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Structure of multialkali antimonide photocathodes studied by x-ray photoelectron spectroscopy

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Abstract. From a comparison of the relative intensities of photoelectrons with different escape depths for Na, K, Cs, and Sb in several multialkali antimonide photocathodes covering a range of high photosensitivities, a model of the structure of these surfaces can be given. In particular, the results indicate for Na₂KSb(Cs), the S-20, a surface layer consisting of K₂CsSb and NaK₂Sb ~ 30 Å thick over a base layer of Na₂KSb.

1. Introduction

Since its discovery in 1955 by Sommer the Na₂KSb(Cs) or S-20 photocathode has been the subject of many investigations. In his book Sommer (1968) gives a very complete account of the early work done on this surface. In particular, the structure of this surface, including the role of the Cs, has commanded the attention of workers since its inception and continues to this day. The early interpretation was that a Cs film of monatomic dimension formed over a bulk substrate of Na₂KSb causing a favourable dipole formation and thereby a reduced surface barrier. This was based on the finding that the absolute amount of Cs was very small and that optical absorption and crystal structure of Na₂KSb were not changed by the addition of Cs. However, various observations by McCarroll *et al* (1971) showed that in Na₂KSb(Cs) the lattice constant of the cubic Na₂KSb is increased by a small amount from 7.724 to 7.742 Å, indicating a bulk effect of Cs. More recently Dowman (1973) and Dowman *et al* (1975) have proposed from scanning electron diffraction studies that Na₂KSb(Cs) consists of a base layer of Na₂KSb with a surface consisting of K₂CsSb. A similar model has been reported by Dolizy *et al* (1977) from x-ray diffraction studies. Most recently Holtom *et al* (1979) have, from Auger profiling studies, concluded that the low work-function is derived from a Cs–Sb dipole layer.

As part of a much larger study on the fundamental electronic structure of multialkali antimonide photocathodes, using the technique of x-ray photoelectron spectroscopy (XPS), we have obtained results that are consistent with the heterojunction model of this surface. A fairly extensive paper is being prepared for publication on the complete results of our studies on this system. The equipment and measurement techniques have been described previously (Bates *et al* 1980). All surfaces were prepared and analysed in

§ Also with the Stanford–NASA Joint Institute for Surface and Microstructure Research.

ultra-high vacuum ($\sim 1 \times 10^{-10}$ Torr). The data reported were corrected for the kinetic energy dependence of the spectrometer sensitivity, the sensitivity factors of Na, K, Cs, and Sb, and the theoretical photoelectric cross-sections of Scofield (1976) were used. Carbon, oxygen and other contaminants were not detected during our experiments and hence can be eliminated as having any effects on the results.

2. Experimental results

Twelve Na₂KSb(Cs) or S-20 photocathodes were studied. The composition near the surface of these photocathodes, measured by the relative intensities of the characteristic spectra of the component elements, is shown in table 1 along with their photoelectric properties. The data reported were calculated from the xps sensitivity factors or standard relative intensities of the corresponding photoelectron peaks, Na 1s, Na 2s, K 2p, etc. These sensitivity factors were determined (Galan 1980) from experimental data in the literature, obtained with the same type of xps spectrometer as ours, in order to correct for the energy dependence of the spectrometer sensitivity. For the energy dependence of the photoelectron escape depth, the approximate 'universal' relation suggested by Wagner (1978) was used, since no experimental data are available for the alkali antimonides. For further details see Galan (1980).

From a study of results in table 1 the following observations may be made.

(a) These photocathodes appear to be formed by alkali-saturated antimonides of the form A₃Sb. This agrees with other studies (Dowman *et al* 1975, Dolizy *et al* 1977).

(b) The concentration of Na in the bulk below a surface layer of the order of xps escape depths (~ 20 Å) appears to correspond to Na₂KSb. All studies on this surface are in agreement with this.

(c) The concentration of Na in a surface layer of the order of xps escape depths is

Table 1. Photoelectric properties† and composition of Na₂KSb(Cs) photocathodes from xps (Al K α = 1487 eV).

S ($\mu\text{A lm}^{-1}$)	E_T (eV)	Y_m (%)	Apparent atomic density relative to Sb 3d ($L=19$ Å) of:					
			Na		K	Cs		
			2s $L(\text{Å})=26$	1s 10	2p 23	4d 26	3d 16	3p 10
230	1.4	30.0	1.84	1.54	0.84	0.39	0.55	0.54
220	1.5	32.0	1.69	1.15	1.40	0.72	0.81	0.95
200	1.5	28.0	2.0	1.39	0.94	0.77	0.90	—
180	1.4	29.0	1.69	1.36	0.82	0.51	0.75	0.74
180	1.5	27.0	1.31	1.31	0.84	0.83	0.95	0.86
140	1.5	24.0	1.69	0.98	1.52	0.37	0.49	0.60
130	1.5	19.0	1.57	0.72	1.34	1.27	1.06	1.23
70	1.6	10.5	1.75	1.25	0.85	0.27	0.45	—
70	1.5	12.5	1.75	1.19	1.60	0.38	0.50	0.64
65	—	—	1.84	1.19	1.46	0.48	0.59	—
65	1.6	13.5	1.84	0.82	0.72	0.83	0.77	1.01
60	1.6	13.5	1.65	1.15	0.70	0.56	0.71	0.80

† S, photosensitivity; E_T , photoemission threshold; Y_m , maximum quantum efficiency; L, escape depth.

much smaller than that corresponding to Na_2KSb . Hoene (1972) and Garfield (1972) had made similar observations. However, the observed intensity of Na 1s photoelectrons, with very short escape depth, near the lattice constant of alkali antimonides, though small and indicating a smaller concentration than in Na_2KSb , is too large if a surface layer consisting of K_2CsSb alone is assumed, as proposed by Dowman *et al* (1975). If no Na is assumed in the surface layer this would seem to be much thinner than 10 Å.

(d) The relative intensities of the Cs xps spectrum show conclusively, first, that the Cs content of S-20 photocathodes is much larger than would correspond to a monolayer (Cs/Sb relative atomic density smaller than 0.35 when measured by Cs 3d/Sb 3d), and second, that Cs is incorporated in the bulk at least in a thickness of about 15 Å. The relative intensities of Cs 3p, 3d and 4d xps peaks suggest a surface layer whose thickness is of the order of the xps escape depths (20–30 Å) where the Cs and Sb atomic densities are about the same, over a bulk very deficient in Cs.

These results are in very good agreement with the studies by Dowman *et al* (1975) and Dolizy *et al* (1977). They detected the appearance of the K_2CsSb phase after Cs and Sb deposition on Na_2KSb photocathodes during the last stage of S-20 processing. *In situ* microbalance investigations by Garfield (1972) and our own investigations (L Galan and CW Bates Jr 1975, unpublished results, Galan 1980) give strong support to the theory that Na_2KSb photocathodes probably consist of a thin NaK_2Sb surface layer with K excess, over a Na_2KSb bulk with an alkali deficiency. When Cs and Sb are added on the surface Cs_3Sb is not formed because it is probably unstable in the presence of NaK_2Sb and Na_2KSb . By diffusion of K, Cs and Sb the phase K_2CsSb and Na_2KSb are formed out of the NaK_2Sb layer. This interpretation of the S-20 processing is supported by two experimental observations. First, Dowman *et al* (1975) found that by Cs and Sb deposition, a NaK_2Sb film transformed into Na_2KSb and K_2CsSb , while its sensitivity increased nearly two orders of magnitude. Second, it has been reasonably well established that the best S-20 photocathodes are obtained from optimised Na_2KSb photocathodes (Garfield 1972, Feldner *et al* 1971), the optimisation consisting of surface activation by K and Sb deposition.

However, there are some experimental observations difficult to interpret with the mode $\text{K}_2\text{CsSb}/\text{Na}_2\text{KSb}$ first proposed for S-20 photocathodes by Dowman *et al* (1975). First, they detected the NaK_2Sb phase in all S-20 photocathodes. Second, Dolizy *et al* (1977) found that when adding Cs and Sb to a photocathode made of Na_2KSb and NaK_2Sb , the phase K_2CsSb appeared but the Na_2KSb and NaK_2Sb phases did not vary in intensity. Third, our xps intensity measurements show that Na is present together with Cs in the surface layer (see (c) above, and (g) and (h) below).

(e) A calculation using Cs 3p, 3d, 4d relative intensities, assuming Cs is only in a surface layer of thickness D , gives values for D from 15 to 95 Å, with an average value of $D \sim 30$ Å. For this calculation no assumption is necessary about the Cs content of the surface layer.

(f) If the ratio of Cs to Sb atomic densities is assumed 1:1 in the surface layer, then a calculation from Cs 3d relative intensities yields D from 10 to 60 Å, with an average value $D \sim 20$ Å. A correlation is obtained with values calculated in (e) above, their ratio being $1.5 \pm 20\%$. This may mean either a systematic error in the sensitivity factors or that the Cs/Sb relative atomic density is smaller than 1, i.e., that at least another phase not containing Cs is present in the surface layer.

(g) If no assumption is made about the ratio of Na to Sb atomic densities in the surface layer then a calculation from Na 1s relative intensities yields D from 1 to 10 Å, with an average value $D \sim 5$ Å. Hence, the presence of Na together with Cs in the surface layer

has to be accepted. Recent AES investigations by Lindfords (1977) also detected the presence of Na in the surface layer of S-20 photocathodes.

(h) Assuming for D the values calculated in (e) and (f) above, a calculation of the Na/Sb relative atomic density in the surface layer from Na 1s relative intensities yields values from 0.7 to 1.5, with an average value of $1.1 \pm 30\%$. In the bulk it was assumed that the Na/Sb relative atomic density = 2.

Considerations (c), (g), and (h) above indicate that the high-yield ($\sim 200 \mu\text{A lm}^{-1}$) photocathodes of table 1 had a high Na content in their surface layer. In the last stage of S-20 processing, when Cs and Sb are deposited on a photocathode formed by NaK_2Sb over Na_2KSb , one can expect diffusion of all the elements, with rates decreasing from Cs, K, Na to Sb. The formation of new phases should also be expected. The possible phases are: Na_2KSb , NaK_2Sb , K_2CsSb , Na_2CsSb and Cs_3Sb . The two first ones seem unlikely in the surface layer after Cs deposition. Cs_3Sb is probably unstable in the presence of K and Na; both Dowman *et al* (1975) and Dolizy *et al* (1977) did not detect the Cs_3Sb phase in any S-20 photocathode, and it is very well known that both Na and K easily displace Cs (Kansky 1972). Hence, it seems reasonable to expect the formation of K_2CsSb and Na_2CsSb in the surface layer. The composition of S-20 photocathodes of table 1 could be explained very well by a surface layer of K_2CsSb and Na_2CsSb over a bulk of Na_2KSb .

However, several experimental observations indicate that the compound Na_2CsSb is not stable and that it does not occur. First, Dowman *et al* (1975) and Dolizy *et al* (1977) did not detect any Na-Cs-Sb compound in any S-20. Second, Dowman *et al* (1975) tried to form a Na-Cs-Sb compound by evaporating Na over Cs_3Sb with no positive result. Third, similar experimental evidence has been obtained by Sommer (quoted by Lindfords 1977), i.e., there is no stable compound in the system Na-Cs-Sb.

An attempt was made in our experimental set-up to synthesise Na_2CsSb with the results given in table 2 with sensitivity $S = 10 \mu\text{A lm}^{-1}$, photoemission threshold $E_T = 1.5 \text{ eV}$, and maximum yield $Y_m = 0.014$. However, xps quantitative analysis revealed the

Table 2. Composition of a $\text{Na}_3\text{Sb}(\text{Cs})$ photocathode from xps (Al $K\alpha = 1487 \text{ eV}$).

Apparent atomic density relative to Sb 3d ($L = 19 \text{ \AA}$)† of	
Na 2s ($L = 26 \text{ \AA}$)	3.0
1s ($L = 10 \text{ \AA}$)	2.8
Cs 4d ($L = 26 \text{ \AA}$)	0.07
3d ($L = 16 \text{ \AA}$)	0.173
3p ($L = 10 \text{ \AA}$)	0.31

† L escape depth.

composition in table 1 and showed that the photocathode was actually Na_3Sb with a Cs monolayer or fraction of monolayer on the surface. Probably this was also the structure of the Na_2CsSb photocathodes reported by Denisov and Klimin (1976), as our sensitivity, threshold and maximum yield were in close agreement with theirs.

It seems that McCarroll (quoted by Lindfords 1977) has given theoretical reasons for the lack of a stable compound in the system Na-Cs-Sb, based on the large differences in the sizes of Na and Cs atoms. Considerations of Madelung energy and ionic radii suggest that a Na-Cs-Sb compound is probably unstable and breaks up into corresponding monoalkali antimonides.

Therefore it can be concluded that there are strong experimental and theoretical reasons indicating that no stable Na–Cs–Sb is possible. The only phases by means of which Na can be present in the surface layer of S-20 photocathodes are NaK_2Sb and Na_2KSb .

Hence, during the last stage of S-20 processing when Cs and Sb are added over the NaK_2Sb surface layer of a Na_2KSb photocathode, the following probably occurs. Cs and Sb diffuse into the NaK_2Sb layer, forming K_2CsSb . K atoms diffuse into the layers just formed by Cs and Sb deposition, forming more K_2CsSb . But also Na atoms diffuse toward the surface. Because of this and because Na was already in the surface layer before Cs and Sb deposition and absorption, Na should be expected in the surface layer of S-20 photocathodes. Na_2KSb , NaK_2Sb and K_2CsSb are probably the only phases in equilibrium when Na, K, and Cs are present, and these phases can be expected in the surface layer of S-20 photocathodes. These phases are the only ones detected by x-ray and electron diffraction (Dowman *et al* 1975, Dolizy *et al* 1977). These results are consistent with the work of Dolizy *et al* (1977) who found that K_2CsSb appeared but that the Na_2KSb and NaK_2Sb phases did not vary in intensity.

The net effect of all these phenomena is the diffusion of K and Na, but mainly K, from the bulk toward the surface layer. The Na_2KSb bulk thus becomes more alkali-deficient and more strongly p-type. This is consistent with the well known fact that the conductivity, already high, of the Na_2KSb photocathode increases further during this

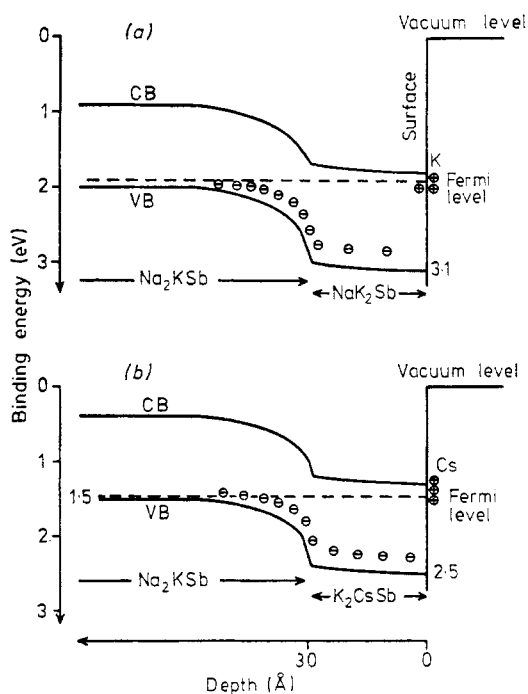


Figure 1. Energy band models proposed for (a) Na_2KSb and (b) $\text{Na}_2\text{KSb}(\text{Cs})$ photocathodes. Several experimental observations suggest that the NaK_2Sb phase is present in the surface layer of $\text{Na}_2\text{KSb}(\text{Cs})$ photocathodes, and therefore the band diagram (a) should also be considered in the model for $\text{Na}_2\text{KSb}(\text{Cs})$ photocathodes. The average depth of the surface layer was estimated from xps intensity measurements. CB, conduction band; VB, valence band.

stage of the formation process of S-20 photocathodes (Sommer 1968, Garfield 1972, McCarroll *et al* 1971).

NaK_2Sb has a hexagonal structure (McCarroll 1960) and is n-type. It is well known that the cubic alkali antimonides Na_2KSb , K_3Sb , and Cs_3Sb have a very definite composition and are unstable under alkali excess. On the contrary, hexagonal alkali antimonides are stable under a high alkali excess (Sommer 1968). Hexagonal alkali antimonides have lower alkali diffusion rates than cubic ones. The relation of crystal structure with defect formation, self-diffusion type of conduction, relative phase stability and their explanation by an ionic model will be discussed in a forthcoming publication. Hence, the presence of a NaK_2Sb surface layer in S-20 photocathodes probably contributes to the equilibrium with a strongly p-type bulk due to alkali vacancies. Moreover, NaK_2Sb can be in equilibrium with an alkali excess or a K-rich surface, producing strongly n-type material. Everything can be repeated again for K_2CsSb . K_2CsSb is cubic, but this compound has many characteristics of the hexagonal phases. It is stable under alkali excess and it probably has low diffusion rates due to its low concentration of alkali vacancies. Hence it can be easily alkali-doped to produce n-type material. But K_2CsSb has also some unique properties that make it the optimum alkali antimonide for a photocathode overlayer. Due to its large lattice constant it has a small valence band binding energy, and hence a small real photoemission threshold. Its band-gap is larger than that of Na_2KSb , being between 1.2 and 1.4 eV (Ghosh and Varma 1978, Hoene 1972). A large band-gap decreases the probability of electron-hole pair creation and increases the photoelectron mean free path. Thus, a Na_2KSb bulk and a K_2CsSb surface layer are the optimum combination of alkali antimonides that produces the heterojunction configuration for a low photoemission threshold material. A band diagram showing the heterojunction model of the optimum S-20 from this work is shown in figure 1.

3. Conclusions

This study, by means of x-ray photoelectron spectroscopy, on multialkali photocathodes prepared in ultra-high vacuum, supports the theory that high-yield S-20 photocathodes consist of a base layer of Na_2KSb and a surface layer of K_2CsSb and $\text{NaK}_2\text{Sb} \sim 30 \text{ \AA}$ thick. Because of the larger band-gap and lower photoemission threshold of K_2CsSb , and because the formation of the K_2CsSb surface layer involves strong alkali diffusion from the Na_2KSb bulk, a combination of Na_2KSb and K_2CsSb gives the optimum combination for high-yield multialkali antimonide photocathodes.

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