In situ surface study of the activating layer on GaAs (Cs, O) photocathodes

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Abstract. An *in situ* study of the activating layer on GaAs (Cs, O) photocathodes has been made using Auger electron spectroscopy, relative work function, photo-emission and spatial resolution measuring techniques. The layer thickness, composition and work function reduction have been measured for both single- and two-temperature activations. In order to account for the electron transmission probability and the transverse energy of the emitted photo-electrons it is necessary to consider both the work function lowering and the scattering properties of the activating layer. Further it has been shown that neither the heterojunction or dipole models provide an adequate explanation of the properties of the layer which are more consistent with the cluster model of Burt and Heine.

1. Introduction

A photocathode based on the activation of GaAs to a state of negative electron affinity (NEA) by exposure to monolayer quantities of caesium and oxygen was first demonstrated by Turnbull and Evans (1967). Since then, because of the cathode's high quantum efficiency and good long wavelength response, it has been the object of several theoretical (Burt and Heine 1978, Bell 1973) and experimental (Goldstein 1975a,b, Stocker 1975) studies. However there still remains some uncertainty as to such basic parameters as the quantities of caesium and oxygen in the activating layer. One reason for this may lie in the fact that the cathode is not inherently stable in ultra-high vacuum and is easily affected by electron beams or by a slight contamination of its environment. Previous workers have modelled the Cs/O layer in several different ways, notably as a heterojunction, a dipole layer or a cluster system but the uncertainty as to the layer's basic composition and properties makes it difficult to assign relative degrees of confidence to these models. In particular there is, at present, no explanation for the 'two-temperature effect' (Stocker 1975) where activation of the cathode, followed by partial cleaning and reactivation, can give higher sensitivities than a single activation. This effect was initially reported for the (100) face where improvements in sensitivity of up to 40% have been observed but has since been observed by us to also occur on the (111)B face, although here the improvement is only 5–10%. This is particularly important for, although the (111)B face has the highest surface escape probability (James *et al* 1971), it is now common to use the (100) face in devices because of the high cosmetic quality obtainable on this face with the metal organic chemical vapour deposition (MOCVD) technique.

There is also no explanation for the fact that the component of the velocity of the emitted electrons parallel to the sample surface as measured in practical devices (Holeman *et al* 1976) is up to an order of magnitude higher than the theory indicates (Pollard 1972, Bell 1973, Burt and Inkson 1976).

The object of this work was firstly to measure the thickness, composition, work function reduction and mean transverse emission energy associated with the caesium/ oxygen layer necessary for optimum photo-emission and secondly, by examining the effect of varying the layer thickness and composition, to draw some conclusions regarding the behaviour and nature of the layer. In particular we have examined the effects of thick caesium/oxygen layers and the processes involved in the decay of the cathode sensitivity with time.

2. Experimental details

The work was carried out in a 300 mm diameter stainless steel vacuum chamber of the form shown in figure 1, this having a smaller side chamber attached for sample imaging.
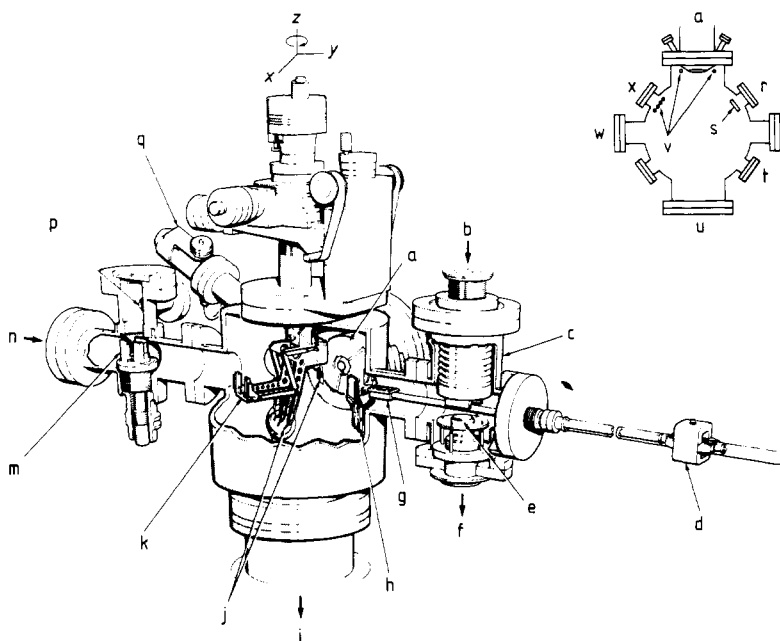

Figure 1. The photocathode activation and imaging system. (a), CMA; (b), window for resolution pattern projection; (c), cathode imaging pot; (d), magnetic transfer drive; (e), phosphor; (f), imaging system; (g), sample holder; (h), sample heater; (i), primary pump system; (j), caesium channels; (k), offset flip manipulator; (m), airlock system; (n), window; (p), to secondary pump system; (q) oxygen inlet value; (r), sapphire window; (s), heater; (t), transmission activation window; (u), viewport; (v), Cs channels; (w), airlock; (x), reflection activation window.

The vessel was pumped with a sorption/ion/titanium sublimation pump system in order both to keep the level of hydrocarbons present to a minimum and to allow the system to be continuously operated over periods of several months. The base pressure of the

system was $<2 \times 10^{-11}$ Torr but, with the use of caesium to activate the cathodes, this would fall by approximately an order of magnitude (measured by a Trigger–Penning gauge). Samples were introduced to the system by means of an all metal sealed transfer mechanism with a cycle time of approximately 90 min. During this operation the chamber pressure rose briefly to no higher than 5×10^{-10} Torr and the base pressure was re-established within 30 min of sample insertion.

The photocathodes were in the form of thin ($\approx 2\ \mu$m) epitaxial layers of p-type GaAs thermocompression bonded to glass (Corning 7056) with an intervening buffer layer of GaAlAs (Antypas and Edgecumbe 1975) and were prepared as shown in figure 2. The
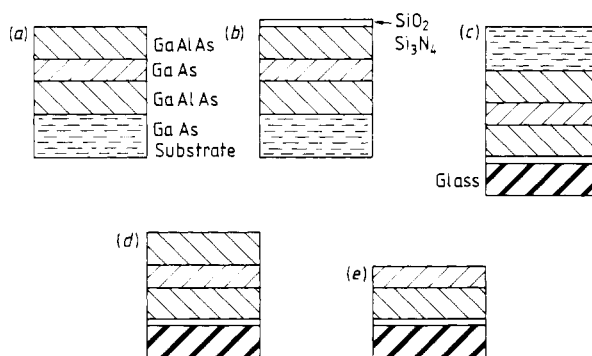
Figure 2. Preparation of a GaAs transmission photocathode structure. (a), Growth; (b), SiO_2/Si_3N_4; (c), Glass bonding; (d), $H_2O_2:NH_4OH$ etching; (e), HF etching.

cathode layers were Zn doped, typically at 2×10^{18} cm^{-3} and had a minority carrier diffusion length of 1.5–4 μm. The active faces of the cathodes were either (100) or (111)B and were grown either by LPE [(100) or (111)B] or MOCVD [(100) only] techniques. Prior to being introduced into the vacuum the cathodes were thoroughly degreased and etched in 3:1:1 ($H_2SO_4:H_2O:H_2O_2$) for 15 s at 20 °C. After admission to the chamber the cathodes were heat cleaned for 10 min at 580 °C using radiation from a heated rhenium filament, the effectiveness of the cleaning being checked by Auger spectroscopy. This preparation technique gave a typical surface carbon level of $<5\%$ of a monolayer, this being the only contaminant seen, and no increase in the surface carbon level was observed even after several hours of Auger measurements. Since the layers were transparent at normal pyrometer wavelengths the cleaning temperature was measured by using a pyrometer operating at 5 μm where the glass substrate is opaque (Rodway et al 1978).

After cleaning the cathodes were activated by exposing them to caesium vapour (from caesium chromate channels that had previously been thoroughly outgassed) to an initial photo-emission maximum and then to both caesium and oxygen (99.98% from a bottle via a leak valve) either alternately or simultaneously. The results reported here were obtained using co-evaporation of caesium and oxygen rather than alternate deposition as our studies have shown no difference in the final activation between the two methods and co-evaporation is better suited to the study of the work function variation with layer thickness. The caesium coverage at the initial photo-emission maximum has previously been established as $\frac{2}{3}$ of a monolayer (Rodway (1984)) (where a monolayer is defined as 7.9×10^{14} atoms cm^{-2}) and this figure has been used to correct all the results

given here to a constant incident caesium flux (in this case 1 monolayer in 12 min) throughout the work. Oxygen admission was typically at a partial pressure of 1–5×10^{-11} Torr.

In the case of a two-temperature activation a cathode that had been activated as above was heat cleaned at a temperature of 450 °C and then reactivated. This gave an increase in photosensitivity of $\simeq 40\%$ with (100) and 5–10% with (111)B cathodes. The levels of photosensitivity were typically 300–1000 $\mu A\,l^{-1}$ in transmission, 800–1300 $\mu A\,l^{-1}$ in reflection. Photo-emission measurements were made in transmission using a 1 mlm light source at a colour temperature of 2854 K, with a 0.5 mm diameter spot, the lamp being so aligned that the beam was coaxial with the Auger analyser. The cathode was biased at −67 V with respect to the chamber and photocurrent measurements were made using a Keithley 602 electrometer. No attempt was made to optimise the cathode thickness or to allow for reflection losses at the vacuum windows and GaAs/glass interface, hence some of the transmission photosensitivities are quite low (i.e. <500 $\mu A\,l^{-1}$). However all material was first checked in reflection prior to the measurements detailed here to ensure its quality. After the chamber had been conditioned by repeated activations the cathodes were stable to within 20% of the maximum sensitivity over a period of 1 h.

Auger analysis was carried out using a standard Varian 3 kV cylindrical mirror analyser with an electron beam spot size adjustable from 150 μm to 1 mm. This work was carried out at a beam voltage of 3 kV and a spot size of 1 mm unless otherwise stated. Quantitative measurements were made from the Auger spectra using the data in the *Phi Handbook of Auger Electron Spectroscopy* (1976) and the compilation of Seah and Dench (1979). Prior to the measurements reported here, it was necessary to assess the effect of the electron beam on the activating layer. An electron beam can affect a surface in one of several ways—by causing dissociation of the surface, stimulating adsorption of residual gases, desorption of one or more constituents of the surface or by simple thermal desorption effects (Pantano and Madey 1981). It has also been demonstrated that, in the case of GaAs (Cs), the presence of oxygen can markedly affect the degree to which this takes place (Madey and Yates 1971). In order to assess the extent to which this occurs in the GaAs (Cs, O) system a series of subsidiary experiments were undertaken. These showed that the minimum practicable beam current of 1 μA (in terms of the signal/ noise ratio) caused no degradation of a single-temperature activation but degraded the emission of a two-temperature activated cathode by $\simeq 40\%$ over a 5 min period. The mechanism for this degradation appeared to be the adsorption of residual gas from the electron gun, but even at beam currents >5 μA the effect upon the observed caesium and oxygen levels was negligible over the period of the measurement.

Measurements of the change in work function were made by the retarding potential technique of Nathan and Hopkins (1974) using the integral electron gun of the CMA. This technique was chosen in preference to the Kelvin probe for two reasons. Firstly the need to condition the experimental chamber with caesium, in order to stabilise the cathodes, means that any reference electrode may become contaminated, even if flash heated before each measurement and secondly the work function changes involved in the deposition of Cs on GaAs are both rapid and large (Clemens *et al* 1978, Rodway 1984). The retarding potential method does lack an absolute reference point for the work function (the effective reference being the hot filament of the electron gun), thus the values given on the *y* axis of the work function plots in this paper are the measured potential differences between the sample and the gun filament (referred to as relative work function in the text and diagrams) and are uncorrected. Work done by Bell (1973)

and repeated by one of us (MA) has shown, by examination of the spectral response of cathodes, that GaAs activated to a photo-emission maximum with caesium alone is in a state of near zero affinity (either zero or slightly NEA). Whilst this is not an accurate result it can provide a very approximate calibration for the work reported here. On this basis the work function reduction below the value at the minimum with Cs only is equivalent to the NEA. The measurements were carried out at a beam current of 10^{-8} amps and a beam voltage of 150 V. The system was stable to 5–10 meV after a 1 h warm-up and the results were reproducible to ±25 meV over a period of several months (as measured by examination of the filament–sample potential difference at the photo-emission maximum with caesium alone), including at least two vacuum system bakes. It is possible that the activation layer on GaAs may not be evenly distributed over the surface. Weber and Peria (1969) have shown that it is possible to detect patchiness of the work function, for patches typically in the size range 0.01–0.5 mm, using the retarding potential technique. If the sample bias is varied and the sample current plotted as a function of this, then the effect of a patchy surface is to cause a shoulder to appear on the diode characteristic curve. A check for such an effect was carried out for all activation conditions.

The spatial resolution of a photodevice depends on several parameters, but the physical quantity of importance, as far as the cathode is concerned, is the mean emission energy of the electrons parallel to the cathode surface ($\bar{E}_T$). Resolution measurements were made by moving activated cathodes into the side chamber where they were placed in close proximity to a phosphor (type P20). This phosphor was on an insulated mount and could be raised to a high positive potential. An optical image of a standard bar pattern was focused onto the cathode and the smallest resolvable pattern on the phosphor was determined as a function of the applied voltage (V) and the cathode–phosphor separation (d), which was measured using a travelling microscope. The relationship between the limiting resolution of the cathode–phosphor system (f_L) and E_T is of the form:

$$f_L = k[(V/d^2)/\bar{E}_T]^{1/2}$$

where k is a constant determined by the form of the electron distribution function (Bradley *et al* 1977). Thus by plotting $\log(f_L d)^{1/2}$ against $\log(V/d)^{1/2}$ for a range of values of d, a straight line of unity slope is obtained, the position of the line determining $\bar{E}_T$. This method gave a typical standard deviation of 10 meV and, provided that the current drawn from the cathode did not exceed 1 μA cm^{-2}, there was <5% degradation of the photo-emission during the measurement.

3. Results

3.1. The single-temperature activation

Activation of the cathode to maximum sensitivity requires a total time of 1.8–2.2 times the time taken to reach the initial maximum with caesium alone. During the activation the caesium Auger signal rises linearly, at the same rate as for the initial deposition of caesium, and with no change in the relative proportions of the high-energy (563 eV) and low-energy (47 eV) caesium Auger peaks (Rodway 1984). Since the scattering length for the 47 eV electrons is considerably less than that for the 563 eV electrons ($\lambda_m \approx 1.5$ as opposed to 3–4 where λ_m is the electron–electron scattering length in monolayers)

any significant screening of the caesium would result in a change in the ratio of the two peaks. As this does not occur we may deduce both that the majority of the caesium remains on top of the layer and that the sticking coefficient remains unchanged. The oxygen Auger signal also rises linearly, but the lack of screening of the caesium Auger signal may indicate that the oxygen is 'burrowing' under the caesium, as suggested both by Goldstein (1975a,b) and Stocker (1975). The apparent Cs/O ratio in the layer is 4.1:1, the variations in the Cs/O ratio observed from activation to activation being of the order of 5–10%. This is less than the 30–40% reported by Goldstein (1975a,b). Examination of the Ga and As Auger spectra for chemical shifts or preferential screening show no effects at high energies but there are effects at low energies (i.e. <100 eV). This area of the spectrum is heavily masked by the $CsN_{4,5}O_{2,3}O_{2,3}$ peak at 47 eV and stripping of this peak from the spectrum is necessary. The reference peak for this was obtained using a spectrum obtained from depositing a thick layer of caesium on a suitable substrate (e.g. CdTe see Rodway *et al* 1983). This gives the results shown in figure 3. It is possible
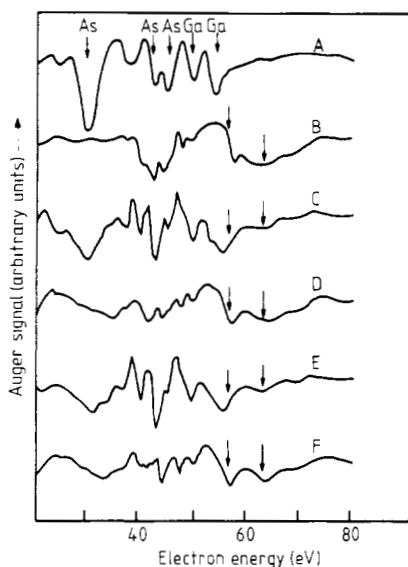

Figure 3. Low-energy Auger spectra of a cathode during processing, after stripping of the Cs 47 eV peak. A, Clean GaAs; B, single activation; C, low heat clean; D, two-temperature activation; E, second low heat clean; F, double activation.

here to discern features at 58 and 63 eV whose strength is associated with the presence of oxygen on the surface but, given the limitations of the stripping technique, it is not possible to be positive as to the origin of these features.

   The heat cleaned sample shows a work function variation over the surface of ±150 meV away from the sample edges (see figure 4) which may be due to variation of the surface carbon contamination. The activated sample shows an equivalent variation of ±10 meV which indicates that the activation is uniform. Examination of the diode response of the cathode-gun system (figure 5) shows no evidence of the structure that would be expected from a patchy surface although there is structure in the secondary electron spectrum, centred at a cathode-gun potential difference of 2 eV. The strength of this feature appears to be related to the presence of oxygen on the cathode surface,
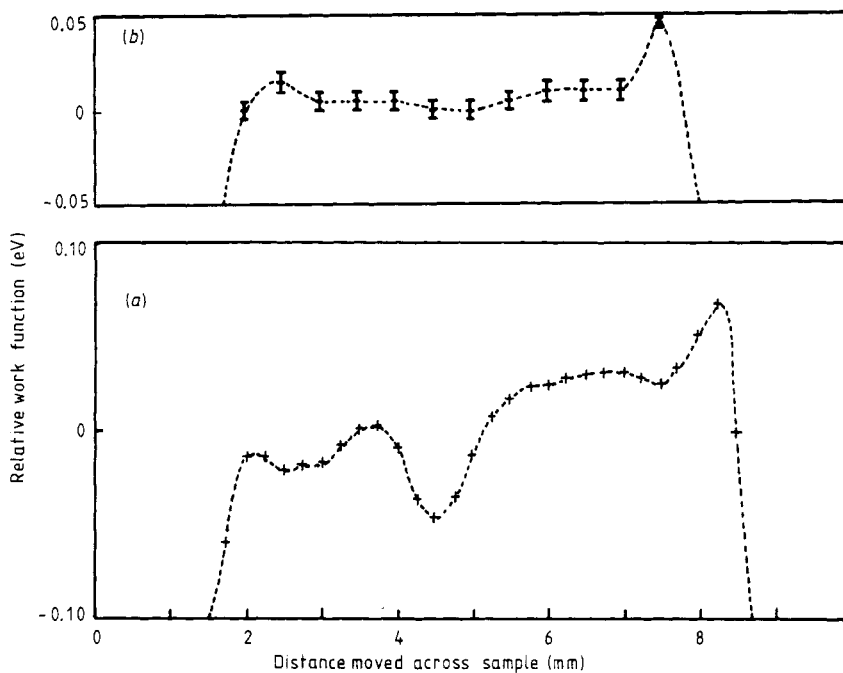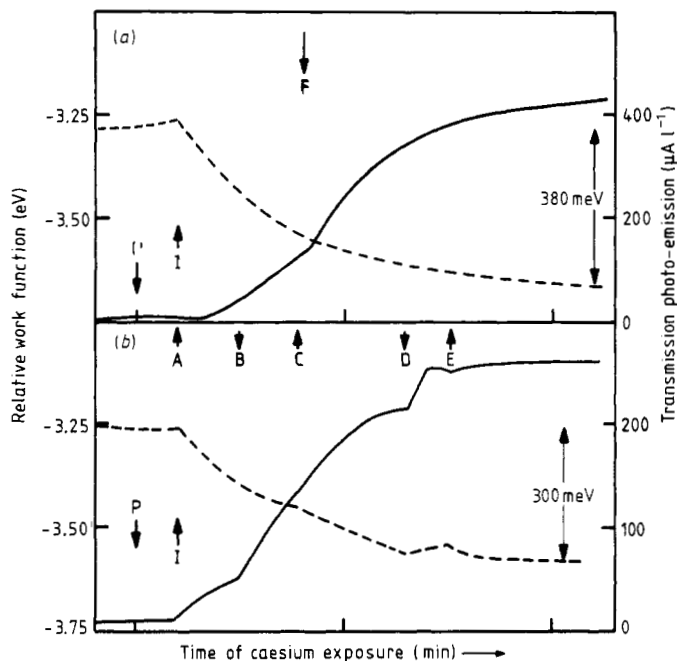
Figure 4. Variation of work function over the cathode surface after (*a*) a 580 °C heat clean and (*b*) after activation.
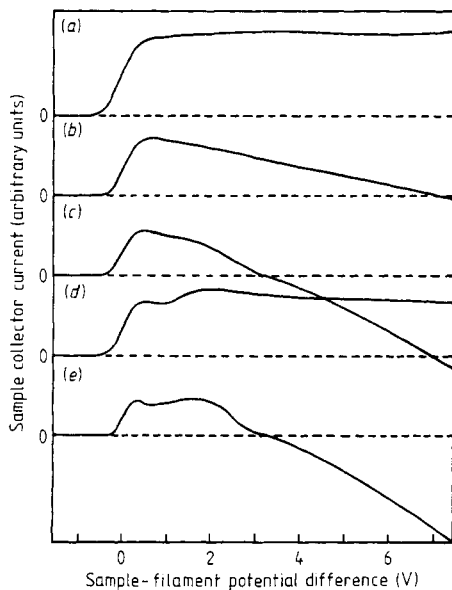
Figure 5. Diode response characteristic of a cathode at various stages in processing. (*a*), Clean GaAs; (*b*), caesium peak; (*c*), first activation; (*d*), low heat clean; (*e*), second activation.

but the beam energy spread of the gun is large (~0.6 eV) so the feature is not well resolved. Also clearly shown is the change of polarity in the collector current resulting from the change in secondary electron coefficient caused by the deposition of caesium.

Figure 6 shows the variation of the work function through the course of typical activations for both the (100) and (111)B faces. The final values of the work functions are also typical. The decrease in work function from the caesium-only case is 380 meV for the (111)B face and 300 meV for the (100) face with a variation of ±40 meV from


Figure 6. Variation of the cathode photosensitivity and work function during activation after a 580 °C heat clean. The arrows indicate points of change of the oxygen admission rate about the optimum stochoimetry. ↑ and ↓ being respectively increases and decreases in the oxygen pressure. P↓ denotes the photo-emission peak with caesium only, ↑I the initial admission of oxygen. ---, work function; ——— photosensitivity. (a) (111)B; (b) (100).

sample to sample. The most striking feature is the effect of variations in the oxygen admission rate on both the rate of fall of the work function and the rate of rise of the photo-emission. Whilst an increase in the oxygen deposition rate causes an increase in the rate at which the work function falls it actually decreases the rate of rise of the photo-emission (see points A and E in figure 6) whilst a decrease in the oxygen deposition rate has the opposite effect (see point B in figure 6). In an extreme case the work function can actually rise while the photo-emission also rises (see point D in figure 6). The variations in the oxygen pressure in the chamber are only of the order of 1×10^{-11} Torr and the changes take place in a few seconds, indicating a very high degree of sensitivity to the Cs/O stoichiometry.

Figure 7 shows the variation of $\bar{E}_T$ for the cathode during the course of an activation. Both (100) and (111)B cathodes have a value for $\bar{E}_T$ of 35 ± 5 meV at the initial caesium
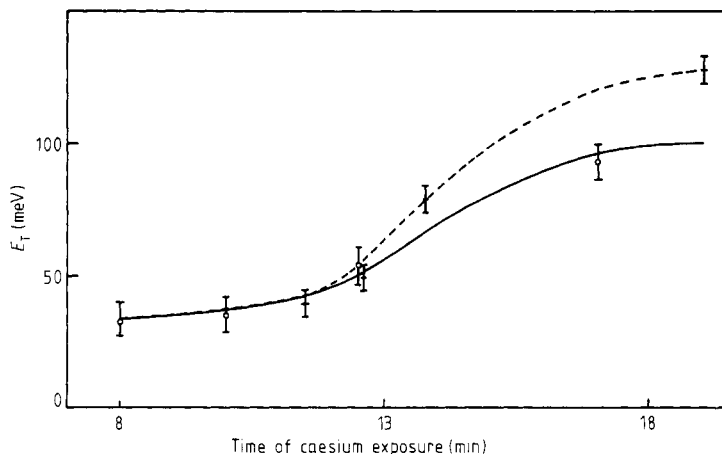
Figure 7. Variation of mean transverse emission energy during activation, following a 580 °C heat clean. The line is fitted on the basis that E_T remains largely unchanged as the layer thickness increases beyond the optimum for photo-emission (see § 4). (+), (111)B; (○), (100).

peak. Although $\bar{E}_T$ increases during the activation the initial onset is slow and, despite the fact that $\bar{E}_T$ stabilises at approximately the same surface coverage as the photo-emission, it is obviously not in a simple relationship either to this or to the work function. Values of $\bar{E}_T$ for the fully activated (100) face were 100 ± 10 meV whilst those for the (111)B face were 110 ± 30 meV.

3.2. Two-temperature activation

Heat cleaning of the activated cathode at 450 °C causes the caesium Auger signal to be reduced to $\frac{1}{3}$ of its original value, whilst the oxygen signal remains virtually unchanged. The photo-emission is reduced to zero and the work function rises by 1–2 eV. The structure in both the low-energy Auger spectra and the secondary electron spectra remains (see figures 4, 5) but slightly weakened. Exposing the partially cleaned surface to caesium now results in photo-emission behaviour similar to that observed on the completely cleaned surface (see figure 8), except that the new initial photo-emission maximum occurs more rapidly than in the single-temperature case (i.e. ~2 min as opposed to 8 min) and the photo-emission at this point is typically 1.5–2 times the corresponding value in the single-temperature activation. The work function at this point is now typically 50–100 meV below that in the single-temperature case and the caesium Auger signal is identical to that observed at the initial caesium peak for a deposition on a completely cleaned surface.

The activation time from the initial admission of oxygen to full sensitivity is now 1.2 to 1.4 times that for the single-temperature activation. The oxygen Auger signal has nearly doubled ($\times 1.5$–1.7), the caesium signal is also larger (by $\simeq 10$–20%) and the measured Cs/O ratio is now $\simeq 2.9:1$, although there is still no significant change in the proportion of the high- and low-energy caesium peaks. This is surprising in view of the quantities of caesium and oxygen deposited and suggests that the activating material does not go down in a simple layer structure but may well be in some form of cluster.
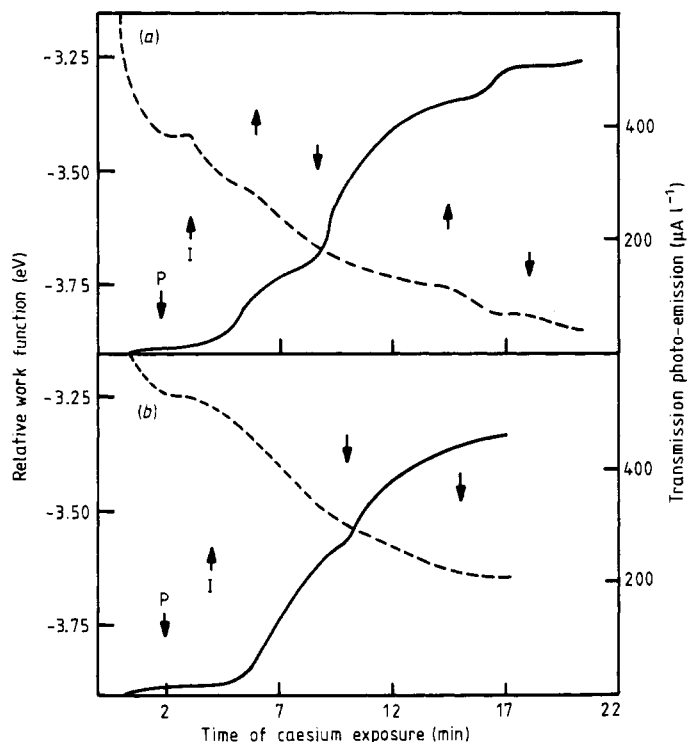
Figure 8. Variation of cathode photosensitivity and work function during activation following a 450 °C heat clean which was preceded by an activation as in figure 4. Notation as in figure 4. (*a*) (111)B; (*b*) (100).

The structures seen in the low-energy Auger and the electron reflection spectra are both stronger.

The new final work function for both the (100) and (111)B faces is now 100–150 meV lower than that observed in the single temperature activation. However it may also be observed that the photosensitivity for a given work function is now higher—indicating that the transmission through the surface layer is higher. The behaviour of the activation with variations in the Cs/O balance is very much the same as for the single-temperature activation.

Measurements of the resolution show no measurable change in $\bar{E}_T$ from the value seen in the initial single-temperature activation—a surprising result in view of the fact that the layer thickness, composition and work function have all changed.

3.3. Multiple activation

The fact that the two-temperature process gives a gain in photosensitivity raises the question of what repeating the process will achieve. A second 450 °C heat clean again reduces the caesium Auger signal by approximately $\frac{2}{3}$ whilst leaving the oxygen signal unchanged. Re-activation of the cathode gives the result shown in figure 9. The caesium Auger signal is again only slightly changed from previous activations, as is the ratio of the high- and low-energy peaks. The oxygen signal has now increased to 2.5–3 times that
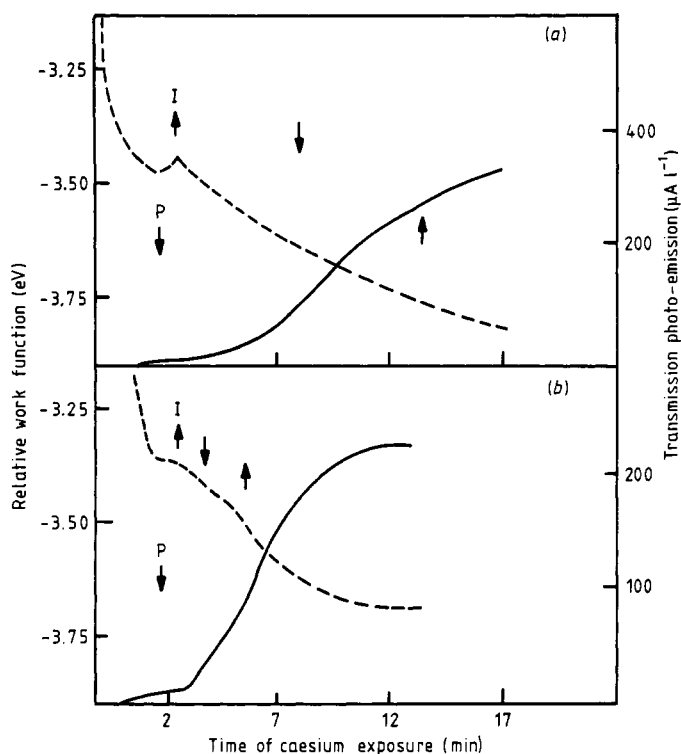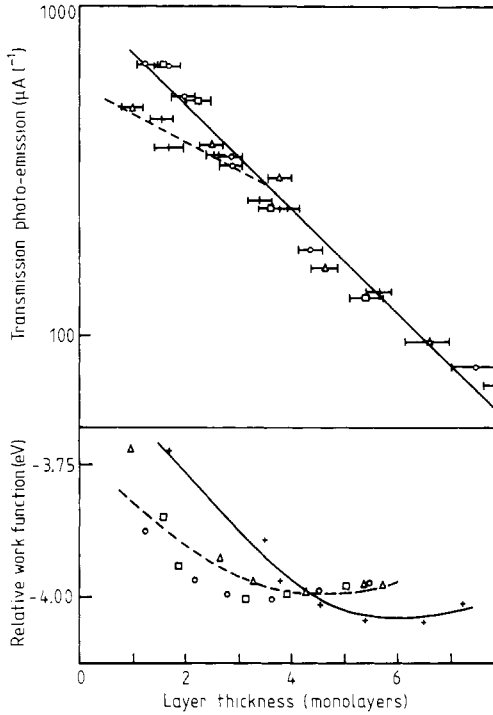
Figure 9. Variation of cathode photosensitivity and work function during activation following a 450 °C heat clean which was preceded by an activation as in figure 8. Notation as in figure 4. (*a*) (111)B; (*b*) (100).

of the single-temperature activation whilst the structure in the low-energy Auger peaks is again unchanged. The Cs/O ratio is now of the order of 2.1 : 1. Although the reduction of the work function follows the same pattern as before and the final value is similar to that for the two-temperature activation, the photosensitivity is lower. The emission for a given NEA is higher than that for a single activation but lower than that for a normal two-temperature activation. This indicates that the transmission probability has been reduced.

3.4. Thick Cs/O layers

Although the photosensitivity peaks at between 1 and 2 monolayers thickness for both the single- and two-temperature activations, the work function is still falling. We therefore continued the activation beyond the optimum point. Figure 10 shows the results of overactivating both single- and two-temperature activated cathodes. This was done by maintaining the caesium deposition rate and controlling the oxygen admission in order to keep the photosensitivity at the highest possible instantaneous value. In this graph the x axis has been calibrated in monolayers rather than time of deposition. The calibration was obtained by examination of the reduction of the Auger signal from the 1070 eV $L_3M_{4,5}M_{4,5}$Ga peak, using the relationships and data given by Seah and Dench (1979). This does in fact vary linearly with the time of deposition indicating that the
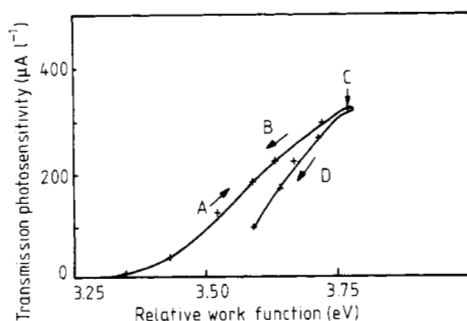
Figure 10. Variation of cathode photosensitivity and work function during the deposition of a thick caesium/oxygen layer. (100): (+), single temperature; (○), two temperature. (111)B: (△), single temperature; (□), two temperature.

sticking coefficient remains constant throughout: a fact that was assumed by Uebbing and James (1970) and Sonnenberg (1972) but not proven. Auger examination of the layer indicates that, as the thickness increases, the composition of the layer surface for (100) and (111)B, both single and two temperature, tends towards a common value. This is confirmed by the behaviour of the work function which also tends to a common value although in the case of the (100) single-temperature activation this is only achieved at a greater layer thickness. The most noticeable result from figure 10 is the fact that a semi-logarithmic plot of the photo-emission against thickness gives a good fit to a straight line, with the single-temperature activations on the (100) face deviating from this near to the photo-emission maximum. This linearity would be expected if the layer were a uniform photo-electron scatterer. In the case of single-temperature activations on the (111)B face the degree of deviation from linearity appears to be related to the improvement shown in the two-temperature process, in that a cathode that only shows a slight improvement gives the best fit to the straight line.

$\bar{E}_T$ for the cathode remained largely unchanged from the value at maximum photo-emission up to a thickness of five monolayers and then began to decrease, falling to approximately $\frac{2}{3}$ of its original value at seven monolayers. During this time the dark current increased to the point where measurements became impossible beyond this thickness. However the effect of this increase would be to give an artificially high value of $\bar{E}_T$ so this indicates that the change is almost certainly more pronounced than that observed.

3.5. Deviations from optimum Cs/O balance

In order to assess the importance of the Cs/O balance in the layer we deliberately exposed the activated cathode to an excess of caesium or oxygen, the results of which are plotted in figure 11. Here we have plotted the relationship between the work function and photo-emission as this better illustrates the different effects of the two elements. It

Figure 11. Effect of excess caesium or oxygen on the photosensitivity and work function of a cathode, activated after a heat clean at 580 °C. A, activation; B, excess Cs; C, full activation; D, excess O_2.

may be seen that the effect of excess caesium is to apparently reverse the course of the activation. This requires comparatively large quantities of caesium (several minutes exposure at the rate used throughout this work), indicating that the sticking coefficient for caesium on a completed layer is fairly small. The cathode also recovers quickly from an overdose of caesium to within 5% of the original photosensitivity. The effect of excess oxygen is severe, a few seconds at 2×10^{-11} Torr causing a drop in sensitivity of tens of per cent whilst the work function changes only a few meV. The cathode only partially recovers from this. The slight initial decrease seen in the work function (i.e. an increase in relative work function) is almost certainly due to the activation technique leaving the cathode slightly caesium rich.

Transverse emission energy measurements were difficult on these cathodes as the modified Cs/O layer was not entirely stable. However such measurements as were possible showed no change due to over caesiation whilst over oxygenation caused a reduction in $\bar{E}_T$.

3.6. Cathode decay

One of the most important factors in the production of a practical photodevice is whether or not the cathode can be stabilised in a tube environment. We have therefore examined some of the cathode changes involved in the decay process. Although long-term life tests and tests at high caesium overpressures cannot easily be carried out in a research chamber it was possible to obtain useful information on the quantities of activant involved in the decay by using the channel calibration previously obtained (Rodway 1984).

Figure 12(*a*) shows typical decays for single- and two-temperature activated cathodes in a chamber that has been passivated by the admission of oxygen at a pressure of 1×10^{-7} Torr for 1 h prior to activation to reduce the caesium overpressure. It may be
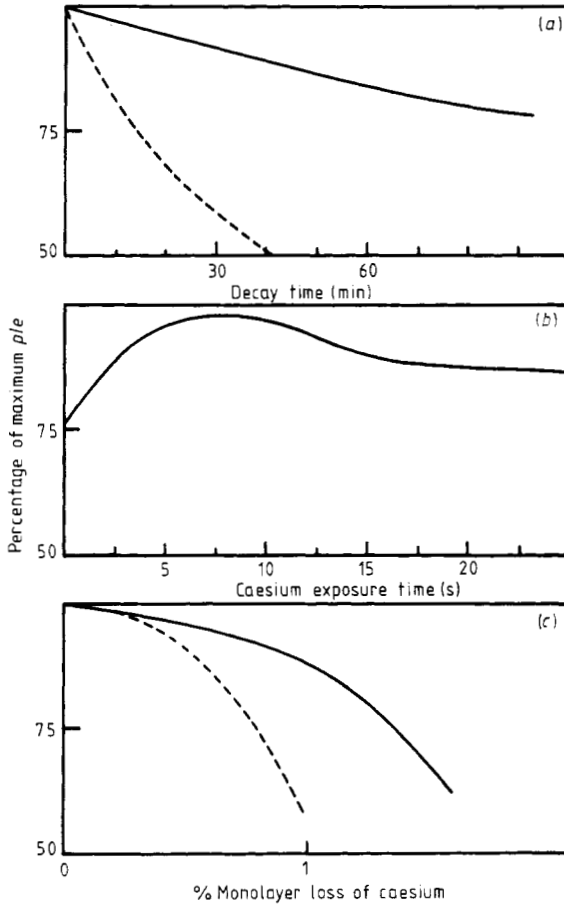
Figure 12. (*a*) Decay of the photosensitivity of a cathode with time; (*b*) effect of caesium exposure on the decayed cathode; (*c*) variation of cathode sensitivity with loss of caesium. —, single temperature; ----, two temperature.

seen that the two-temperature activation decays more quickly than the single-temperature. In both cases a 50% decrease in photo-emission was accompanied by a work function increase of a few tens of meV. Comparison with figure 11 shows that this behaviour was in accord with either Cs loss or O_2 gain although we are unable to resolve which of these two mechanisms applied. The observed work function change was too small to be caused by Cs gain or O_2 loss.

Figure 12(*b*) records the restoration of photosensitivity after decay by exposing the photocathode to Cs. The Cs flux was known (Rodway 1984) and thus the equivalent Cs loss during decay could be derived (figure 12(*c*)). This shows that the (Cs, O) layer is very sensitive to deviations from the optimum stoichiometry and that only a small percentage of the layer appears to control the photosensitivity. Figure 12(*c*) shows that for a single-temperature activation a loss of 1.5 to 2% of a monolayer of caesium (or 1–1.25% of the total amount of Cs on the surface) causes a loss of 50% of the photo-emission. The two-temperature activation is even more sensitive requiring the loss of only 1% of a monolayer (or $\frac{1}{2}$% of the total) for the same loss of sensitivity.

4. Discussion

It is possible to make an estimate of the quantities of caesium and oxygen in a single-temperature layer from the time needed for the activation. It has previously been reported (Rodway 1984) that the caesium coverage at the initial photo-emission maximum is $\frac{2}{3}$ of a monolayer. It has also been reported (van Bommel *et al* 1978) that the sticking coefficient for caesium up to this first maximum is unity. Since the total activation time for the cathode is twice that required to reach the first caesium peak, the *maximum* total coverage of caesium is $1\frac{1}{3}$ monolayers. As the rate of rise of the caesium Auger signal remains constant throughout the activation and there is no apparent change in the ratio of the high- and low-energy peaks, it also follows that the sticking coefficient during the period of oxygen admission remains constant at unity and that at least the majority of the caesium remains on the surface of the layer (as suggested by both Stocker (1975) and Goldstein (1975a,b)). If it is assumed that the activant is deposited on the surface in the form of a simple layer structure, i.e. there is the maximum screening of the oxygen signal then, using this as a basis it is possible to estimate the true Cs/O ratio in the layer. The relevant equations for the screening effect have been given by Seah and Dench (1979) and by using these in conjunction with the data in their compilation, it is possible to assign maximum and minimum bounds to the Cs/O ratio. This gives a value for the Cs/O ratio in the single-temperature activation layer of between 4.1:1 and 2.7:1, i.e. an oxygen coverage of $\frac{1}{3}$ to $\frac{1}{2}$ of a monolayer. Whilst the measured ratio is within the range of values observed by Goldstein (1975a,b) and straddles the value of $\approx 3:1$ given by Sommer *et al* (1970), it is rather higher than the value of 2:1 obtained by Phillips *et al* (1984). However, it must be noted that the results of Sommer and co-workers were obtained by very different methods whilst the cathode preparation techniques used by Phillips and co-workers were untypical of those used for practical photodevices. NEA is achieved at low surface coverage (<1 monolayer total), and this indicates that the layer may not be treated as a heterojunction. The work function continues to fall as the coverage increases, and there is no evidence of depolarisation during any of the activations which one would expect for a dipole layer, for example. Depolarisation effects can be seen quite clearly in the case of caesium only (Rodway 1984) where, beyond a coverage of $\frac{2}{3}$ of a monolayer, the mutual depolarisation of the dipoles causes a rise in the work function. The greater work function reduction achieved with (Cs, O) would imply a stronger dipole and hence depolarisation should be more apparent, but no rise in work function is seen until the layer is over five monolayers thick.

In the case of the two-temperature activated cathode, there is a greater final quantity of both caesium and oxygen present on the surface. During the course of the activation the emission for any given work function reduction is greater than for the single-temperature case. This indicates that the transmission probability of the photo-electrons through the activating layer has been increased. At the photo-emission maximum the work function has been reduced by a further ≈ 100 meV over that achieved in the single-temperature cases. Making the same assumption as to the layer structure as above, then the final caesium coverage is $1\frac{1}{2}$ monolayers with a Cs/O ratio of between 3:1 and 1.9:1, i.e. $\frac{1}{2}$ to $\frac{3}{4}$ of a monolayer of oxygen. The stronger features in the low-energy Auger spectra are in agreement with the greater oxygen coverage.

In neither of these activations is there any evidence of patchiness in the layer (in the size range 0.01 mm to 0.5 mm) and both show a very high sensitivity to deviation from the optimum Cs/O balance. In both cases a change of <2% of a monolayer in the

composition (either a gain of oxygen or a loss of Cs) reduces the sensitivity to near zero with very little change in the work function. This observation is not readily explained by the dipole model of the layer.

One of the most revealing results in this work is the behaviour of the photo-emission as the layer becomes thicker. This shows an exponential fall in sensitivity as the coverage increases beyond the photo-emission maximum, similar to that observed by Uebbing and James (1970) but differing from the results of Sonnenberg (1972). However, the range of layer thicknesses here is less than that covered by Sonnenberg and there is some suggestion of a deviation from the simple exponential behaviour at the greatest thickness. Such behaviour is consistent with the layer being a strong scatterer, as has been suggested by Korotkikh and Musatov (1978) and Musatov and Korotkikh (1982), and Uebbing and James (1970) derived an attenuation length for the Cs/O layer based on the behaviour on continuing the activation. The improvement in emission seen by the addition of oxygen to a caesium rich layer, despite only a small (few meV) change in NEA, is then explainable in terms of a reduction in the scattering in the layer. This scattering process is unlikely to be electron–electron scattering as, at these low energies, the scattering length is many monolayers (Seah and Dench 1979). However LEED examination of activated cathodes indicates that the layer may well be amorphous (Goldstein 1975a,b), or possess only short-range order, and it has been observed in other systems possessing only short-range order (e.g. Rodway 1978) that the scattering length for electron–phonon interactions (l_p) can be very short (of the order of a few ångströms). Such a process with its low interaction energy could also explain the high values of E_T observed. In order to examine this further we have constructed a Monte Carlo scattering model based on the work of Stuart *et al* (1964) and this gives the results shown in figure 13. This is a very simple model of the scattering process but it may be seen that its agreement with experiment is good.

Figure 13 shows the variation of the escape probability (E_p) and $\bar{E}_T$ with NEA for a
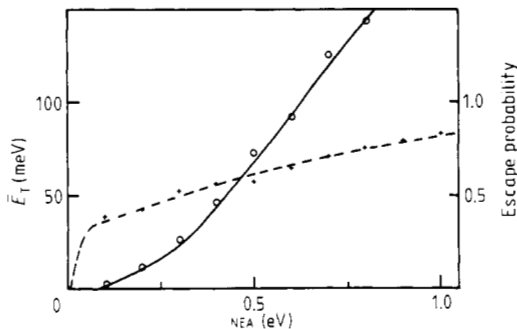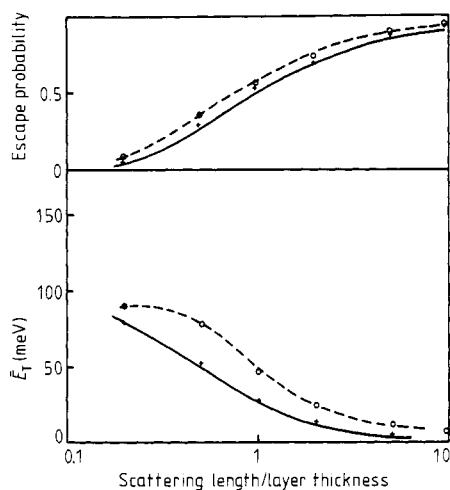

Figure 13. Monte Carlo model prediction of the variation of cathode escape probability and mean transverse emission energy with NEA. (O), $\bar{E}_T$; (+), E_p.

single-temperature activation. The value of 20 meV for the electron–phonon interaction energy was chosen on the basis of typical values obtained in other systems. The relative values of layer thickness and scattering length were chosen to give a fit to the experimental results obtained here. The choice of a suitable zero for the electron energy is more difficult as little is known about the electronic structure of the Cs/O layer. In this case the zero was arbitrarily chosen to be the top of the valence band in the GaAs as this

appeared to give model results consistent with those obtained experimentally. The model indicates that a scattering length approximately equal to the layer thickness at optimum emission gives a reasonable agreement with experiment. This, given a layer thickness of approximately two monolayers, is not inconsistent with the attenuation length of 9 Å quoted by Uebbing and James (1970). Figure 13 shows that the rate of rise of the escape probability becomes more gradual as the NEA increases and indicates that the change in NEA observed between the single- and two-temperature activations is not adequate to explain the rise in photosensitivity. However if it is assumed that the two-temperature process also causes a reduction in the scattering by improving the ordering of the layer (see figure 14). This could not only account for the rise in sensitivity but also

Figure 14. Monte Carlo model prediction of the variation of escape and mean transverse emission energy with electron scattering length in the Cs/O layer. (○), 0.4 V NEA; (+), 0.3 V NEA.

for the fact that there is no variation observed in $\bar{E}_T$—the two changes having opposite effects upon it. The values of $\bar{E}_T$ given by the model are somewhat lower than those measured and we believe that there may be some contribution to $\bar{E}_T$ due to the GaAs surface otherwise it would be expected that $\bar{E}_T$ at zero affinity would be near zero. The scattering process will tend to mask variations in $\bar{E}_T$ due to variations in surface topography and this is in agreement with the results of earlier work (Rodway and Bradley 1984). In the Si (Cs, O) system the layer is highly ordered and l_p would be expected to be long. Clarke *et al* (1976) have derived an attenuation length of 50 Å for this layer and this is not inconsistent with the value for $\bar{E}_T$ of 40 meV observed in this system (Howarth *et al* 1979). The comparative lack of effect of the two-temperature process upon the (111)B face is also understandable as it is apparent from figure 11 that this starts out with a lower scattering than the (100) in the single-temperature case and thus any improvement in emission will be mainly due to the change in NEA.

Whilst our observations conflict with the heterojunction and dipole models of the layer they are more consistent with the model devised by Burt and Heine (1978). This model, based upon the work of Ebbinghaus and Simon (1976, 1979), proposes that the

surface is covered with clusters of $Cs_{11}O_3$ with further caesium interstitial to these clusters. The clusters are highly repulsive to the conduction electrons and the resultant channelling of the electrons gives an effective rise in their momentum and Fermi energy. The interstitial caesium represents a relatively small percentage of the total surface coverage and the channelling of the emission through this part of the layer means that the loss of emission upon the adsorption of excess oxygen by these interstitial atoms will be higher than would be expected from the total quantities of caesium and oxygen present on the surface. This would also explain why the effect of excess oxygen is so much more damaging to the emission than that of excess caesium, as the adsorption of oxygen onto an interstitial caesium atom would create a strong reversed dipole on this site effectively shutting off the emission whilst an extra caesium atom would not create such a dipole, would have less effect on the emission, would be weakly bound and relatively easily desorbed.

The adoption of a cluster model rather than a simple layer model will affect the Auger results. Exact quantification of this would need extensive calculation but examination of a model for the $Cs_{11}O_3$ cluster (see Simon 1976) shows, that, from geometric considerations, the effect upon the observed caesium level should be comparatively small as only one of the caesium atoms will be fully screened. In the case of the oxygen the model indicates that the screening will be rather less than for a simple layer.

As the layer becomes thicker the effect of the GaAs surface on the layer composition and structure will become less and the layer woud be expected to tend towards a bulk oxide of the form reported by Simon. It does appear to be the case that both single and two temperature tend towards a common composition as the layer thickness increases beyond 4–5 monolayers.

5. Summary and conclusions

We have shown that the total thickness of the single-temperature activating layer on the GaAs (Cs, O) photocathode for optimum photosensitivity is $\simeq 1\frac{2}{3}$ monolayers with a Cs/O ratio of between 4:1 and 2.7:1. This produces a typical work function reduction of 275 ± 40 meV on the (100) face and 350 ± 40 meV on the (111)B face relative to that obtained with caesium only. We have further shown that this layer acts as a powerful scatterer, the emission dropping off exponentially as the layer thickness is increased. In the case of the two-temperature activation we have shown that the layer is thicker ($\simeq 2$ monolayers) with a Cs/O ratio of between 3:1 and 1.9:1 and the work function is reduced by a further 100 meV. We have further shown that the improved emission observed with the two-temperature activation is due not only to the greater NEA but to a reduction in the scattering in the layer. This scattering process can also account for the fact that the values of $\bar{E}_T$ exhibited by this cathode are much higher than the theoretical prediction of Burt and Inkson (1976).

Both types of activation are very sensitive to loss of caesium or gain of oxygen, the total photo-emission being controlled by $\simeq 3\%$ of the total surface coverage. The behaviour of these layers is more consistent with the cluster model of Burt and Heine than with the heterojunction or dipole models.

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