PHOTOEMISSIVE MATERIALS—A REVIEW

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ABSTRACT

This review surveys the development of photoemissive materials used in practical devices. The phenomenon of photoemission and the criteria for obtaining good photoemission from materials are discussed. The available photoemissive materials and the preparation techniques are described. Alternative phenomena employed for enhancing the photoemission efficiencies, like interference, high field, and grating tuning are outlined. Finally the present status of work and future trends are indicated.

Key words: Photoemission, Photocathodes.

1. INTRODUCTION

Photoemission, like photoconduction and photovoltaic effect, is a powerful tool for photodetection. In this paper we shall review the developments of various photoemissive materials leading to improved efficiency and detection limit as are available today. The phenomenon of external photoelectric effect was discovered in the year 1887 when Hertz[1] had observed that a spark can be produced between two electrodes at a longer distance when the negative electrode was exposed to ultraviolet radiation. After the discovery of the electron it was realised that the incident light of proper frequency gives rise to the emission of electrons from the surface of materials. The phenomenon was explained by Einstein[2] by his famous photoelectric equation

$$h\nu = E_T + E_K. \qquad (1)$$

In the first quarter of the 20th century, though the potential of this phenomenon from application point of view was realised to some extent, the application was rather limited because of the absence of materials with good photoelectron emission efficiency. The quantum efficiencies of most of the photoemissive materials known then were of the order of 10^{-4} electrons per incident photon. Therefore, even though photoemitters were being used for some applications like switches and relays, the interest in the phenomenon was mostly academic in nature.

The discovery of the photoemissive compound Ag–O–Cs in 1930[3,4] changed the situation radically. This material had a quantum efficiency of 10^{-2} electrons per incident photon. This was about two orders of magnitude higher than any of the materials then available. With the discovery of this material (photocathode) many different types of applications, like those in image converters, television camera tubes and low light level measurement meters, came into existence.

The discovery of Ag–O–Cs photocathode indicated the possibility of the development of other photoemitting compounds and hence more intensified effort was put towards that end. This has resulted in the development of a large number of materials with varying degree of usefulness. We shall discuss the photoelectric properties of those materials within the scope of this review. Table I shows the milestones in the development of photoemissive materials.

TABLE I

Photocathode	Year of discovery	Maximum quantum efficiency electron/photon
Ag–O–Cs	1930	10^{-2}
Cs_3Sb	1936	$1 \cdot 5 \times 10^{-1}$
Bi Ag–O–Cs	1939	$8 \cdot 0 \times 10^{-2}$
Na_2 K Sb (Cs)	1955	$3 \cdot 0 \times 10^{-1}$
NEA : Ga As	1965	$4 \cdot 0 \times 10^{-1}$
NEA : Si	1970	$4 \cdot 0 \times 10^{-1}$

2. THE PHENOMENON OF PHOTOEMISSION

The Einstein equation provided an appropriate explanation for the phenomenon which the classical electromagnetic theory had failed to achieve. This was due to the simplistic assumption that every material had a characteristic threshold energy of photoemission. In the case of metals, this threshold energy was found to be equal to the work function of the material;

which was the difference between the vacuum level and the Fermi energy. In semiconductors, this was found to be the difference between the vacuum level at the surface and the top of the valence band in the bulk. The Einstein's equation, however, did not provide any better insight into the problem than clearly stating the phenomenon. Many questions (from material preparation point of view) like, why should a specific material have a higher quantum efficiency than the other and what should be the criteria for a material to be prepared for obtaining a particular type of response, etc., still remained unanswered. The answers, however, eventually came from a closer examination of the phenomenon.

The phenomenon of photoemission is conceived as a three step process (Fig 1).

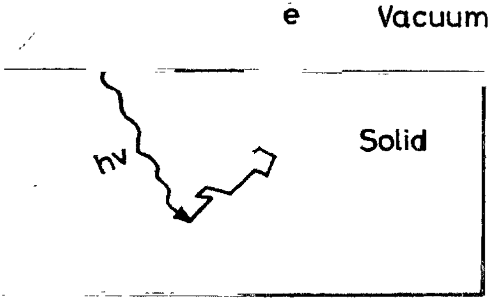

FIG. 1. Generation and escape of photoelectron from the solid.

These are:

(1) Absorption of photons and the generation of photoelectrons.

(2) Diffusion of the electrons from the point of generation to the surface.

(3) Escape from the surface.

Let us examine these three processes one by one.

1. When a beam of light is incident on a solid, its intensity I at a depth d from the surface is governed by the exponential law

$$I = (I_0 - R) \exp(-Kd) \tag{2}$$

where I_0 is the incident intensity, R is the reflected component and K is the absorption coefficient of the material. For obtaining good photoemission from a solid it is necessary that the material should absorb as large a fraction of photons as possible within a depth from the surface from which the electrons generated can be emitted. This demands that the absorption coefficient K should be as large as possible. In fact it has been observed that the good photoemitters have an absorption coefficient as high as 10^6 cm^{-1} in the wavelength range where they have good quantum efficiency.[5, 9] This requirement of a large absorption coefficient indicates that the materials in which the optical transitions are predominantly of the indirect type, cannot be good photoemitters. This implies that the band structure of a material which determines the probability of optical transitions from the filled bands to the empty ones has a strong influence on photoemission. The band structure should be such that there should be good probability of vertical (k-conserving) transitions. Of course, non-direct transitions without involving phonons have been observed in certain photoemissive materials like Cs_3Sb and Cs_3Bi.[10] In either case a high probability of optical transitions is a necessary condition to good photoemission.

2. The diffusion of the electrons from the point of generation to the surface with appropriate energy would be dependent on the number and the type of scattering events the electrons suffer on their path. The scattering may take place with lattice atoms, the defect sites, and with the free and bound electrons. The concentration of the free electrons is very high in metals which gives rise to a very small mean free path for scattering of the photogenerated electrons. As a result, very few of the electrons can reach the surface, with enough energy to surmount the potential barrier and therefore metals as a class are not likely to be good photoemitters.

In semiconductors and insulators also, the materials which offer too many scattering centres for free electrons are not likely to be good photoemitters. Therefore, good photoemission has not been observed in amorphous solids. It is believed that the materials which exhibit good photoemission in the polycrystalline form, *e.g.*, alkali antimonides, etc., could emit more photoelectrons if they were available in single crystalline form. One reason for obtaining very high photoemission from single crystalline films of gallium arsenide and silicon is the large scattering length of the electrons and consequently the large depth from which photoelectrons can escape (escape depth).

Two types of scattering are important for the photogenerated electrons in poly- or single crystalline semiconductors or insulators. One is the lattice scattering and, the other, electron-electron scattering with valence band electrons. In lattice scattering the mean free path depends relatively little on the energy of the primary electrons and the energy loss per event is small (typically 0·01 ev). The mean free path for this is typically more than 10 nm.

In electron-electron scattering (pair production), on the other hand, the mean free path of the primary electron is very small and depends on the energy of the primary electrons. The loss of energy per collision is also very large, the minimum being equivalent to one band gap of the material. Therefore the electrons suffering this type of scattering lose energy very rapidly. The mean free path also being smaller (a few nm) the electrons rapidly lose energy to a point where its probability of emission becomes negligible. This scattering has a threshold value, the minimum of which is equivalent to twice the band gap from the top of the valence band. In a good photoemitter the electron-electron scattering should not affect the emission of photoelectrons. This condition imposes certain constraints regarding the band gap and electron affinity of the materials which could be good photoemitters.

Let us suppose that there are three classes of materials as indicated in Fig 2. In (*a*) the threshold of pair production, E_{th}, is less than the electron affinity. In this case all electrons which can escape can undergo electron-electron scattering by which their energy may be reduced below vacuum level. This type of material is likely to be a very poor photoemitter. In type (*b*) E_{th} is higher than electron affinity but not very much more.

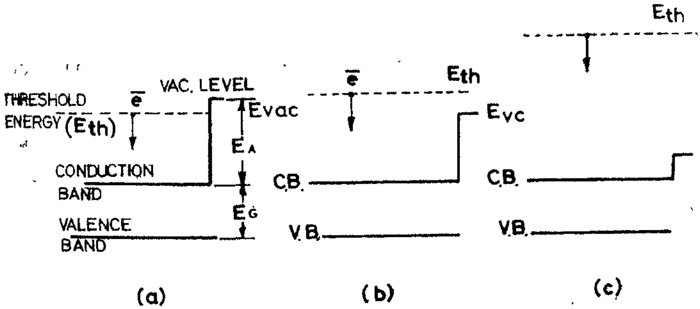

FIG. 2. Classification of solids as photoemitters (*a*) poor photoemitters, (*b*) photoemitters better than class (*a*), (*c*) very good photoemitters.

Therefore, only the electrons with energy slightly above E_{vac} would be exempted from electron-electron scattering. This type of material would be a better photoemitter than class (*a*) but photoemission would not be high. In type (*c*) material the E_{th} is very much larger than the electron affinity E_A such that once scattered electrons with loss of energy of E_g have an energy higher than E_A. This would be the ideal material for photoemission. This requires that the band gap of the material should not be very high and the electron affinity should be low, such that once scattered electrons (energy loss $> E_g$) are able to be emitted. It is seen that these conditions are fulfilled by the good photoemitters presently developed.

3. The electrons with energy larger than the electron affinity have a good probability of escape from the surface. The other condition that the component of energy normal to the surface should be higher than the electron affinity, decreases the probability of the electrons with energy very near to electron affinity. They can be emitted only if they impinge on the surface at very small angles to the normal. The higher energy electrons can be emitted if their impingement angle is large. These give rise to the complexity of the escape functions.[11] In simple models of photoemission, however, the escape function is taken as a step function.[7]

To derive an expression for quantum yield of a photoemitter, we can use the absorption law as described by eq. (2) and also combine together the diffusion and escape process by using an escape function of the form[7]

$$F_{esc} = X e^{-gx} \tag{3}$$

where X is the probability of an electron reaching the surface to escape from it. The exponential form indicates the probability to reach the surface from a depth x in the material. g is not a constant but is dependent on the initial energy of the electron and a quantity $1/g$ is termed escape depth of the electrons.

If we consider a thin film of photoemitter as usually most photocathodes are, and consider the light to be incident from the substrate side (semi-transparent mode) then the quantum efficiency could be stated by the expression[9]

$$Y(h\nu) = \frac{(I-R)\, Kp\, X\, e^{-K_T d}}{g-K_T} [1 - e^{-(g-K_T)d}] \tag{4}$$

d is the thickness of the film, K_T is the total absorption coefficient and K_p is the contribution to it due to the transitions in which the final states are above vacuum level.

Theoretically, if the diffusion of the photogenerated electrons in the solid is isotropic and they are not able to produce secondaries, the maximum quantum efficiency attainable could be 0·5 el/photon. This is because an electron generated very close to the surface has equal probability to escape to vacuum and diffuse inside the volume. But if the photogenerated electrons are capable of producing secondaries the upper limit of quantum efficiency could be enhanced. However, the maximum quantum efficiency of various photocathodes which have been used so far, in practical applications ranges from 0·01 to 0·4 electrons per photon.

3. The Various Conventional Photoemissive Materials

The photocathodes which are important from the application point of view would now be discussed.

Ag-O-Cs or (S-1) photocathode

This was the first compound photocathode with good quantum efficiency. The maximum quantum efficiency is about 0·01 el/photon. Though the quantum efficiency is poor compared to the photocathodes which have been subsequently developed, this photocathode has the longest cut off wavelength in the infrared which is about 1·25 μm. The general usefulness of this cathode is limited because of its poor quantum efficiency in the visible region and high thermionic emission ($10^{-11}-10^{-13}$ A/cm^2). Mostly it is used for infrared image conversion and other applications as infrared detector. The spectral response of this and other photocathodes are illustrated in Fig 3.

Cs_3Sb (S—11)

The Cs_3 Sb photocathode was the first high quantum efficiency material to be developed.[12] The maximum quantum efficiency was about 0·15 el/photon and the threshold was at 600 nm. The thermionic emission from this photocathode was also very low (10^{-16} A/cm^2). This has been surpassed by materials discovered later not only in quantum efficiency but also in threshold wavelength. Therefore, from technical point of view it can be considered obsolete. However, because of the simplicity of the manufacturing process resulting in lower cost it is still widely used for applications where optimization of performance is not important.

Bi-Ag-O-Cs (S-10)

This cathode was developed[13] specifically for obtaining a spectral response approaching that of the eye for use in photoemissive camera tubes.

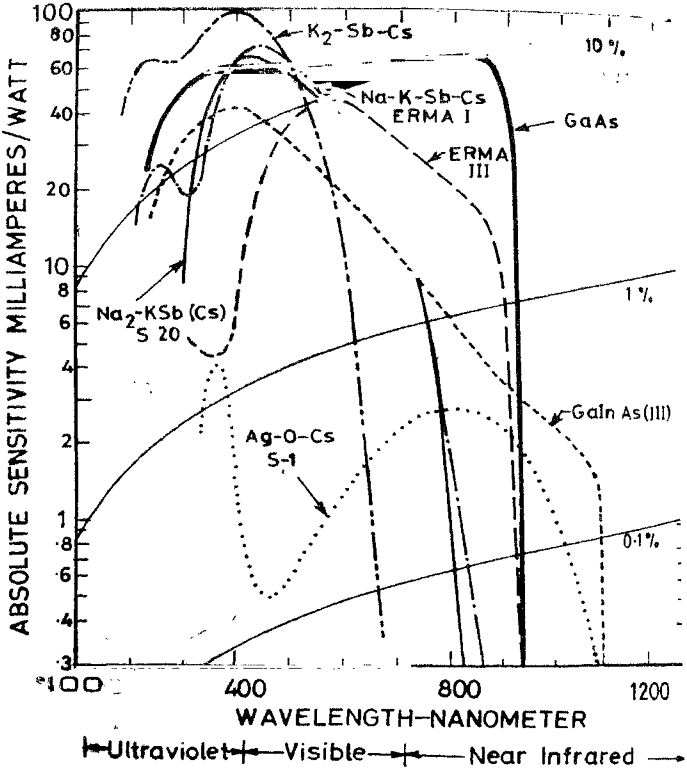

FIG. 3. Spectral response of the photocathodes.

This is still useful for color television camera tubes like image orthicon. For other applications it is inferior to other types of photocathodes because it has got a relatively higher thermionic emission ($\sim 10^{-12}$ A/cm^2) and lower peak quantum efficiency ($\sim 0\cdot08$ el/ph).

K_2Cs Sb

This cathode[14] is characterised by a high quantum efficiency in the 400 nm region ($\sim 0\cdot3$ el/ph), combined with a very low dark current ($< 10^{-17}$ A/cm^2). This makes the cathode very suitable for detection of very low light levels, photon counting and scintillation counting where the radiation to be detected is in 400 nm region.

Na_3KSb

This cathode has a spectral response very similar to K_2 Cs Sb with a longer threshold wavelength. This also has a high peak quantum efficiency (0·3 el/ph). This is the only photocathode known in which the response throughout the visible region is obtained without the presence of Cs or Rb. The absence of Cs gives rise to the most important property of this photocathode, *viz.*, its stability at higher ambient temperature. It can operate at an ambient temperature as high as 160° C whereas other photocathodes become unstable above 60° C. Therefore, it is used in detectors meant to work at higher temperatures.

Na_2 K Sb (Cs) (S–20, S–25)

This is the only conventional photocathode which has both high peak quantum efficiency throughout the visible range and useful response in the near infrared.[15] The maximum quantum efficiency is about 0·3 el/ph and the cut off ranges from 800–950 nm. This has got a low dark current ($< 10^{-15}$ A/cm^2) also. This is used in most of the present-day applications involving photocathodes. The disadvantage with this cathode is the complexity of the manufacturing process and therefore it is expensive.[16] The dark current of this photocathode is higher than that of K_2 Cs Sb.

4. NEGATIVE ELECTRON AFFINITY PHOTOCATHODES

It was well known that band bending takes place at the surface in *p* type materials with *n* type of surface states. The possibility of obtaining large band bending such that the effective electron affinity is reduced to zero or some negative values was realised and the first photocathode of this type with negative electron affinity was developed by Scheer and Van Laar.[17] They obtained band bending by using *p* type GaAs single crystals with a surface layer of cesium. Better negative electron affinity photocathodes were obtained by oxidising the cesium layer on the surface of GaAs.[18] Later, the negative electron affinity has been established in a large number of materials like silicon,[19,20] gallium phosphide[21] and the ternary and quaternary compounds like (GaAl)As,[22] Ga(As, Sb),[23] In(As, P)[24], (In, Ga, As, P),[25] etc. All these materials have to be activated with cesium and oxygen to produce the required band bending at the surface for negative electron affinity (NEA).

It has been possible to obtain a quantum efficiency of about 0·4 el/ph and a threshold wavelength of about 1 μm. The band bending model with Cs_2O layer on p type GaAs is shown in Fig 4.

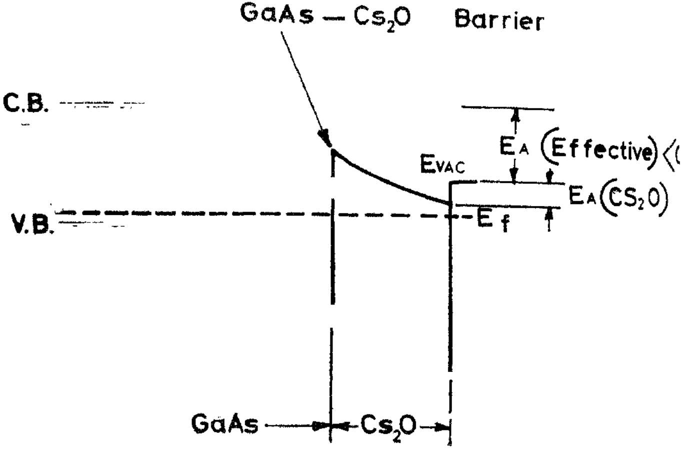

FIG. 4. The hetero-junction model for band bending in GaAs with Cs_2O on the surface.

This is the heterojunction model to explain the band bending. The Cs–O layer on the surface is considered to have the characteristics of bulk n-type Cs_2O.[26–28] The band profiles of the two materials adjust at the interface in such a manner as to satisfy equilibrium charge conditions. The result is an interfacial barrier that the bulk generated electrons might either overcome or tunnel through. Once in Cs_2O they can be emitted as hot electrons over the small 0·4 to 0·6 ev positive electron affinity barrier of the Cs_2O. The effective electron affinity is negative.

The negative electron affinity helps to improve the quantum efficiency in two ways. Firstly all the electrons excited to conduction band in the bulk can be emitted as photoelectrons unlike in positive electron affinity emitters where the electron excited to states below the vacuum level cannot escape. Secondly in positive electron affinity photoemitters the electrons which are emitted are hot electrons, having much higher energy than an electron thermalised at the bottom of the conduction band. Because there is a continuum of lower available energy levels the hot electron can lose energy quickly through interactions with lattice optical phonons[29,30]. The hot electron lifetime before it is thermalised is typically about 10^{-13} secs. This means that the photogenerated electron should reach the surface within this time in order to escape. On the other hand, the thermalised electrons at the bottom of the conduction band (within a few kT above the minimum of the band) have a lifetime ranging from 10^{-10} to 10^{-8} secs in III–V compounds and may be as long as 10^{-6} secs in silicon. Thus they can diffuse from a much larger depth to the surface and consequently be emitted. Therefore the escape depth of photoelectrons in NEA emitters is about 1 μm or higher compared to about few tens of nm for the conventional photoemitters.

Though very high quantum efficiency and extended range of response have been obtained from NEA photocathodes the practical applications have so far not been very encouraging. This is because in applications like those in imaging devices, etc., the use is required in transmission mode which is rather difficult with NEA materials. For use in transmission mode the single crystal has to be grown on a transparent substrate. Epitaxial growth of III–V single crystals has been possible on sapphire and spinel but the quantum efficiency in the transmission mode of operation is much poorer than in the reflection mode. Secondly, for using electron lenses for focusing of electron image the photocathode should be curved. To deposit single crystal films on curved substrates appears to be difficult at this stage. Therefore the only type of imaging device using NEA photoemitter could be proximity focused with a flat input photocathode. This has been attempted in developmental tubes.[31, 32] As photodiodes NEA cathodes with long threshold wavelength up to a maximum of 1·1 μm ($In_x Ga_{1-x} As$) with low dark current ($\sim 10^{-16}$ A/cm^2) are used for Raman Spectroscopy[33], for detection of Nd–YAG laser radiation at 1·06 μ[16], etc.

5. PREPARATION TECHNIQUES

The conventional positive electron affinity photocathodes are prepared by techniques which are similar for different materials despite their differences in chemical composition. The different metals comprising the photocathodes are reacted at different temperatures in carefully controlled fashion to obtain the compound of the desired composition. The chemical reactions are carried out in contamination free high vacuum, the pressures being 10^{-7} torr and lower. The pure metals are generated *in situ* from some chemical compounds or evaporated from some beads. For generation of alkali metals like cesium, sodium, potassium, etc., the chromates or dichromates of the respective metals are mixed with some reducing agents and filled in nickel tubes.[34] These tubes are heated to generate controlled quantities of the metals. Antimony is generated from antimony beads formed on platinum clad molybdenum wires. Oxygen is generated by heating potassium chlorate or manganese oxide and where a very controlled generation of oxygen is required in UHV as in the case of NEA cathode, a UHV leak valve is used. The source of oxygen to feed the input of the leak valve is obtained by permeation of oxygen through silver foil.[35]

To illustrate, the conventional processing technique of a photocathode will be described. To process other photocathodes the temperature of activation and the materials would be different. The technique described[8] is for processing multialkali photocathode which is the most complex and difficult. To start with, a base layer of antimony is evaporated the thickness of which corresponds to a loss of transmission of 45%. This antimony layer is activated with potassium vapour at a temperature of 185° C. The photosensitivity starts rising when the Sb layer is activated and after a peak sensitivity is reached potassium is cut off. The resulting film is activated with sodium at 220° C and then with potassium and antimony alternately. Finally the film is activated with cesium and antimony at 160° C and the photocathode is completed. Fig. 5 shows the different steps of photocathode processing and how photosensitivity varies during this period. There are variations of this processing technique and recently a method of preparation for a few alkali antimonide photocathodes has been developed[36,37] which is more advantageous from device application point of view and gives higher sensitivity.

The preparation of NEA photocathode involves preparation of a good epitaxial single crystal at the surface which is prepared by liquid or vapour phase epitaxy.[38, 39] Imperfections in the crystal can reduce the diffusion length of the electrons and thus reduce the large escape depth which is the reason for its high efficiency. After preparing the single crystal the wafer is mounted in the photodiode and the surface is cleaned by resistive heating or electron bombardment to near the decomposition temperature (*e.g.*, 675° C for GaAs). Then it is activated by Cs and O_2 alternately at room temperature[22] to a point such that the sensitivity does not increase further. For activation, usually a base pressure below 1×10^{-9} torr is needed.

6. ENHANCEMENT OF PHOTOEMISSION BY OTHER TECHNIQUES

There are other means by which photoemission from photoemitters can be enhanced. Methods using interference, grating tuning and high

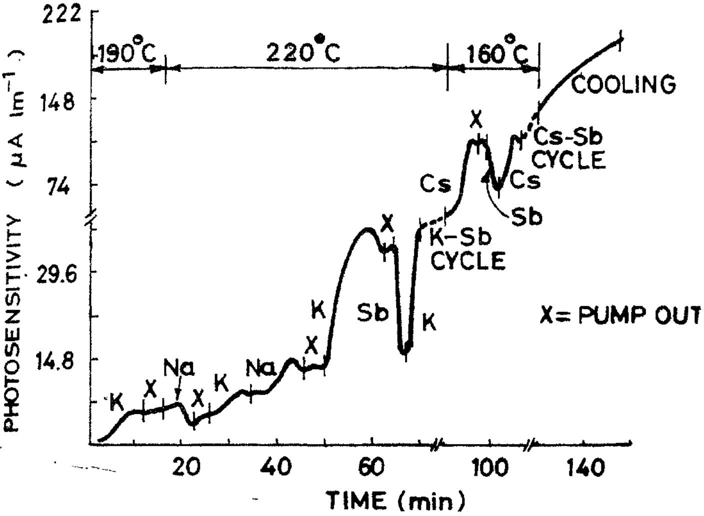

Fig. 5. The processing sequence of a multialkali photocathode.

field lowering of surface barrier have been used to achieve higher photoemission. These methods will be described briefly.

1. *Interference photocathodes*

It is well known that, if the absorption of light can be increased in the photoemissive material within the depth of the attenuation of electrons then the photosensitivity can be enhanced. In interference photocathode[40–43] this is done by using some dielectric films between the substrate and the photocathode so that the reflection from the composite system is minimised and the absorption is increased.

In the case of transmissive interference cathode, usually two layers of dielectric are used to satisfy the amplitude and the phase condition (Fig. 6), *e.g.*,

Amplitude condition $\gamma_{34} = \gamma_{21}$

Phase condition $n_1 t_1 + n_2 t_2 + n_3 t_3 = \lambda/2.$

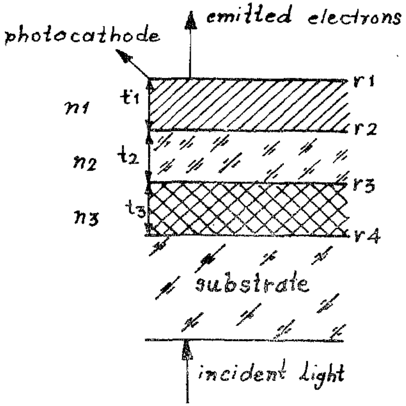

FIG. 6. Arrangement of the adapting films in a two layer interference photocathode.

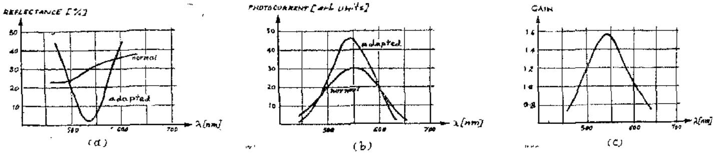

FIG. 7. Reflectance (*a*), photocurrent (*b*) and gain (*c*) of a second order TIC with cesium antimony film *versus* wavelength.

These conditions being satisfied, the decrease in reflectance and consequent increase in photocurrent can be seen in Fig. 7. This was obtained with cesium antimonide photocathode with SiO_2 as phase adapting and TiO_2 as amplitude adapting film.[43] Similar enhancement has been obtained for other types of photocathodes also.[42]

There are other modes in which interference photocathodes can be used like reflective interference cathodes (RIC) and totally reflective interference photocathodes (TRIC). The most important advantage with interference photocathodes is that the peak position of the photoresponse can be tailored by having an appropriate thickness of the dielectric layer.

2. *Grating tuned photocathodes*

It was observed that by resonant excitation of surface waves or surface plasmons an enhancement of photoemission was obtained.[44,47] This principle was utilised[48] for obtaining enhancement of photoemission from Ag-O-Cs photocathodes by depositing this on a grating substrate having discontinuities in the 10–30 nm range. The periodicity of the grating was 890 nm and the resonant coupling was seen to occur at normal incidence for the somewhat lower frequency characteristic of 930 nm free space wave length as can be seen from Fig. 8. The enhancements for other angles of incidence are shown and compared with the photocathode deposited on smooth substrate. This method of tunable enhancement of quantum efficiency would be useful in detection of laser radiation.

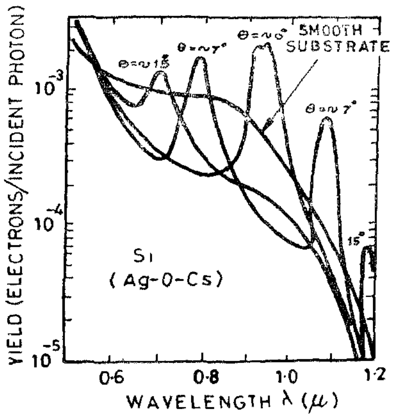

FIG. 8. Quantum efficiency of a grating tuned S-1 photocathode. The quantum efficiency *vs.* wavelength is shown for *p*-polarized light at normal and other angles of incidence.

3. *High field enhancement of photoemission*

The application of high electric field is known to increase the photoemission by lowering the surface barrier for the photoexcited electrons.[49–52] A large enhancement of photosensitivity resulting in an increase of white light sensitivity from 235 μa/lm to 500 μa/lm has been observed for multialkali photocathode.[51] An enhancement in quantum efficiency by as much as as a factor of six has been reported[50] at the long wavelength photoemission. This advantage cannot be fully utilised in d.c. applications because of a consequent increase in dark current. However, for pulsed applications like detection of pulsed laser, etc., this gain can be effectively utilised. Fig. 9 illustrates how photoemission enhancement takes place for multialkali photocathodes.[51]

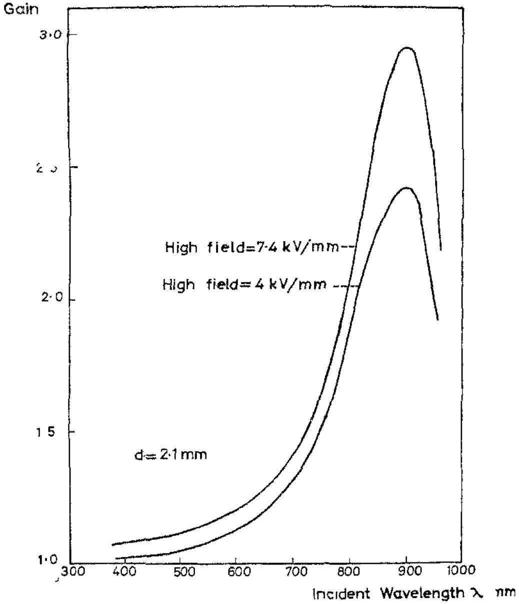

FIG. 9. The quantum efficiency gain curve for an extended red multialkali photocathode having a white light sensitivity of 235 μa/lm.

7. SOME RECENT TRENDS IN THE DEVELOPMENT OF PHOTOEMISSIVE MATERIALS

In recent years some new concepts have been introduced and research is continuing in those fields. For example work was continuing on photosensitive field emission from silicon point arrays at Westinghouse research labs.[53–55] Surface of silicon is etched by photolithography to produce a number of sharp edges which gives good photocurrent on illumination under electric field. But the dark current is too high for use of these photoemitters in practice and till now no satisfactory solution has been found.

Work on transferred electron photoemission from InP[56] and from InP/In GaAs/InP[57] type of structures is being tried at Varian Associates. Band bending at the surface is achieved by the action of electric field by which the photoelectrons generated in the volume are transferred to the bent band region from where they can energetically escape. Some improvement in quantum efficiency on biasing has been reported.

A similar principle is utilised on a double hetero-junction type of device[58] which is biased to obtain higher photoemission. The future of these types of photocathodes would depend on how much photoemission improvement can be achieved and also, how expensive they would be, as these involve several of the techniques of microelectronics. Probably, for quite some more time, the supremacy of the conventional photocathodes like bialkali and multialkali, etc., would remain unchallenged for device applications.

8. CURRENT STATUS OF RESEARCH IN INDIA

Experimental work on conventional photoemissive materials is being carried out at Bhabha Atomic Research Centre. In this laboratory starting from Ag-O-Cs photocathode[59] almost all the extensively used photocathodes have been prepared. Improved processing techniques have been developed for processing of alkali antimonide and Ag-O-Cs photocathodes.[36, 60] Detailed investigations have been carried out into the various aspects of processing of various photocathodes and other physical parameters.[60–66, 8, 9] Work is also being continued in the field of negative electron affinity and interference photocathodes.[67]

9. CONCLUSION

The development of the photoemissive materials from the discovery of Ag-O-Cs photocathode to the present day is reviewed.

Most notable of the materials which were developed were Ag–O–Cs, Cs_3Sb, Na_2 K Sb(Cs), K_2 Cs Sb and NEA materials. The NEA materials, however, have so far not been able to replace the conventional photocathodes for device applications. Attempts are in progress to develop other types of photoemitters based on the principle of transferred electron effect, etc., and at the same time to improve on the efficiency of the conventional photoemitters, particularly of Na_2 K Sb(Cs). The research on materials of future would probably be directed to facilitate the transport of all the photogenerated electrons to the surface, or would help the photoelectrons to produce secondaries so that the upper limit of quantum efficiency could be enhanced.

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