscolo, I. and Michelato, P., 2000, *Nucl. Inst. Methods A*, **445**, 389–393.
[29] Yong-Le Pan and Chang, R.K., 2001, *Laser Focus World*, **May**, 235–240.
[30] Lerner, E.J., 2001, *Laser Focus World*, **July**, 155–159.

Professor Townsend's scientific career has concentrated on studies and applications of imperfections in insulating materials. The spread of topics has ranged from mechanisms of colour centre formation from alkali halides to explosives, thermoluminescence and radiation dosimetry, ion implantation to form optical waveguides and waveguide lasers etc., new routes to periodic poling, ion implanted sunglasses and car mirrors, luminescence detection of phase transitions, and most recently, to enhancements in the performance of photocathodes. The work has involved very many collaborators and resulted in five books, 450 papers and 50 theses. In spare moments he plays the violin and is a keen fencer, including recently being National Veterans foil champion in 2000 and 13th in the World Veterans sabre.