Preparation and study of properties of a few alkali antimonide photocathodes

C. Ghosh and B. P. Varma

Optoelectronics Section, Bhabha Atomic Research Centre, Bombay-400 085, India

A new processing technique for a few alkali antimonide photocathodes is described. This technique does not require an initial antimony layer as in the conventional techniques. Electron microscopic examination of the antimony film shows that the antimony film is affected by ambient gases, and the improvement of senistivity which results in this technique is thought to be due to the absence of it. The band gaps of the photocathodes are determined by photoconductivity measurements. The threshold energy and, hence, the electron affinity is calculated from the threshold region photoemission of these photocathodes. The activation energy of the defect levels is determined by the measurement of the electrical conductivity at a low temperature in a specially designed cryostat. Finally, the role of cesium in a multialkali photocathode is discussed, and a model of band bending which assumes a K_2CsSb layer at the top is proposed. This gives the threshold energy value observed experimentally.

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I. INTRODUCTION

The technique of processing the high-sensitivity photoemitting compound Ag-O-Cs was discovered in 1930.[1,2] Many more compounds have since been discovered, the most important of which are Cs_3Sb by Gorlich,[3] Bi-Ag-O-Cs,[4] and $Na_2KSb(Cs)$ and K_2CsSb by Sommer.[5,6] Recently, a new class of high-sensitivity negative electron affinity photoemitting materials have appeared.[7-9] However, the search for new materials and processing techniques which give higher photosensitivity continues.

Almost all methods described in the literature for the fabrication of alkali antimonide photocathodes start with a base layer of antimony film of a predetermined thickness deposited at room temperature.[3-6] The method of monitoring the film thickness by observing optical transmission may pose practical problems for many devices, e. g., where fiber optic windows are used. We have, therefore, developed a new processing technique in which there is no need for the deposition of the initial layer of antimony and for monitoring its thickness. This new method gives very high sensitivity as well. The photocathodes thus prepared have been studied for spectral response, photoconductivity, and temperature dependence of conductivity. Results of an electron microscopic investigation of the antimony film which helps to explain the high photosensitivity is described. The band gap, electron affinity, and activation energy of the defect levels have been measured.

II. EXPERIMENT

All the photocathodes, e. g., K_3Sb, $Na_2KSb(Cs)$, and K_2CsSb were prepared by the new technique developed in the laboratory. Potassium, generated by heating a potassium dispenser, is deposited on a phototube[10] heated to 180 °C. When a very small photosensitivity is registered with the potassium film on the substrate, the antimony metal is evaporated onto it in small controlled amounts by resistively heating an antimony bead formed on platinum-clad molybdenum wire. The sensitivity starts rising and the antimony supply

is discontinued after a peak sensitivity has been reached. If a K_3Sb photocathode is to be formed, the phototube is cooled, the potassium generation being continued at a slower rate for some time to compensate for the loss of potassium from the photocathode. A white-light sensitivity up to 25 $\mu A/lm$ has been achieved this way.

To prepare a K_2CsSb photocathode, the K-Sb photolayer is formed to get maximum sensitivity after which the activation with Cs and Sb is started. Cesium and antimony are simultaneously generated, and the rate of generation is so adjusted that a steady rise of sensitivity is maintained. An integral sensitivity of 100—120 $\mu A/lm$ has been obtained in this way.

For the preparation of a Na_2KSb photocathode, the K_3Sb layer is activated with sodium at 200 °C until the photosensitivity reaches a peak and begins to decrease. Simultaneous evaporation of potassium and antimony is then started at a temperature of 185 °C. The rate of
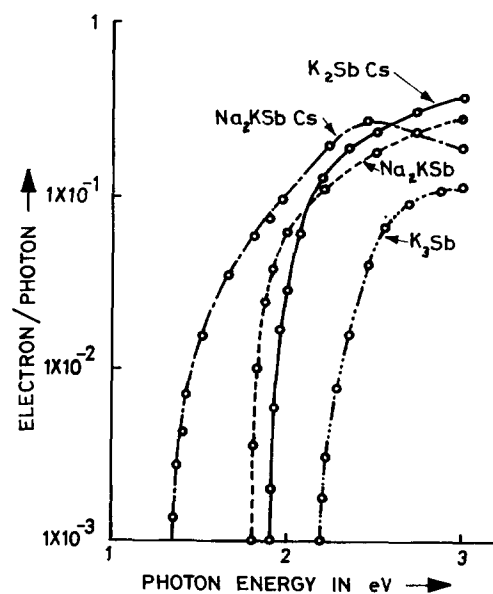

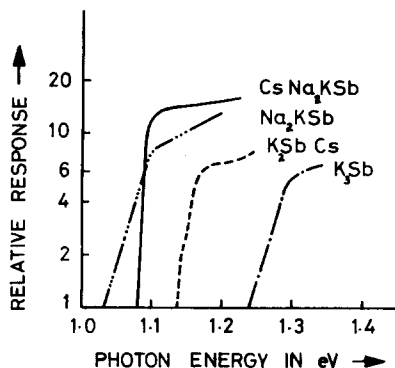FIG. 1. Spectral response of the photocathodes.

FIG. 2. Photoconductive response of the photocathodes.

the evaporations are carefully controlled to maintain a steady increase till it reaches the maximum value. An integral sensitivity of 100–120 $\mu A/lm$ has been achieved.

The preparation of a $Na_2KSb(Cs)$ cathode involves a further step. After the Na_2KSb cathode is formed, the temperature is brought down to 160 °C when the cesium addition is started. When the sensitivity starts falling from the maximum obtained by cesium addition, Sb evaporation at a controlled rate is started. This simultaneous evaporation increases the sensitivity to high values. The cathode is cooled after a little overcesiation. The integral sensitivity of this cathode is between 200–300 $\mu A/lm$. Figure 1 gives the spectral response of the different photocathodes described above.

To determine the band gap of the photocathodes, a measurement of photoconductivity was carried out. Since the photoconductivity was small, a standard compensation circuit was used for accurate measurement.[11] Figure 2 gives the photoconductive response of the photocathodes in the threshold region.

The location of the impurity levels in the forbidden gap of the photocathodes was determined by measurement of the electrical conductivity and its variation with temperature in the range of temperature from 90 °K to room temperature. A cryostat was specially designed for this purpose on the principle of gas cooling. In the

standard cold-finger method,[12] the photocathode is separated from the cold finger by a glass disk of a thickness of 1 mm or more. Also, the photocathode absorbs radiation from warmer surroundings so that its temperature is greater than that of the cold-finger tip where the temperature is measured. In our cryostat the ambience is at the same temperature as the photocathode so that the difference of temperature between the substrate and the photocathode would be negligible.

The design of the system is illustrated in Fig. 3. Liquid nitrogen was boiled by means of a heater immersed in the liquid-nitrogen container. The nitrogen gas coming out of the container was passed through the system in which the phototube was kept for measurement. Electrical connections were made through glass to metal seals. The system was evacuated to rotary vacuum before introducing cold nitrogen gas through it. The temperature was measured by sensitive $p-n$ junction thermometers. Any desired temperature from 90 to 300 °K was obtainable by adjusting the flow of nitrogen gas through the cooling chamber by controlling the power to the heater. The temperature was stabilized for a few minutes before the resistance was measured. The different photocathodes were examined for low-temperature electrical conductivity. During the measurement, a small voltage was applied across the photocathode through Ohmic contacts. A plot of the log conductivity versus $1/T$ is given in Fig. 4 for these photocathodes. This system was also used for measuring the photosensitivity at low temperature.

The electron microscopic examination of the film was done using a Siemen's Elmiskop-1 electron microscope in the usual way.[13,14]

III. RESULTS AND DISCUSSION

The high sensitivity of the photocathodes appears to be due to the high sensitivity of the initial K-Sb layer. Using the conventional technique[15] an integral sensitivity of about 7 $\mu A/lm$ was obtained, whereas an integral sensitivity of about 25 $\mu A/lm$ has been obtained by the method reported here. It has been observed that in the conventional technique for the processing of

A : HEATER POWER SUPPLY.
B : HEATER
C : LIQ. NITROGEN DEWAR
D : DIAPHRAGM VALVE
E : DOUBLE WALLED CHAMBER.
F : EXIT PORT OF INNER
    CHAMBER.
G : PHOTO TUBE
H : CONDENSATION PREVENTING
    OUTER CHAMBER.
I : GLASS VIEWING PORT
J : LEEDS FOR ELECTRICAL
    CONNECTION THROUGH
    GLASS TO METAL SEALS.
K : FOAM RUBBER CLADDING.
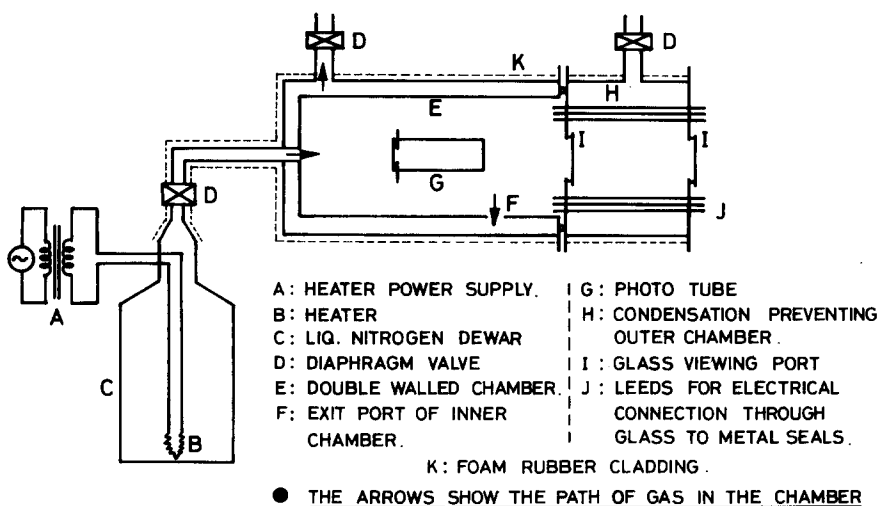● THE ARROWS SHOW THE PATH OF GAS IN THE CHAMBER
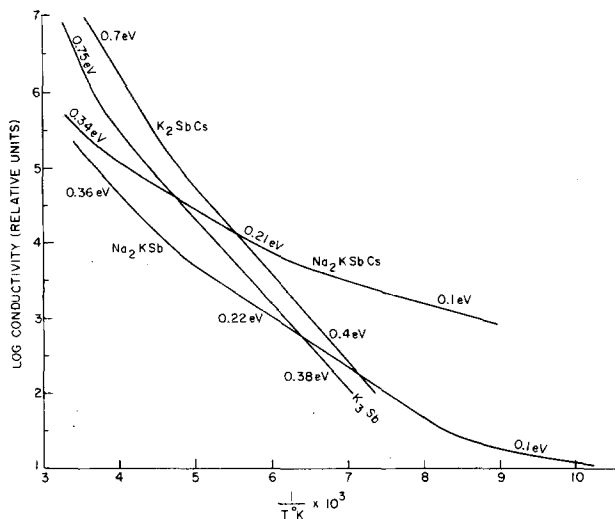
FIG. 3. The schematic diagram of the cryostat.

FIG. 4. Log(conductivity)-vs-1/T plot. The conductivity values are not absolute as the curves are displaced vertically for the sake of convenience.

multialkali photocathodes, the sensitivity of the photo-cathode is very poor if the initial antimony layer is exposed to the atmosphere before the activation with potassium.[16] It may be inferred that the action of atmospheric gases on the antimony film has an adverse effect on the final sensitivity of the photocathode. In the conventional technique the activation of the antimony film with potassium normally starts quite some time after the evaporation of the antimony film. During this time it is exposed to the gases from the alkali dispenser at a pressure of $(2-3) \times 10^{-7}$ Torr. It was felt necessary to see whether the gases at this pressure have any effect on the antimony film. The study of the antimony film by electron microscopy was therefore undertaken.

The growth of antimony films was studied in three vacuum ranges, e.g., low $(1 \times 10^{-5}$ Torr$)$, high $(5 \times 10^{-8}$ Torr$)$, and ultrahigh $(1 \times 10^{-9}$ Torr$)$ vacuum on carbon substrates.[13,14] It was observed that the antimony thin films grew initially with the formation of isolated rounded islands which became gradually elongated as the thickness increased. Finally, these islands coalesced abruptly to form an electrically continuous film. It was observed that at low and high vacuum the coalescence thickness was about 120 Å, while in ultra-high vacuum it decreased to about 100 Å. The films were amorphous in all cases before coalescence, but they turned crystalline on coalescence only in cases of high and ultrahigh vacuum. Thus, it is obvious that the residual atmosphere affects the antimony film growth considerably. To see the effect in the conventional method of photocathode processing, an antimony film of the same thickness as deposited in the conventional method (~ 70 Å) was deposited in ultrahigh vacuum and then exposed to gases from alkali channels. The film was exposed for about 20 min at about $(2-3) \times 10^{-7}$ Torr, and then antimony was further evaporated on this film until there was coalescence. It was found that the coalescence thickness was about 120 Å and that the film did not crystallize. This clearly shows that the antimony film is affected considerably by the

ambient gases before it reacts with potassium. The gases in the ambient vacuum[17,18] possibly react with the antimony film in its island form when the effective surface area of the film is very large. Moreover, the islands of the metal films are not completely flat at the surface,[19] and, therefore, some amount of gas could always be trapped between the substrate and the metal islands. A portion of the trapped gas is likely to be dissolved in the film when it becomes continuous with the deposition of more antimony or with potassium atoms to make a K_3Sb photocathode.[20]

Additionally, due to the island nature of the film a substantial portion of the surface area of the substrate is not covered by antimony. When potassium is added there is a possibility of free potassium being deposited in the open areas resulting in an inhomogeneity in the composition of K-Sb over the surface. Moreover, since the average size of the islands is quite large (~ 300 Å) at that average thickness, the reaction of potassium vapor with the islands may make the surface layer of the islands richer in potassium compared to the core of the islands. Thus, the nonuniformity of composition of the K-Sb layer may be a further reason for its poor sensitivity.

In contrast to this, potassium and antimony are evaporated simultaneously in the new method and there is little likelihood of antimony being affected by the reactive gases before it reacts with potassium. Moreover, there could not be much deviation from the correct composition required for the highest photoemission as the deposition of both metals are controlled to obtain maximum photoemission. These factors make it possible to obtain a K-Sb layer of such high sensitivity.

Similarly, the simultaneous evaporation of the two components at other stages of processing improves the sensitivity by depositing the optimum quantity of the two materials with a precision which is not possible in sequential evaporation.

The band gap in the photoconductivity measurement was taken to be the energy value at which the photo-conductive response ceases to rise very fast. The threshold-energy values for photoemission is computed by using the Kane formula[21] which is applicable to photoemission near threshold. According to this

$$Y \propto (E - E_T)^n,$$

where Y is the quantum yield, E_T is the threshold energy, E is the incident photon energy, and n is a constant whose value will be different for different modes of excitation and scattering. Fisher[22] computed

TABLE I. Values of the band gap, threshold energy, n, and electron affinity for the different photocathodes investigated.

Photocathode	Band gap	Threshold energy	n	Electron affinity
K_3Sb	1.8	2.2	1.28	0.4
K_2CsSb	1.2	1.9	1.08	0.7
Na_2KSb	1.1	1.8	1.35	0.7
$Na_2KSb(Cs)$	1.1	1.34	0.94	0.24

the photoemission threshold for the Na_2KSb photo-cathode in this way. He obtained 1.37 eV for the photo-emission threshold and 1.35 for n. In our Na_2KSb photocathodes the value of n was the same, though the threshold was slightly different. The electron affinity of the materials was determined from the threshold and the band-gap values. Table I gives the values of the band gap, threshold energy, n, and electron affinity for the different photocathodes investigated.

The band gaps of Na_2KSb and $Na_2KSb(Cs)$ are the same as those measured by our experiment. Spicer[23] also found the band gaps of these two materials to be the same, but equal to 1.0 eV. The electron affinity of the multialkali photocathode was reported by Spicer as being 0.55 eV, a value much higher than our values.

It is well known that the alkali antimonide photo-cathodes are extrinsic semiconductors.[24,25] The photo-emission near the threshold region is found to decrease if the photocathode is cooled. In our measurement of the multialkali photocathodes also, a large reduction in the threshold region photoemission was observed if the photocathode was cooled to 90 °K; it decreases to a value of 0.3 times the value at room temperature for the multialkali photocathode at 9000 Å. Such a decrease is possible only if photoemission from defect levels has a significant contribution near the threshold region. We determined the activation energies of the defect levels by studying the dependence of electrical conductivity on temperature at low temperatures.

The activation energy for the defect levels has been obtained from a plot of log(conductivity) versus $1/T$ and taking the slope as $\frac{1}{2}\Delta E$. This corresponds to the case where the Fermi level at a lower temperature lies in between the impurity levels and the nearest band.[26] The activation-energy values are indicated in Fig. 4. It can be seen that there are three distinct activation energies, e.g., 0.1, 0.21, and 0.34 eV for the multialkali photocathode. The activation energies for Na_2KSb photocathodes were nearly the same as those for multialkali photocathodes. The activation energies for K_3Sb and K_2CsSb were also found to be similar. This shows that the addition of cesium to Na_2KSb does not change the band gap and probably does not affect the defect-level scheme also.

The addition of cesium and antimony to a Na_2KSb photocathode lowers the electron affinity from a value of 0.7 to 0.24 and thereby increases the threshold wavelength and integral sensitivity. There has been some controversy about the role of cesium in multi-alkali photocathodes. Spicer[24] concluded from his measurements of optical properties and band gaps that cesium forms a monolayer on the surface of Na_2KSb and lowers the electron affinity; but other experiments performed later do not seem to support this monolayer theory. We shall discuss some of the important obser-vations which have been reported so far.

McCarroll et al.[27] observed using careful x-ray analysis that the lattice constant of Na_2KSb was 7.727 ∓ 0.003 Å, which after cesium addition increased to 7.745 ± 0.004 Å. They therefore concluded that some cesium must have been incorporated in the volume of
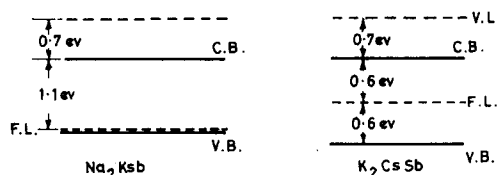
the material which is responsible for the increase in the lattice constant. By using Vegard's law the quantity of cesium was estimated to be 1% of the volume.

Hoene[28] reported a chemical analysis of high-sensi-tivity photocathodes. He found that the Cs content was between 3 and 7%. This amount was much more than required for monolayer formation by cesium. Garfield[29] also found by using a microbalance technique that about 10% of the weight of the whole cathode was due to the last few additions of Cs and Sb. This means that the cathode contained a much higher quantity of cesium than is necessary to make a monolayer at the surface.

Oliver[30] reported that the vapor pressure of cesium over the S-20 photocathode was four orders of magni-tude lower than it should be if one assumed free cesium at the surface.

Perhaps the most interesting information is provided in a recent paper by Dowman et al.[31] They observed by a scanning-electron-diffraction system that crystal-lites of Na_2KSb, NaK_2Sb, and K_2CsSb coexist in S-20 photocathodes, and that the high-sensitivity photo-cathodes are primarily composed of Na_2KSb with a layer of K_2CsSb at the surface. They also observed that the surface layer of K_2CsSb was formed during the last stage of photocathode processing when cesium and antimony were added. Since no potassium is added at this last stage and a large amount of free potassium is required to form the K_2CsSb layer, the potassium atoms should migrate from the Na_2KSb material to the surface.

The Na_2KSb material is known to be a highly p-type material and the K_2CsSb as near intrinsic.[32] It is possible to construct a band-bending scheme at the surface with the assumption that the volume of the multialkali material is Na_2KSb and the surface layer is K_2CsSb (Fig. 5). Using the band-gap and the elec-tron affinity values of our measurement we obtain a threshold energy of 1.3 eV, which is in good agreement with our experimentally measured value of 1.34 eV.

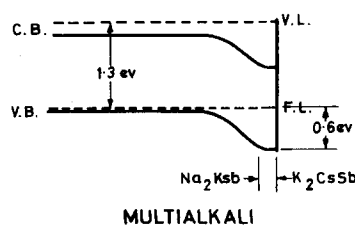ENERGY BAND DIAGRAM OF Na_2KSb & K_2CsSb

MULTIALKALI

FIG. 5. The band bending at the surface of multialkali photocathodes.

The assumption of the formation of a surface layer of K_2CsSb instead of free cesium explains the experimental observations. The amount of cesium required would be much more than one monolayer for the formation of a K_2CsSb layer.

Potassium atoms required to form the K_2CsSb layer is obtained from the volume of Na_2KSb, probably as a result of substitution by cesium atoms. According to Kansky,[33] the cesium atoms can replace the potassium atoms as the equilibrium constant for this reaction is very high. As cesium atoms are larger in size than the potassium atoms, an expansion of the lattice is expected which has been observed experimentally. Also, the vapor pressure of cesium over K_2CsSb would be very much lower than could be expected with free cesium at the surface.

IV. CONCLUSION

A new technique for the processing of alkali antimonide photocathodes has been presented. It does not require any initial antimony layer and is capable of giving high sensitivity because the antimony film is not affected by gases as in conventional techniques. The band-gap, electron affinity, and defect-level activation energies of these photocathodes have been determined. The role of cesium has also been explained; it is concluded that cesium does not exist as free atoms on the surface but in the form of a K_2CsSb layer.

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