Activation of the Na_2KSb photocathode with Cs and O_2 at lowered temperatures [1]

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Abstract

Several attempts to activate the Na_2KSb photocathode with Cs and O_2 at RT failed due to the growth of a thick intermediate oxide layer, consisting of Sb, Na and K oxides, and thus to the formation of a highly alkali-deficient Na_2KSb base layer. The spectral sensitivities in the near IR region were very low because these defects had contributed to a reduced escape depth of excited electrons and an increased photoelectric threshold energy. A novel activation at 140 K has therefore been performed in order to promote the adsorption of Cs and to prevent the harmful diffusion of O into the near-surface region of the Na_2KSb and the strong diffusion of K from the interior of the Na_2KSb towards its surface. During cooling-down from RT to 140 K, the photosensitivity of the Na_2KSb dropped to about one third of the initial value measured at RT, due to an increase in the electrical resistivity of the Na_2KSb, thus causing a space charge to arise, which attenuated photoemission. The $Cs-O_2$ cycles resulted in a relatively high photosensitivity of 250 $\mu A/lm$, if its initial drop is taken into account. During heating to RT, the photosensitivity first increased to 370 $\mu A/lm$ at about 210 K, and then, in the range between 210 K and RT, it unexpectedly decreased from 370 to 100 $\mu A/lm$. This behaviour was attributed to defects which caused the build-up of a surface potential barrier, such as the reduction of Cs (sub)oxides, which was enabled by the enhanced diffusion of K from the interior of the Na_2KSb into the deposited Cs.O surface film at temperatures above 210 K.

1. Introduction

The photoemission properties, in the near IR region, of the thick, polycrystalline, p-type bialkali–antimonide Na_2KSb films with a forbidden band gap of 1.0 eV and an effective electron affinity of 0.7 eV can be improved when they are activated with Cs and Sb. If the so-called 'yo–yo' procedure, which takes place at elevated temperatures in UHV and consists of alternating introductions of Cs vapour and evaporations of Sb, is used, then an integral sensitivity of over 500 $\mu A/lm$ can be achieved, while the effective electron affinity of a $Na_2KSb(Cs,Sb)$ photocathode amounts to 0.3 eV [1].

It is well-known that some compounds of the O–Cs binary system, such as Cs (sub)oxides which are richer in Cs and contain O^{2-} ions, are very effective when lowering the effective electron affinity towards negative values, as is the case with various III–V photocathodes [2]. In order to study the deposition of Cs and O_2 onto a textured and homogeneous Na_2KSb film, we have constructed a cluster model of a high-efficiency $Na_2KSb(Cs,O)$

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photocathode, consisting of a strongly p-type doped Na_2KSb base layer, and an overlayer of the caesium suboxide $Cs_{11}O_3$, about one-cluster size thick. The latter has already proved to be the most effective in lowering of the effective electron affinity to a negative value when deposited onto a p-type GaAs monocrystal [3]. A small increase in photosensitivity was also observed in the case of slightly oxidized Cs_3Sb [4] and $Cs_{2.5}K_{0.5}Sb$ [5] due to the growth of $Cs_{11}O_3$, which was detected by means of XPS in the near-surface region of Cs_3Sb and $Cs_{2.5}K_{0.5}Sb$, with a thickness of 2 and 1.4 nm, respectively.

The structure of the $Cs_{11}O_3$ exhibits O atoms occupying internal positions surrounded by Cs atoms at different atomic distances. The outermost Cs atoms have a quasi-metallic structure due to the quantum size effect of the conduction electrons [6]. Considering the slight oxidation of the $Cs_{2.5}K_{0.5}Sb$ photocathode [5], some conclusions have been extended to the Na_2KSb photocathode. The formation of a very thin $Cs_{11}O_3$ surface film on the Na_2KSb substrate can thus improve the photoemissive properties of the latter by two mechanisms:

(1) Real electron affinity is reduced by two combined effects: the electron quantum size effect in the $Cs_{11}O_3$ clusters, and the strong electric dipole field formed by the interface bialkali antimonide/caesium suboxide.

(2) The amount of downward band-bending increases, as well as the band-bending region becomes narrower, since the bialkali–antimonide bulk becomes more p-type. This is due to the increased density of alkali vacancies (acceptor centres) arising through diffusion of mobile alkali atoms into the thin $Cs_{11}O_3$ surface film.

Both mechanisms contribute to lowering of effective electron affinity. The approximate energy band diagram is presented in Fig. 1, assuming that the photoelectric threshold energy of the $Na_2KSb(Cs,O)$ photocathode is reduced to about 1.0 eV, and that the average thickness of the optimum $Cs_{11}O_3$ overlayer amounts to 1.5 nm [5].

At a temperature of 140 K, one monolayer of $Cs_{11}O_3$ was formed on a metallic Cs film, deposited on Cu(110), when exposing its surface to 0.3 L O_2 [7]. These data were used when we calculated the amount of Cs contained in one monolayer of $Cs_{11}O_3$. Supposing a sticking coefficient of O_2 equal to 1 at
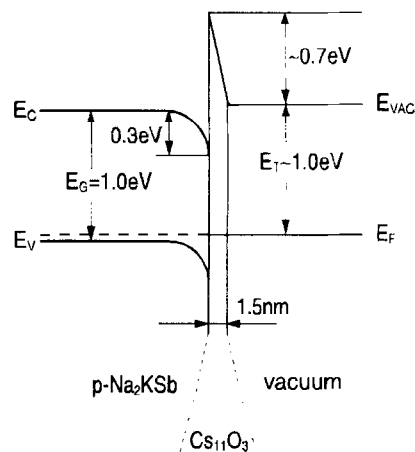

Fig. 1. The approximate energy band diagram for the cluster model of a high-efficiency $Na_2KSb(Cs,O)$ photocathode, consisting of a strongly p-type doped Na_2KSb base layer and an overlayer of $Cs_{11}O_3$ about one-cluster size thick.

140 K, then 0.2 ML O_2 was adsorbed during the formation of 1 ML $Cs_{11}O_3$, since 1 ML $O_2 = 7.7 \times 10^{14}$ cm^{-2}. The amount of Cs in 1 ML $Cs_{11}O_3$ was estimated to be a little less than 3 ML Cs, if 1 ML Cs $= 4.2 \times 10^{14}$ cm^{-2}.

The aim of the preliminary experiments was to study the deposition of Cs and O_2 onto a textured and homogeneous Na_2KSb base layer, following the yo–yo procedure, used in the case of GaAs(Cs,O) photocathodes, which took place at RT in UHV [3]. After some trials, it was clear that the Na_2KSb photocathode was not inert during the deposition of Cs and O_2 at RT. A major part of the experimental work therefore comprised the activation of the Na_2KSb with Cs and O_2, which took place at temperatures much lower than RT, in order to promote the adsorption of a Cs overlayer consisted of about three monolayers, and to prevent the harmful diffusion of O into the near-surface region of the Na_2KSb and strong diffusion of mobile alkali atoms from the interior of the Na_2KSb towards its surface. This is because both diffusion processes were believed to take place at RT, enabling much faster growth of the intermediate oxide layer. By lowering temperature below RT, we expected a greater condensation coefficient of Cs, as well as decreased mobilities of O and alkali atoms by several orders of magnitude, as the relating diffusion constants are exponentially dependent on temperature.

2. Experimental

A homogeneous, semitransparent Na_2KSb base layer with a strong texture was synthesized in situ by a standard procedure, at elevated temperatures in UHV, on the curved fibre-optics cathode lens of a second-generation image-intensifier tube. A cross-section of the tube assembly is schematically shown in Fig. 2. A low work function coating was deposited at a temperature of 140 K onto the Na_2KSb photocathode by alternately exposing its surface to Cs and O_2 until the photocurrent signal was maximized, whereas the image tube was pumped by an appendage sputter-ion pump (SIP), containing a hot filament to strike the discharge in UHV. During activation, the residual pressure in the tube was in the range of 10^{-10} mbar.

High-purity Cs was evaporated by resistive heating from a sliding Cs source. This contained a standard Cs dispenser (SAES Getters) embedded in a closed metal pipe with a small aperture. The evaporating divergent Cs atomic beam covered only the photocathode's surface and left the walls of the image tube practically Cs free. The Cs dispenser was thoroughly degassed at elevated temperatures while synthesizing the Na_2KSb photocathode.

O_2 was introduced from a solid state O_2 source based on a thermally decomposable copper oxide. This source consisted of a resistive wire with a thin, spirally wound Cu wire. Its surface was oxidized to CuO at elevated temperatures in an O_2 residual atmosphere. Before arriving at the activation site, O_2 readily reacts with the residual gases, such as H_2 and CH_4, adsorbed on the internal walls. To prevent a decrease in purity, the O_2 source was mounted in an additional housing connected to the image tube with a short section of Cu tubing. During the $Cs–O_2$ cycles, the partial pressure of O_2, which was measured by means of the appendage SIP [8], amounted to between 2×10^{-9} and 5×10^{-8} mbar.

Photosensitivity was observed continuously in the transmission mode by illuminating the fibre-optics cathode lens with an incident white light, which was transferred directly to the deposited photosensitive layer, and measuring the photocurrent between the photocathode and the anode cone.

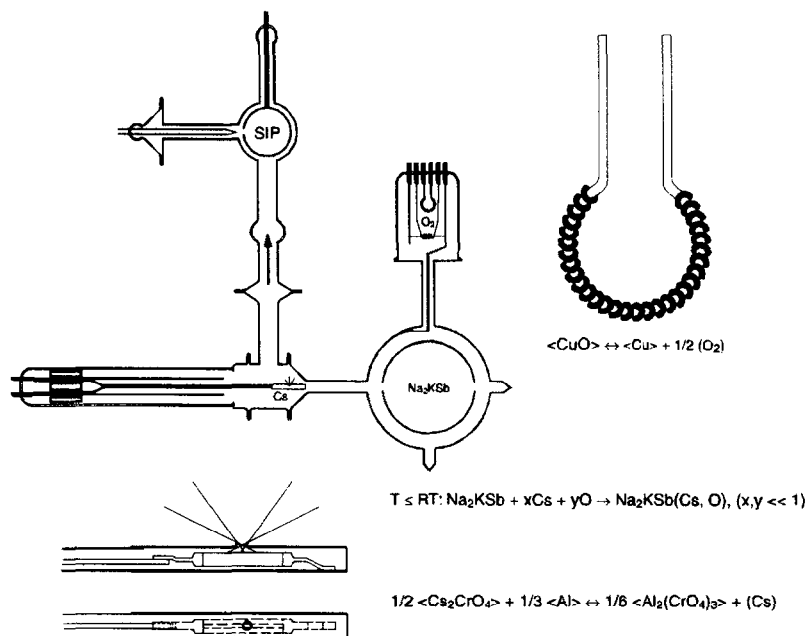The deposited Na_2KSb photocathode was cooled down indirectly by cooling-down the fibre-optics

$<CuO> \leftrightarrow <Cu> + 1/2\ (O_2)$

$T \le RT: Na_2KSb + xCs + yO \rightarrow Na_2KSb(Cs, O),\ (x,y \ll 1)$

$1/2\ <Cs_2CrO_4> + 1/3\ <Al> \leftrightarrow 1/6\ <Al_2(CrO_4)_3> + (Cs)$

Fig. 2. The cross-section of the tube assembly, consisting of an image tube with the incorporated Na_2KSb photocathode, a solid state O_2 source, a sliding Cs source and an appendage sputter-ion pump (SIP) with a hot filament.

cathode lens from outside using a laboratory cooling system. It consisted of two hermetically untight chambers, separated by a glass window, and attached to the cathode lens and the light source, respectively, and of two thin metal pipes, one connecting the first chamber and a Dewar flask filled with liquid N_2 (in order to cool down the photocathode layer), and the other connecting the second chamber and a cylinder filled with dry gaseous N_2 (in order to prevent condensation of water vapour onto the glass window). The temperature was measured by a thermocouple, which was attached to the cathode lens in order to assure a good thermal contact.

3. Results

3.1. RT activation

Several attempts were made to activate the Na_2KSb photocathode with Cs and O_2 at RT, but they ended in failure, i.e. the obtained integral sensitivities and the spectral sensitivities in the near IR region, especially, were very low. Regarding photosensitivity (S) during the course of the activation process at RT, the corresponding photocurrent (I) reached its maximum value in the first Cs–O_2 cycle.

The latter consisted of one evaporation of Cs, lasting until I first rose to a peak value and then dropped to 10 to 20% of this peak value, and of one introduction of O_2, lasting until I finally increased to a value which was only somewhat higher than the previous peak value. Such a small increase in S led us to the conclusion that some oxidation of the base layer must have taken place. This conclusion was also supported by measurements indicating that O_2 was introduced at a relatively high partial pressure of O_2, which was of the order of 10^{-7} mbar, whereas the Na_2KSb with deposited Cs was exposed to about 10 L O_2 before the final I rise.

3.2. Low temperature activation

The activation of the Na_2KSb with Cs and O_2 which was performed at 140 K, in order to experimentally approach the cluster model of the $Na_2KSb(Cs,O)$ photocathode, is presented in Fig. 3. During the activation process, S in the transmission mode and temperature of the cathode lens, as well as the residual pressure and the partial pressure of O_2, were measured. The behaviour of the corresponding I was as follows:

• During the cooling-down of the Na_2KSb photocathode, from RT to 140 K, I first rises a little
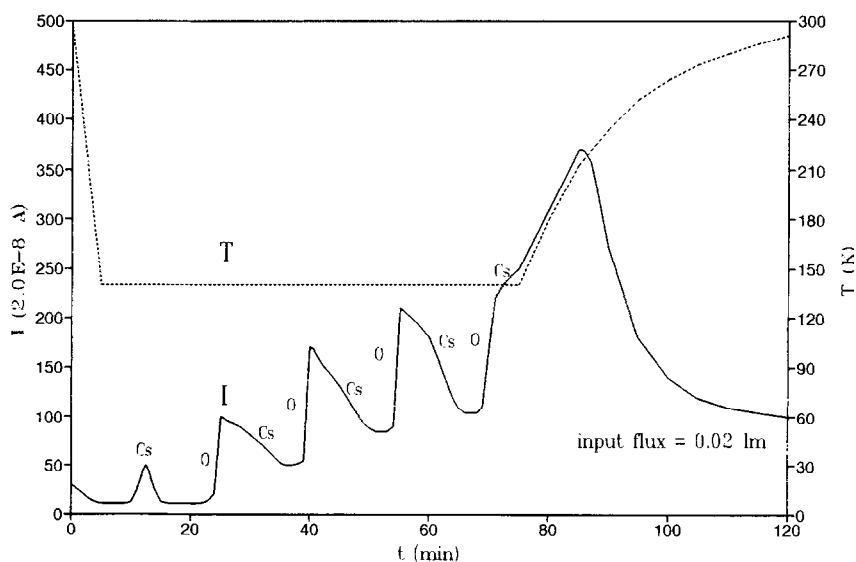
Fig. 3. Variation in photocurrent (I) and temperature (T) during: cooling-down of the Na_2KSb photocathode, from RT to 140 K, activation of the Na_2KSb photocathode with Cs and O_2 at 140 K, and heating of the $Na_2KSb(Cs,O)$ photocathode, from 140 K to RT. The photocathode layer was illuminated by an incident white light flux of about 0.02 lm intensity.

(not visible in Fig. 3) and then drops to about one third of the initial value measured at RT.

• The activation process starts with the evaporation of Cs accompanied by an I rise to a peak value. Cs is continuously evaporated until I drops to 10 to 20% of this peak value. Introduction of O_2 then follows, and lasts until I reaches a first maximum value.

• The Cs–O_2 cycles are repeated until I no longer increases. Each cycle comprises one evapora-

Fig. 4. The oxidation process of the Na_2KSb photocathode covered by a thin Cs overlayer during the first introduction of O_2 at RT: (i) Partial oxidation of the thin Cs overlayer, and diffusion of O towards the Na_2KSb, is enabled by the dissociative adsorption of O_2 onto the outermost Cs layer and the distribution of O beneath this layer. (ii) The growth of a thick intermediate oxide layer consisting of Sb, Na and K oxides is enabled by the diffusion of O through a growing K (sub)oxide layer into the near-surface region of the Na_2KSb, and the strong diffusion of K from the interior of the Na_2KSb into its near-surface region and further into the partly oxidized Cs overlayer. (iii) The final growth of a thin Cs.O surface film starts after the intermediate oxide layer some nm thick (in which the diffusion processes cease) has been grown.

tion of Cs lasting until I drops to about 50% of the previous maximum value, and one introduction of O_2 lasting until I rises to a new maximum value. An S of about 250 $\mu A/lm$ is obtained at 140 K.

• During the heating of the activated photocathode, from 140 K to RT, I first increases, until a maximum S of about 370 $\mu A/lm$ is obtained at about 210 K. During heating from 210 K to RT, I unexpectedly decreases and an S of about 100 $\mu A/lm$ is obtained at RT.
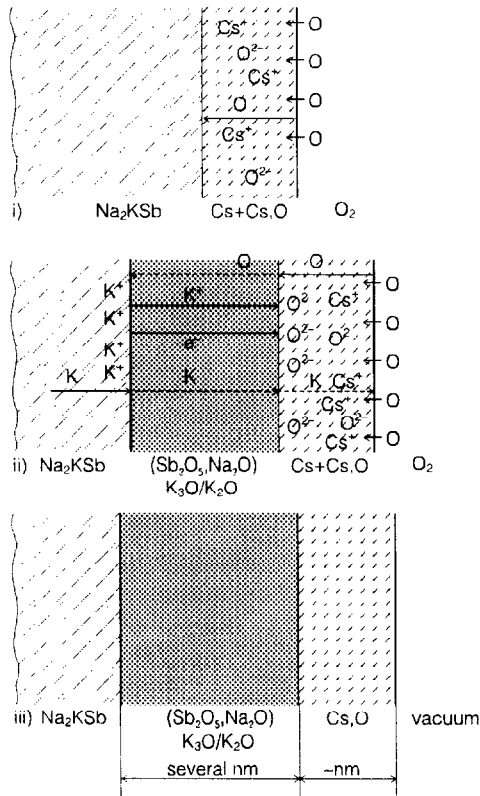
4. Discussion

4.1. The oxidation kinetics of Na_2KSb–Cs at RT

The low S obtained when activating the Na_2KSb photocathode with Cs and O_2 at RT has been attributed to the growth of a thick intermediate oxide layer, consisting of Sb, Na and K oxides, with a large forbidden band gap, a high work function and a reduced photoelectron mean free path for electron–phonon interactions (compared to Na_2KSb), and hence to the formation of a highly alkali deficient Na_2KSb base layer, in which the photoelectron mean free path is reduced because of additional energy losses while interacting with alkali vacancies. These defects contributed to a reduced escape depth of excited electrons and an increased photoelectric threshold energy.

Taking into account the Mott–Cabrera theory on the growth of thin n-type oxide films, and an XPS study of $Cs_{2.5}K_{0.5}Sb$ photocathode oxidation where diffusion of the mobile alkali atoms plays an important role [5], then the oxidation process, during the first introduction of O_2 at RT, of the Na_2KSb photocathode covered by a thin Cs overlayer can be described by a three-step model, which is also presented in Fig. 4:

(i) Partial oxidation of the thin Cs overlayer, and diffusion of O towards the Na_2KSb, is enabled by the dissociative adsorption of O_2 molecules onto the outermost Cs layer and the distribution of O atoms beneath this layer [9].

(ii) Growth of a thick intermediate oxide layer consists of:

• initial growth of a thin n-type K (sub)oxide layer between the Na_2KSb base layer and the partly

oxidized Cs overlayer according to the Mott–Cabrera theory;

• oxidation of the Sb^{3-} species to Sb^0 and further to Sb^{5+}, the latter forming Sb_2O_5, and the oxidation of Na to Na_2O, due to the diffusion of O through the thin K (sub)oxide layer into the near-surface region of the Na_2KSb [5];

• the additional growth of a thick K (sub)oxide layer, due to the strong diffusion of K from the interior of the Na_2KSb (which becomes thus alkali-deficient) into its near-surface region, this diffusion resulting in a thick oxide layer, with the following sequence of K compounds of the O–K binary system: K_3O/K_2O (suboxide/oxide), which does not favour photoemission [5].

The growth of the thick intermediate layer is maintained by diffusion of K through the K (sub)oxide layer into the partly oxidized Cs over-layer, where reduction of Cs (sub)oxides by K takes place. The free Cs enables the continuous dissociative adsorption of O_2 and distribution of O beneath the outermost Cs layer.

(iii) Final growth of a thin Cs,O surface film starts after the intermediate oxide layer some nm thick (in which the diffusion processes cease) has been grown [5], and lasts until I rises to a peak value.

According to this model, the kinetics of the thick intermediate oxide layer growth is much faster than the logarithmic rate.

4.2. The photoemission instability of $Na_2KSb(Cs,O)$

The small rise and the following drop of I to one third of the initial value during cooling-down of the Na_2KSb photocathode, from RT to 140 K, can be attributed to certain temperature-dependent semiconduction effects influencing S, such as the position of the Fermi level and hence the amount of favourable band-bending, and the electrical resistivity. This is because an additional lowering of the Fermi level due to the decrease in temperature results in enhanced downward band-bending, reflecting in a small rise of S at the beginning of the cooling-down. In the case of continuous photoemission, the electrons emitted from the crystal must be simultaneously replaced, otherwise an arising space charge can completely prevent photoemission. A certain electrical conductivity of the photocathode film is therefore necessary.

According to our calculations, the electrical resistivity of Na_2KSb can increase by at least three orders of magnitude (from about 1 to about 10^3 Ω cm) during cooling-down from RT to 140 K, thus causing a certain quantity of space charge to arise, which attenuates photoemission.

The $Cs–O_2$ cycles taking place at 140 K are accompanied by normal behaviour of I, increasing gradually to a maximum value. The obtained S of 250 $\mu A/lm$ is relatively high, if the initial drop in the corresponding I was taken into account.

During the heating of the activated photocathode, from 140 to 210 K, S increases from 250 to about 370 $\mu A/lm$, since the electrical conductivity increases strongly, the Fermi level is lowered and the band-bending region becomes narrower. These changes are due to a gradual increase in the density of acceptor centres caused by the diffusion of mobile alkali atoms from the interior of the Na_2KSb into the deposited Cs,O surface film.

During the heating of the activated photocathode, from 210 K to RT, S decreases from 370 to 100 $\mu A/lm$. The decrease in I can be attributed to defects, which cause the build-up of a surface potential barrier and have been already mentioned when explaining the oxidation kinetics, during the first introduction of O_2 at RT, of the Na_2KSb photocathode covered by a thin Cs overlayer. Thus, the resulting S is most probably affected by:

• the reduction of Cs (sub)oxides at temperatures above 210 K, which is enabled by the enhanced diffusion of K, occupying interstitial octahedral crystal sites in the cubic DO_3 microcrystal structure of Na_2KSb, and possible slight diffusion of Na, occupying the corresponding interstitial tetrahedral crystal sites [10], from the interior of the Na_2KSb into the deposited Cs,O surface film. According to thermodynamic considerations, the reduction of Cs (sub)oxides is feasible, since the standard Gibbs free energy of formation of various K (sub)oxides, as well as of Na (sub)oxides, is more negative than that of the corresponding Cs (sub)oxides [11].

5. Conclusion

Activation of the Na_2KSb photocathode with Cs and O_2 at 140 K gave an integral sensitivity of 250 $\mu A/lm$. The expected photosensitivity of about 700

$\mu A/lm$, which might have been obtained, if, during heating of the activated photocathode from 140 K to RT. the photocurrent signal had increased by a factor of three as a consequence of increasing electrical conductivity, was not attained. The Na_2KSb photocathode is obviously not inert to the deposited Cs,O surface film, since this system is not thermodynamically stable at temperatures above 210 K due to the enhanced diffusion of mobile alkali atoms from the interior of the Na_2KSb into the Cs,O surface film, enabling reduction of favourable Cs (sub)oxides. However. if the expected photosensitivity had been attained, it would have been close to a reported photosensitivity obtained surprisingly through the activation of Na_2KSb with Cs and O_2 at RT [12]. Based on our experience with RT and novel low temperature activations of the Na_2KSb photocathode with Cs and O_2, we doubt that such a high value of photosensitivity has ever been experimentally achieved.

Acknowledgements

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