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The Kinetics of Sr on W by DC Field Electron Microscopy

by

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The Kinetics of Sr on W
by DC Field Electron Microscopy

Stable states of Sr on W identified during deposition were also observed in migration and desorption experiments. These studies suggest that the adsorbate consists of a strongly bound layer next to the W substrate and a loosely bound outer layer. Experiments with SrO on W failed to show whether or not Sr influenced transition from one Sr-O-W complex to another for tip temperatures below 1150°K.

(N) Apr[illegible] 5, [illegible]63

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Introduction

The structure of adsorbed layers of SrO on W and its effect on the electron field emission has been studied in detail. Cape and Coomes (1) examined the kinetics of thin SrO films on W by field electron microscopy (FEM). Previously, Moore, Allison and Morrison had examined the chemical reactions which occur when a W filament coated with SrO was heated in vacuum (2). They found that complexes of Sr-O-W were formed with an evolution of gaseous Sr and that the rate of reaction was in agreement with values computed from thermochemical data. In the FEM experiment, changes in micrograph patterns could be observed which were interpreted as the same chemical reactions studied by Moore et al. The results show reaction taking place on the $\{111\}$ and the $\{100\}$ areas together with their environs. The high temperature modifications involving oxygen were identified from the work of other investigators (3, 4).

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(1) J. A. Cape and E. A. Coomes, J. Chem. Phys., <u>32</u>, 210 (1960).

(2) G. E. Moore, H. W. Allison, and J. Morrison, J. Chem. Phys., <u>18</u>, 1579 (1950).

(3, 4) J. A. Becker and R. G. Brandes, J. Chem. Phys., <u>23</u>, 1325 (1955).
E. W. Müller, Elektrochem., <u>59</u>, 372 (1955).

Below 1150°K there was possible evidence for the dissociation of SrO and the migration of Sr to the $\{110\}$ edges where clusters of crystallites form. Lack of FEM data on the behavior of Sr on W single crystals and inadequate temperature calibration made the interpretation of the results at 1150°K and lower temperatures difficult. This is a report on FEM work carried out in the range 300°K to 1150°K.

Moore and Allison had made a study of Sr on a polycrystalline W filament using thermionic emission technique (5). This earlier work measured the average work function decrease caused by the adsorbed strontium and the activation energy of desorption of this adsorbed layer. By repeating this same type of experiment on a single crystal using FEM techniques, details of the crystallographic distribution of adsorbent and the resulting crystallographic variation in work function could be observed. In the FEM technique, observations are made with the tip at room temperature so that the electron emission measurements are independent of the temperature selected for the kinetic process.

The general approach in both the Sr and SrO experiments was the same. One looked for stable states of the absorbent-absorbate system and made measurements of the time and Fowler-Nordheim work function as the activation progressed to the end state.

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(5) G. E. Moore and H. W. Allison, J. Chem. Phys., 23, 1609 (1955).

Results

A. Strontium

Figure 1 shows the sequence of FEM patterns which were observed as strontium was deposited on a heated W tip of the FEM tube. Each row is a sequence of patterns observed at a particular temperature, T_r, of the tip. The first picture in each row was taken before the Sr source was turned on. The arrival rate of Sr at the tip, approximately 3.8×10^{-7} gm/cm^2 hr is the same in all cases. The orientation of the source with respect to the tip is different in each of the sequences shown. In the second and fourth sequence, the axis of the source was parallel to the axis of the tip, while in the first and third, the two axes were perpendicular to each other.

The first sequence of patterns shown in Figure 1 was observed at a temperature T_r equal to 300°K. The times given in this figure are cumulative deposition times with the tip held at T_r. In the early stages of the deposition the Sr coverage is small enough so that the clean tungsten pattern is still recognizable on the side away from the source. Thus, no detectable adsorbent was incident on this region of the tip. As the Sr accumulates on the side of the tip nearest to the source, the voltage required to draw a given current from this region decreases to the extent that the clean W pattern is no longer visible. Only a bright region on the side nearest the source appears as in pattern B. This bright region changes with increasing deposition time to a bright irregular line across the center of the pattern as in C. Later individual bright spots begin to appear behind the line as it becomes fainter and more irregular. These bright spots are interpreted as clusters of Sr. With the exception of the three $\{110\}$ planes, the bright line lies along a $\langle 111 \rangle$ zone. Since a bright region always surrounds the $\{110\}$ plane, it is suggested that the Sr incident on the $\{110\}$ plane migrates rapidly over the plane to its edges. Further deposition increases the

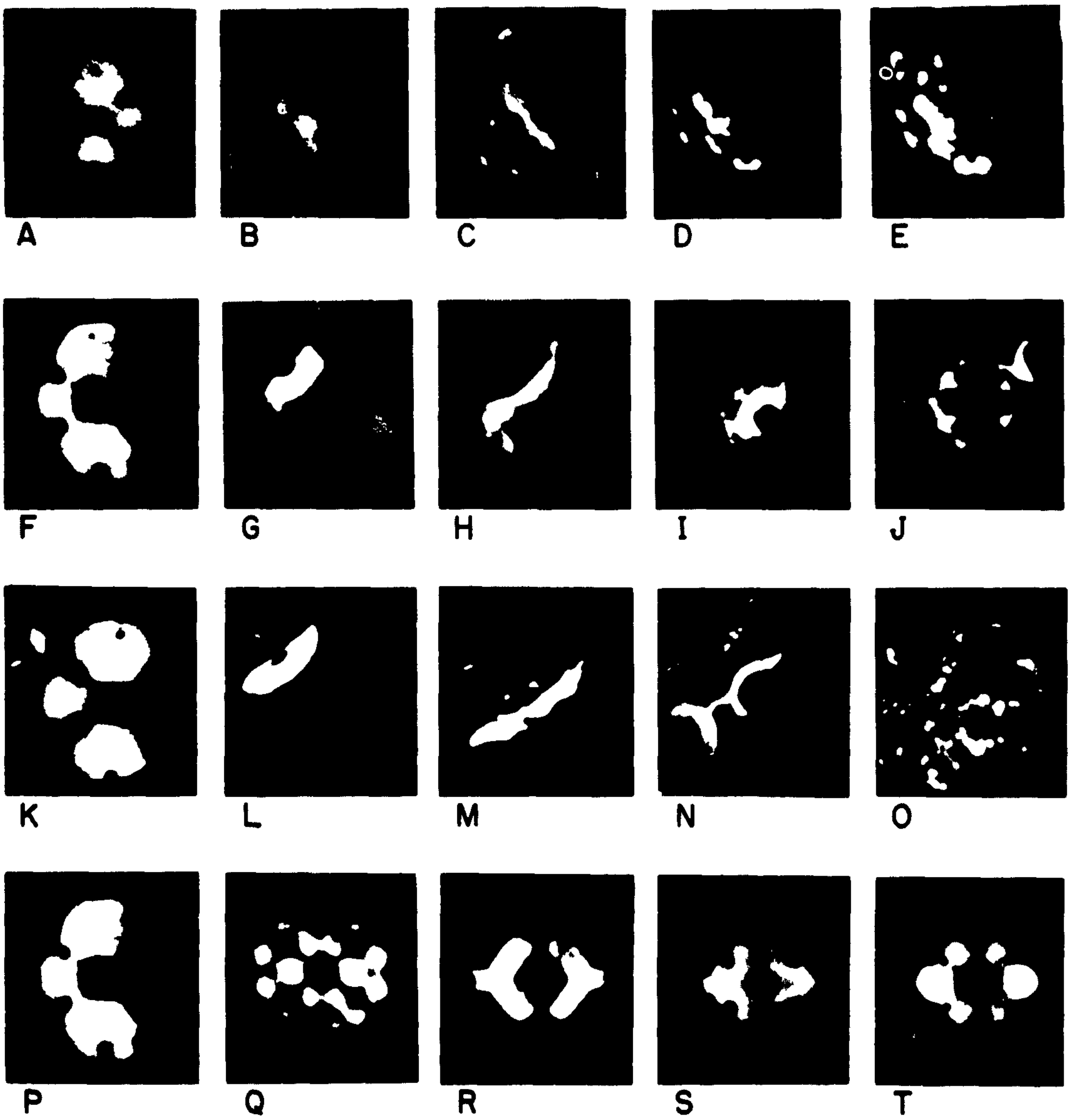
A
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Figure 1

Deposition of Strontium

$T_r = 300^oK$

Pattern	A	B	C	D	E
Time (min)	0	15	35	75	120
ϕ (ev)	4.5	2.80	2.55	2.42	2.2

$T_r = 350^oK$

Pattern	F	G	H	I	J
Time (min)	0	30	60	90	120
ϕ (ev)	4.5	2.56	2.53	2.42	2.49

$T_r = 425^oK$

Pattern	K	L	M	N	O
Time (min)	0	15	42	45	60
ϕ (ev)	4.5				

$T_r = 570^oK$

Pattern	P	Q	R	S	T
Time (min)	0	15	45	90	120
ϕ (ev)	4.5	3.55	2.20	2.30	2.26

size and brightness of the clusters.

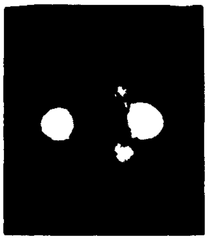
The second deposition sequence was made at T_r equal to 350°K. At this temperature it appears that Sr was mobile and surface migration proceeded at a rate comparable to the arrival rate. As a result of the geometry the initial accumulation occurred along a narrow band, Fig. 1G. For a similar deposit at T_r equal to 300°K in the same geometry, clusters formed at approximately the same position as the bright region in pattern B, but the other portions of the tip remained dark to the end of the deposition time. In this case the migration proceeded with a sharp boundary, Fig. 1G to 1J Fig. 1I shows encirclement of the $\{110\}$ regions by nonuniform migration. The region behind the leading edge appears as a symmetric pattern. After 120 minutes, the deposition was stopped, and the temperature of the tip was held at 350°K until migration was completed. The result is shown in pattern J. Clustering did not occur in this sequence as in the first sequence when the Sr was not mobile.

The third sequence of patterns shows a deposition at 425°K. The Sr was again incident from the upper left. The axis of the source was perpendicular to the axis of the tip and the source was well back from the apex of the tip. Again migration with a sharp boundary occurred during deposition. In distinction to the previous sequence clusters began to appear behind the migrating boundary. The symmetric pattern shown in Fig. 1O is dominated by clusters which are symmetrically located about the $\{110\}$ planes. After depositing strontium for an additional hour beyond that required to obtain pattern O, no changes in the pattern were observed indicating that a steady state condition has been reached by the strontium.

The fourth deposition sequence was made at 570°K. The Sr was incident on the tip from the upper left in precisely the same geometry as used for the second sequence. The patterns remained symmetrical throughout the entire sequence suggesting a migration rate higher than the arrival rate.

The absence of boundary migration in this case may indicate that a large concentration gradient cannot be maintained due to the high mobility of Sr. Attention is called to the following details. In pattern Q, the general shape and form of the clean tungsten pattern was preserved with new dark regions appearing at the $\{103\}$ planes which surrounded the $\{100\}$ planes. The $\langle 111\rangle$ zones developed narrow dark bands and the $\{111\}$ planes became dark. As the deposition continued, the high emission became restricted to a smaller region with little detail except at the $\{211\}$ and the $\{110\}$ planes. The total emitting region then began to expand again as in pattern S until finally after two hours of deposition a pattern similar to that for clean tungsten emerged. The main differences was that the $\{111\}$ planes appeared brighter than the $\{100\}$ regions. The final pattern was stable and did not change with continued deposition.

In Figure 2 it may be observed how the stable states are transformed into one another. The first sequence of patterns in Figure 2 shows the changes which occurred when deposition was continued at a lower T_r after the stable state of Figure 1T was reached. This pattern will be designated as stable state 1. Starting with the tip in stable state 1, deposition was continued at T_r equal to 360°K. In Pattern C clusters appeared principally on the $\{110\}$ plane edges. After deposition for 1 hour the pattern was still symmetric with extensive clustering. A bright spot appeared on the side of the tip near the source, due to an accumulation of Sr. As the deposition continued, the accumulation became larger but no other changes occurred. It is evident in this sequence of patterns that migration occurred without a boundary. On the other hand, beginning with a clean tungsten tip, with T_r equal to 350°K, deposition was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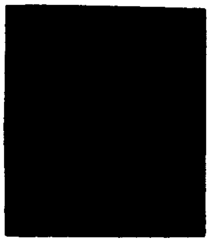
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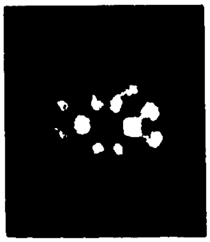
I


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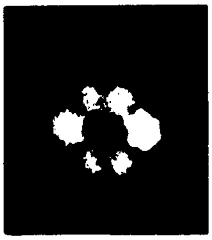
K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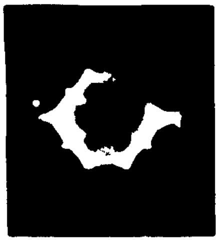
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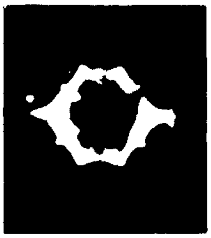
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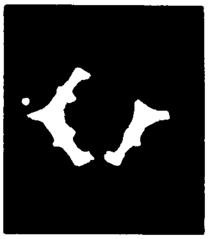
P


Q

Figure 2

Deposition of Strontium

$T_r = 360^{\circ}K$

Pattern	A	B	C	D	E
Time (min)	0	15	30	50	75
ϕ (ev)	2.37	2.60	2.54	2.44	2.40

$T_r = 300^{\circ}K$

Pattern	F	G	H
Time (min)	0	21	57
ϕ (ev)	3.10	3.17	2.62

Time = 60 minutes

Pattern	I	J	K	L	M
T_r ($^{\circ}K$)	1000	900	800	700	635
ϕ (ev)	3.78	2.75	2.48	2.45	2.55

$T_r = 400^{\circ}K$

Pattern	N	O	P	Q
Time (min)	120	120	120	120
ϕ	2.55	2.55	2.55	2.55

accompanied by boundary migration. Therefore, one may assume that the observation of boundary migration depends on the surface conditions of the tip, as well as on the tip temperature, and concentration gradient. This deposition transforms stable state 1 to the end pattern of Figure 1O which will be labeled as stable state 2.

The second sequence of patterns in Figure 2 shows what happens when Sr is deposited on the tip at room temperature beginning with stable state 1. After only one minute of deposition, clustering occurred which obscured the pattern in the region nearest the source. On further deposition, the clusters appeared to form a nearly symmetric ring about the $\{110\}$ plane nearest the source just as in Figure 1D. Continued deposition resulted in nonsymmetrical bright emitting regions. There was no evidence of migration, and it appeared that the adsorbed Sr was immobile at room temperature regardless of whether the substrate was clean W or a symmetric distribution of Sr on W. Thus, an end pattern for a given temperature may be obtained from an end pattern corresponding to an elevated temperature merely by depositing additional Sr with the tip held at the lower temperature.

At temperatures above 500^{o}K a series of steady end states may be obtained. The sequence I, J, K, L, M of Figure 2 shows 5 such states. In this sequence each pattern represents the end steady state observed when Sr was deposited on clean W at a particular temperature. Pattern I was the end pattern observed during deposition at 1000^{o}K. Pattern J was that observed during deposition at 900^{o}K. In all cases, the end steady state pattern was not altered by continued deposition. The end pattern observed for any one temperature is an intermediate state observed during any lower temperature deposition. Clusters did not appear in any of these patterns. If deposition was continued in pattern ~~E~~ L at a lower temperature clusters appeared as in the first and second sequences of Figure 2. Thus it appears that the final state was entirely a function of temperature provided that a certain minimum time of deposition had elapsed.

Patterns N, O, P, Q illustrated in Figure 2 reveal how the exposure time may alter the appearance of the pattern. It shows the pattern observed after a two hour deposition at T_r equal to 400°K. This pattern of stable state 2 was unmistakably identifiable on the microscope itself; however, the photographs can be made to emphasize predetermined aspects. If the negative is highly exposed the pattern shows a faint uniform structure similar to that of clean W underneath an intense symmetric structure apparently superimposed on the former. In some cases faint clusters can be observed on the $\{110\}$ plane edges. If the negative is briefly exposed, the faint structure cannot be seen and more detail can be observed in the previously intense structure. Clusters on the $\{211\}$ planes are a common feature of these additional details. The interpretation is that the Sr was adsorbed in two layers which differ considerably in their distribution and that the outer layer was less dense but exercised a greater control over the electron emission process. The clusters formed a part of the second layer. The similarity of the first layer to clean W indicates perhaps that this layer builds up on sites of the underlying W.

The stable states of Sr on W identified during deposition can also be observed in migration and desorption experiments. FEM patterns for these experiments are illustrated in Figure 3. Strontium was deposited on the side of the tungsten tip from the upper left at the temperature T_r equal to 300°K for two hours. This was equivalent to about 3 layers if spread uniformly over the tungsten tip. Pattern A is that of clean tungsten before the deposition. Pattern B displays the emission immediately after the completion of the deposition.

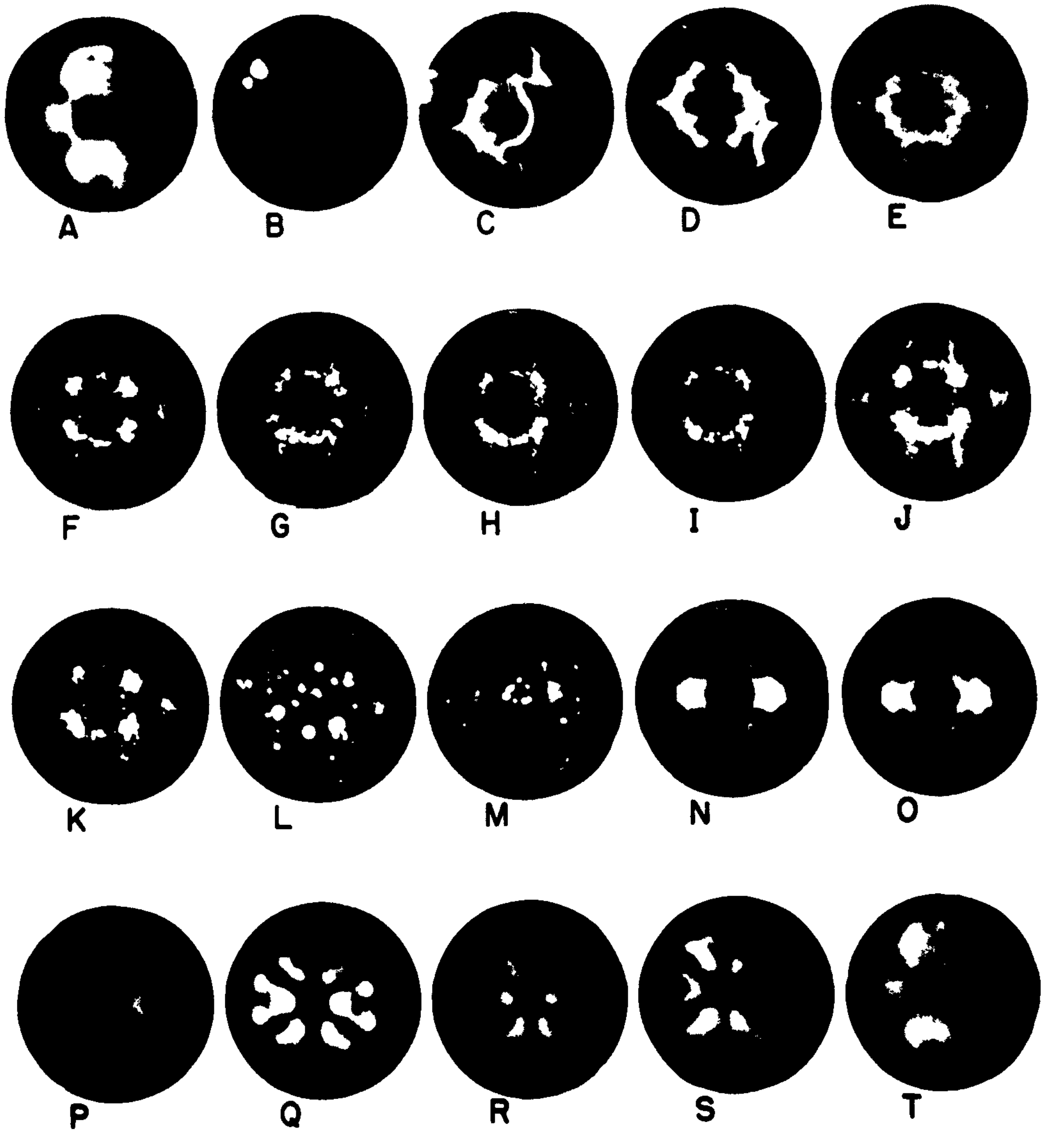
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Figure 3

Migration and Deposition of Strontium

$T_a = 350^{\circ}K$

Pattern	A	B	C	D	E
Time		0	40	240	4400
I(μ a) V (kv)	1.5 11.5	1.5 4.2	1.5 5.4	1.5 5.6	1.5 5.4
φ (ev)	4.5	2.3	2.7	2.8	2.7

$T_a = 450^{\circ}K$

Pattern	F	G	H	I	J
Time (min)	1/2	5	95	1335	2555
I (μ a) V(kv)	1.5 4.9	1.5 4.4	1.5 4.2	1.5 4.1	2.5 4.5
φ (ev)	2.6	2.4	2.3	2.3	2.3

$T_a = 570^{\circ}K$

Pattern	K	L	M	N	O
Time (min)	5	65	75	125	1600
I (μ a) V(kv)	1.5 3.9	1.5 4.1	2.5 4.7	1.5 4.6	1.5 4.5
φ (ev)	2.2	2.3	2.4	2.5	2.4

$T_a = 1200^{\circ}K$

Pattern	P	Q	R	S	T
Time (min)	1	4	12	64	124
I(μ a) V(kv)	1.5 5.2	1.5 6.9	2.0 8.4	2.0 11.0	1.5 11.5
φ (ev)	2.6	3.1	3.6	4.3	4.5

Adsorbed Sr appears as a large cluster on the side of the tip. The remainder of the patterns in the first row show the progress of a boundary migration at 350°K. The bright edge was visible together with the symmetric pattern behind that edge. In pattern D, the migration was almost complete after 240 minutes at this temperature. The symmetric end pattern E is a variation of stable state 2 previously identified in patterns N, O, P, Q of Figure 2.

When the tip temperature was raised to 450°K as in F, the clusters which were faint in pattern E quickly dominate the entire pattern especially on the $\{110\}$ plane edges. There was very little change in the pattern as well as the apparent work function with time. Immediately after the temperature was increased to 570°K the regular array of clusters became randomly distributed as seen in patterns K and L and the pattern lost its symmetry. Later a stable symmetric pattern developed as the clusters disappeared. This is illustrated in patterns M, N, and O. Pattern O may be identified as the same as stable state 1.

Activation at 1200°K caused a decrease in the apparent emitting area and a rapid increase in work function, followed by an increase in emitting area and a less rapid increase in work function. In time this process terminated in the clean W pattern and the work function of W.

A study of deposition, migration, and desorption data suggests the following state of the adsorbate on the W tip. Stable state 2 consists of an inner strongly bound layer and an outer loosely bound layer. At low temperatures the loosely bound layer is held in a relatively uniform symmetric distribution. The Sr atoms are immobile on these uniform layers. At slightly higher temperatures, they move over the tightly bound layer until they are trapped at surface imperfections such as the $\{110\}$ plane edges, where they are held as clusters of atoms.

Stable state 1 is the tightly bound layer of Sr on W. The total quantity of Sr which can be held in this condition depends primarily on the tip temperature.

The concentration of immobile Sr following deposition at 300°K spreads out, at elevated temperatures, to stable state 2 via a boundary migration. Surface migration proceeds by Sr atoms moving over the tightly bound layer until they reach the edge of that layer where they become bound to the clean W surface making it possible for other atoms to migrate over the freshly covered region. Thus the tightly bound layer is gradually extended by the movement of strontium over the tightly bound first layer. The sharp leading edge of the migration implies the lack of mobility of the inner layer at this temperature. The outer layer meanwhile forms on top of the inner layer as rapidly as the boundary proceeds. This type of migration has been reported for oxygen on W tips at 27°K (6) (The oxygen, however, increases the work function of the W tip so that the FEM patterns show a dark region spreading out over the clean W).

The transition from state 2 to state 1 is accomplished by desorption of the weakly bound layer. The transition from state 1 to clean W is one of desorption of the tightly bound inner layer. Transition 2 to 1 occurs at a lower temperature than does transition 1 to clean W.

If the optimum quantity of Sr were deposited, a tightly bound layer could be formed by deposition and migration without desorption. This is illustrated in Figure 4. With the tip held at 300°K, strontium was deposited from the lower left, at the same arrival rate used above, for a period of 35 minutes. Pattern B, which can be identified with Figure 1C, was observed after the source was turned off. By heating the tip to an activation temperature of 515°K,

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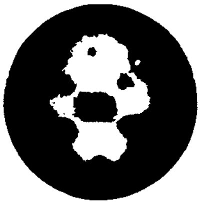
(6) R. Gomer and J. K. Hulm, J. Chem. Phys., 27, 1363 (1957).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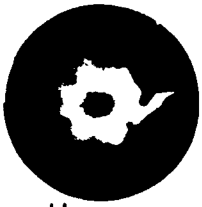

H


I


J

Figure 4

Deposition of Strontium at $T_r = 300^{\circ}K$ for 35 minutes and migration at $T_a = 515^{\circ}K$.

Pattern	A	B	C	D	E
Time (min)		0	3	10	15
I (μ a) V (kv)	5 8.62	100 5.05	100 4.68	100 4.63	100 4.58
ϕ (ev)	4.5	2.6	2.5	2.5	2.5

Pattern	F	G	H	I	J
Time (min)	26	35	41	50	57
I(μ a) V(kv)	100 4.48	100 4.52	100 4.50	100 4.48	100 4.48
ϕ (ev)	2.4	2.5	2.5	2.4	2.4

migration with a sharp leading edge was initiated. The progress of the migration was exhibited by the displacement of the bright region across patterns C - J. As above, the advancing boundary appeared to encircle the $\{110\}$ planes and proceeded outward. Upon completion of the migration the symmetric pattern J showed characteristics only of a tightly bound layer. The work function for this state of the tip was 2.5 ev as was determined from the Fowler-Nordheim plot of Figure 5. For the purpose of determining the activation energy pattern H was selected as the end state. This was easily recognized and reproducible.

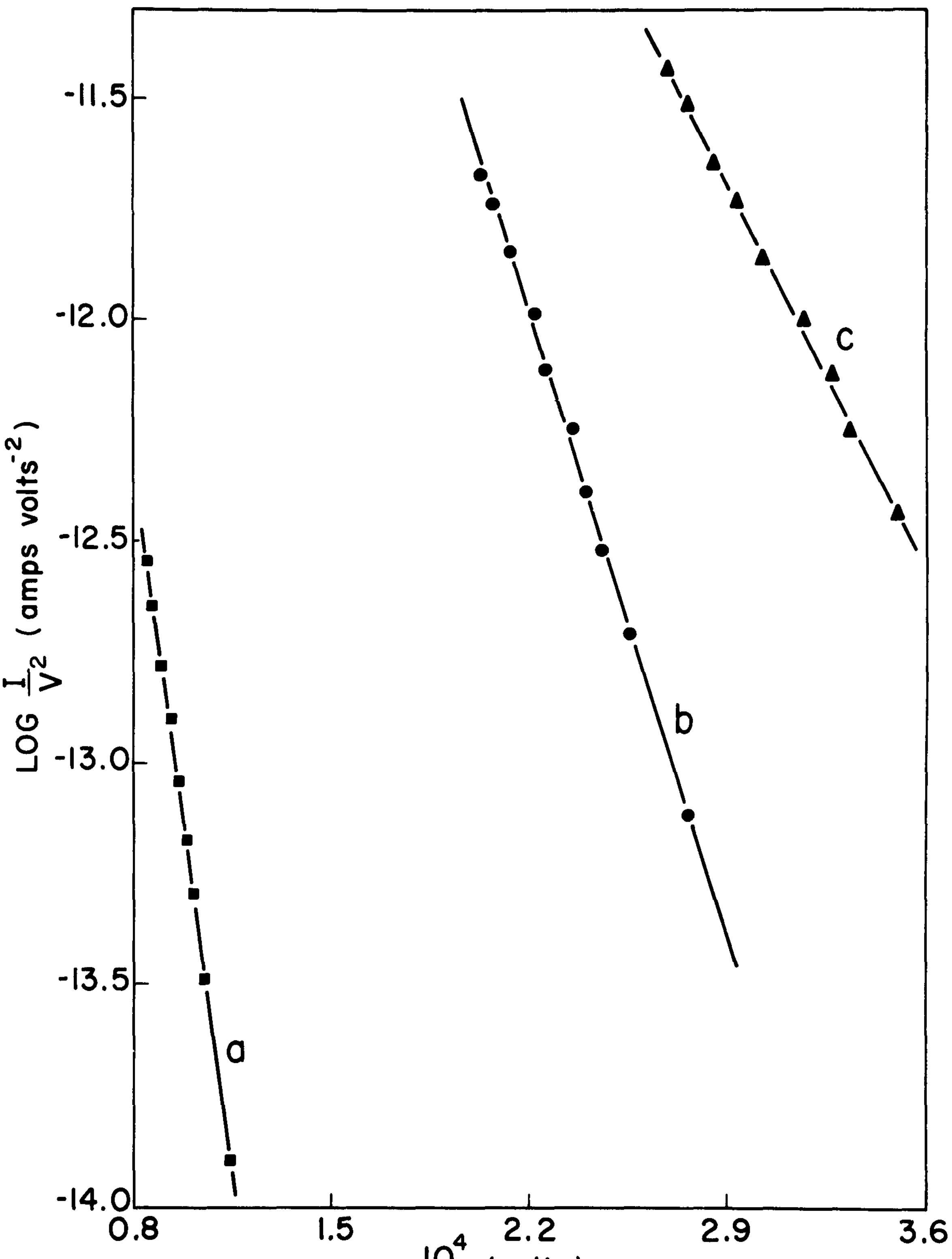
Figure 6 shows the sequence of patterns observed during migration at four activation temperatures between 450°K and 532°K after identical depositions. The first pattern in each row represents the initial state of the migration process while the fourth pattern represents the final state. The last pattern exhibits the condition after the migration was complete. Measurements of this type can be extended up to temperatures of 750°K, however, the migration times are too short for accurate determination. In the temperature range between 570°K and 750°K desorption from the mobile loosely bound layer is competitive with the migration process.

Figure 7 shows an Arrhenius plot from which activation energy of this mode of migration may be determined for the sequence presented in Figure 6. A least squares fit yields an activation energy of 16 kcal/mole or 0.70 ev/atom to an estimated accuracy of ± 3 kcal/mole.

Figure 8 presents patterns of tightly bound layers formed by migration of smaller quantities of Sr. Strontium was deposited with the tip held at a receiver temperature of 300°K. The deposition times were so short that optimum coverage for maximum emission was not achieved. Migration progressed without a boundary. In each sequence the activation temperature

Figure 5

Fowler-Nordheim plot (a) for clean W, ϕ assumed to be 4.5 ev, (b) Sr on W pattern J, figure 4, $\phi = 2.5$ ev, (c) SrO on W pattern I, figure 11, $\phi = 2.0$ ev. The work function computed for (b) and (c) used the form factor determined from (a).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-11.5
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-12.5
-13.0
-13.5
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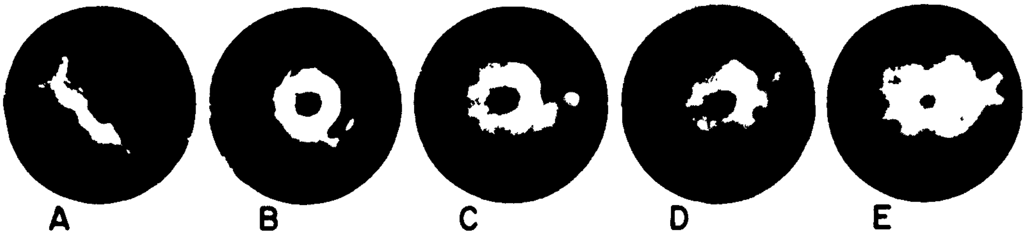
0.8
1.5
2.2
2.9
3.6
$\frac{10^4}{V}$ (volts)
a
b
c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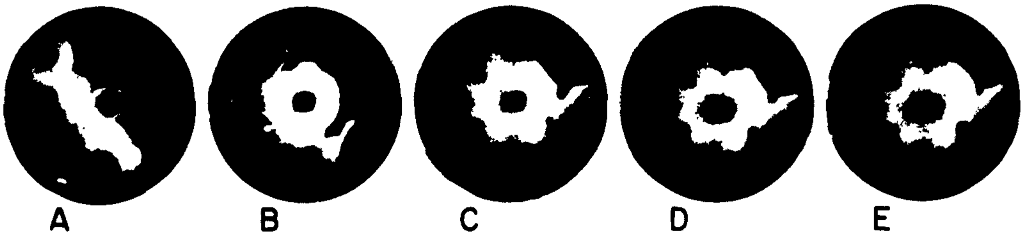
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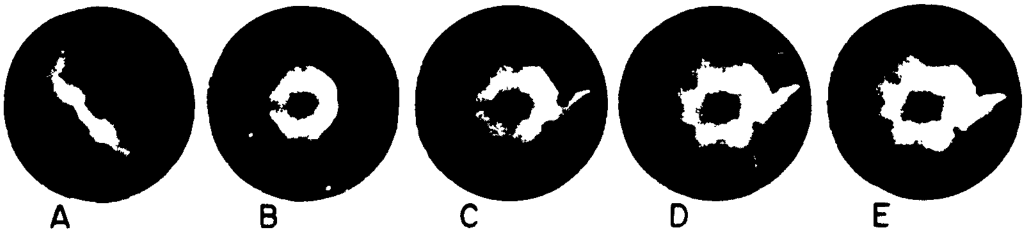
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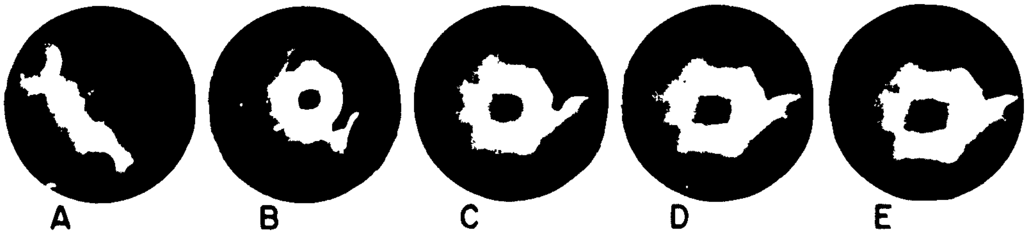
A
B
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E

Figure 6

Migration of Strontium on Tungsten after Deposition at Room Temperature for 35 minutes.

$T_a = 532^{\circ}K$

Pattern	A	B	C	D	E
Time (min)	0	2	10	20	30
I (μa) V(kv)	50 4.80	50 4.52	50 4.40	50 4.30	50 4.42
ϕ (ev)	2.8	2.7	2.6	2.6	2.5

$T_a = 487^{\circ}K$

Pattern	A	B	C	D	E
Time (min)	0	10	53	100	132
I (μ a) V(kv)	100 5.05	100 4.58	100 4.48	100 4.48	100 4.48
ϕ (ev)	2.6	2.5	2.4	2.4	2.4

$T_a = 468^{\circ}K$

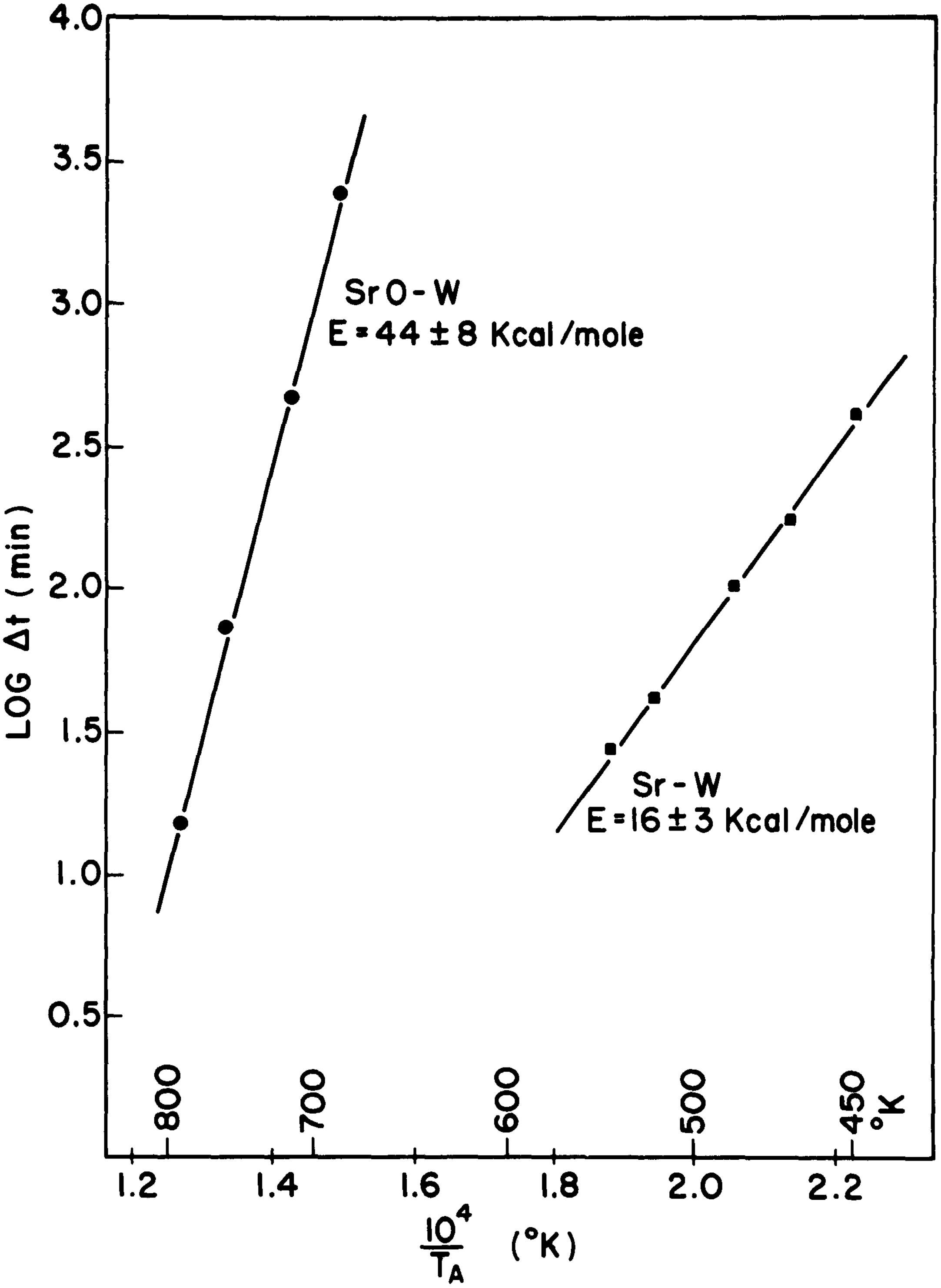
Pattern	A	B	C	D	E
Time (min)	0	20	119	174	194
I (μ a) V(kv)	50 4.70	50 4.28	50 4.22	50 4.22	100 4.55
ϕ (ev)	2.6	2.5	2.4	2.4	2.4

$T_a = 450^{\circ}K$

Pattern	A	B	C	D	E
Time (min)	0	10	265	410	430
I(μ a)V(kv)	100 4.92	100 4.62	100 4.48	100 4.48	100 4.48
ϕ (ev)	2.6	2.5	2.4	2.4	2.4

Figure 7

Plot of log Δt vs. $1/T_a$



4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
LOG Δt (min)
Sr O - W
E = 44 ± 8 Kcal /mole
Sr - W
E = 16 ± 3 Kcal /mole
800
700
600
500
450
°K
1.2
1.4
1.6
1.8
2.0
2.2
$\frac{10^4}{T_A}$ (°K)

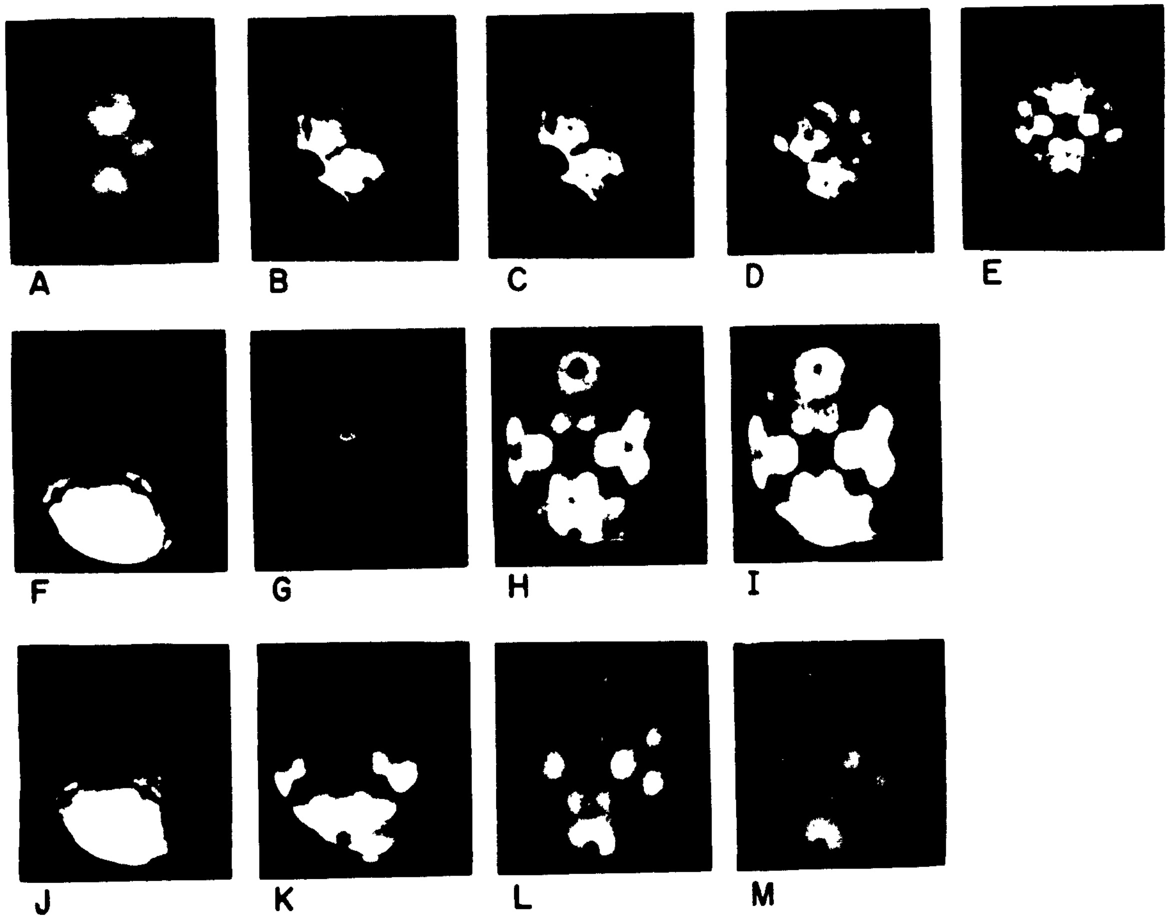

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Figure 8

Migration of Sr on W at $T_a = 632^\circ K$. The tip was at room temperature during deposition.

Deposition time = [illegible] 1 min.

Pattern	A	B	C	D	E
Time (min)		0	1	6	12
ϕ (ev)	4.50	4.37	4.45	4.35	4.31

Deposition time = 2 min.

Pattern	F	G	H	I
Time (min)	0	1	5	17
ϕ (ev)	4.15	4.04	4.15	4.24

Deposition time = 2.5 min.

Pattern	J	K	L	M
Time (min)	0	1	6	15
ϕ (ev)	3.95	3.88	3.90	4.01

for migration was 631°K. The deposition time was one minute, two minutes, and two and a half minutes for the first, second, and third sequence respectively. In the first two sequences the center of the deposition was on a $\{100\}$ plane while in the last the deposition was on a $\{110\}$ plane. As migration proceeded the only observable change in the pattern is on the planes which are normally high emitting from clean tungsten. Larger deposition required a longer time to complete the migration. For these small coverages it was found that the work functions did vary although the final patterns are indistinguishable. Thus the work function was a more sensitive test of coverage than is the FEM pattern.

B. Strontium Oxide

When SrO is deposited on W and then heated to successively higher temperatures, a series of chemical reactions may occur terminating in an oxygen covered W surface. The FEM patterns observed during these processes are shown in Figure 9. A coverage equivalent to about three layers of SrO was deposited from the upper right on the clean W point for a period of two hours. Additional SrO would not change the appearance of the pattern at the end of the deposition not at any stage during the subsequent activations. This is considered a heavy coverage. Pattern A shows the emission from clean W, and pattern B shows the emission from the tip after the deposition was completed. Pattern B has no symmetry, but shows a bright grainy region on the side of the tip nearest the source which is distinctly different from the clusters observed for Sr on W.

Upon activation at T_a equal to 790°K, a series of patterns were observed that were symmetric except for the grainy bright regions which persisted on the side of the tip nearest the source. As seen in patterns C and D, the symmetric part changed with time, becoming stable only after the grainy region had disappeared as in pattern E. This stable pattern was characterized by high

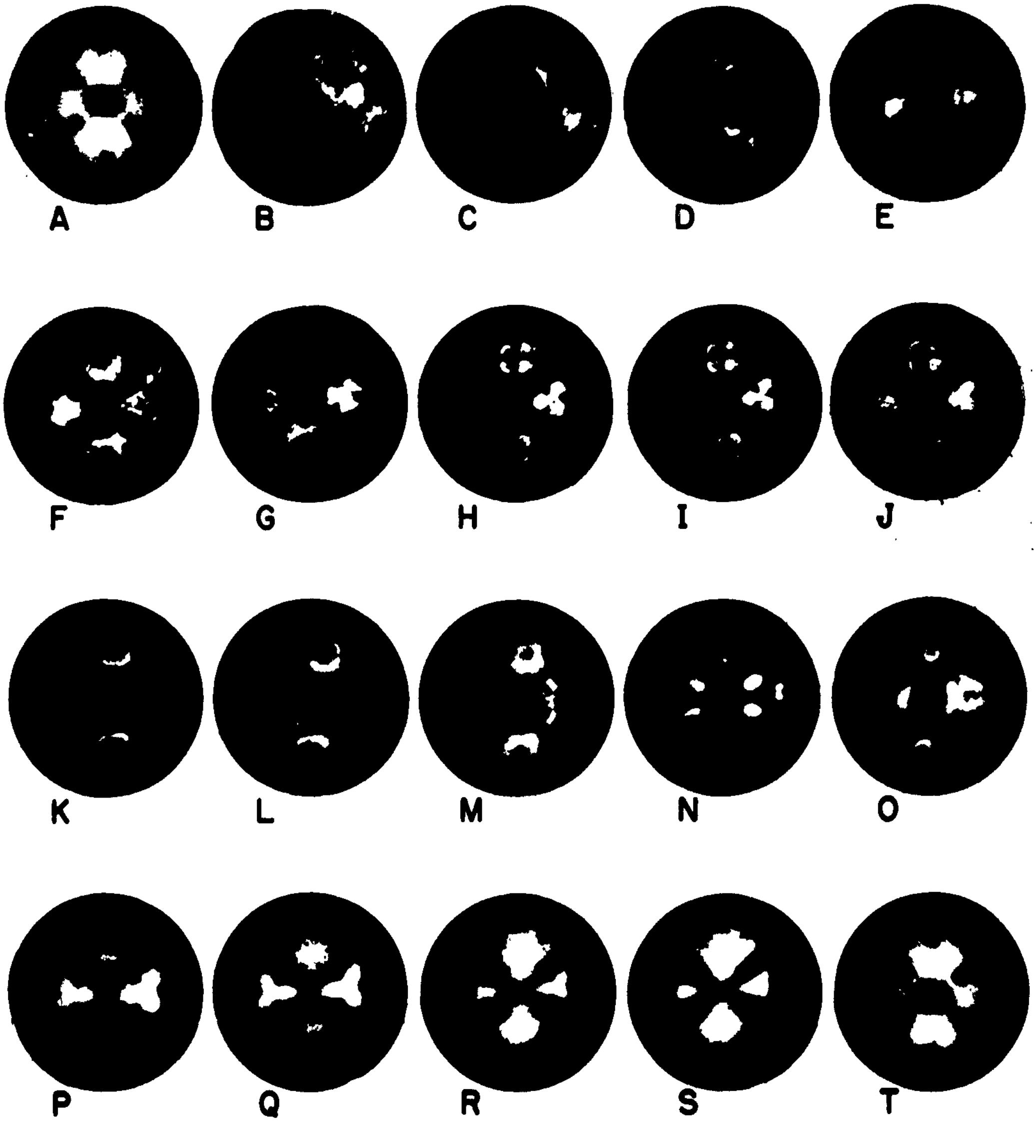
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Figure 9

The FEM patterns observed for successive activation temperatures, T_a, after depositing a heavy coverage of SrO.

T_a = 790°K

Pattern	A	B	C	D	E
Time (min)		0	40	160	412
I (μa) V (kv)	15 9.60	100 3.00	100 2.30	100 2.40	50 3.60
ϕ (ev)	4.5	1.7	1.1	1.4	2.1

T_a = 1000°K and 1185°K

Pattern	F	G	H	I	J
T_a(°K)	1000	1000	1000	1185	1185
Time (min)	60	140	460	5	202
I (μa) V(kv)	100 6.58	140 7.10	25 8.20	25 8.62	25 9.28
ϕ (ev)	3.0	3.3	3.8	4.0	4.1

T_a = 1400°K

Pattern	K	L	M	N	O
Time (min)	67	101	131	185	200
I(μa) V(kv)	15 7.60	25 7.10	50 6.50	25 7.80	100 7.90
ϕ (ev)	3.8	3.5	3.4	3.9	4.0

T_a =1750°K

Pattern	P	Q	R	S	T
Time (min)	1/6	5	20	55	245
I(μa) V(kv)	15 11.40	15 11.10	15 10.55	15 9.95	15 9.60
ϕ (ev)	5.0	4.9	4.7	4.6	4.5

emission from the $\langle 11 \rangle$ direction reducing the work function below the published values of bulk Sr(7). Two activation runs, the first at 1000°K, and the second at 1185°K are shown in the next row. The patterns are similar for the two runs with one exception. All patterns in the first run show emission at the $\{110\}$ edges, but none show this emission in the second. The work function increased in both cases, apparently approaching a value near 4.1 ev. Further heating at 1400°K produced the sequence of patterns reported by Cape and Coomes (1). In this sequence there was a reversal in symmetry about the $\langle 11 \rangle$ direction accompanied by a sharp minimum in the work function. Heating to 1750°K cleaned up the W point, and patterns corresponding to oxygen on tungsten were observed during this process.

The high temperature processes, represented by the last two rows of Figure 9, were identified (1) with chemical reactions between SrO and W, the decomposition of a chemical compound to oxygen on W, and the final desorption of oxygen. Low temperature behavior of SrO on W was investigated by observing changes in the FEM pattern with time as SrO was deposited on W for a fixed tip temperature. Figure 10 shows the patterns observed during four separate depositions at successively higher temperatures. In all cases SrO was incident from the upper right with the same tip-source geometry. Pattern B in the sequence of patterns which was taken with the tip temperature at 300°K, shows that the SrO was incident only on the side of the tip nearest the source. As the SrO accumulated on the tip, a bright region appeared on the corresponding side of the pattern. The clean W pattern, visible at first on the other side, seemingly vanished as a result of the difference in work functions. The bright leading edge and clusters characteristic of Sr did not appear, and instead a grainy bright region developed as shown in pattern C. This pattern maintains some of the

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(7) D. A. Wright, Proc. I. E. E., 100, 125 (1953).

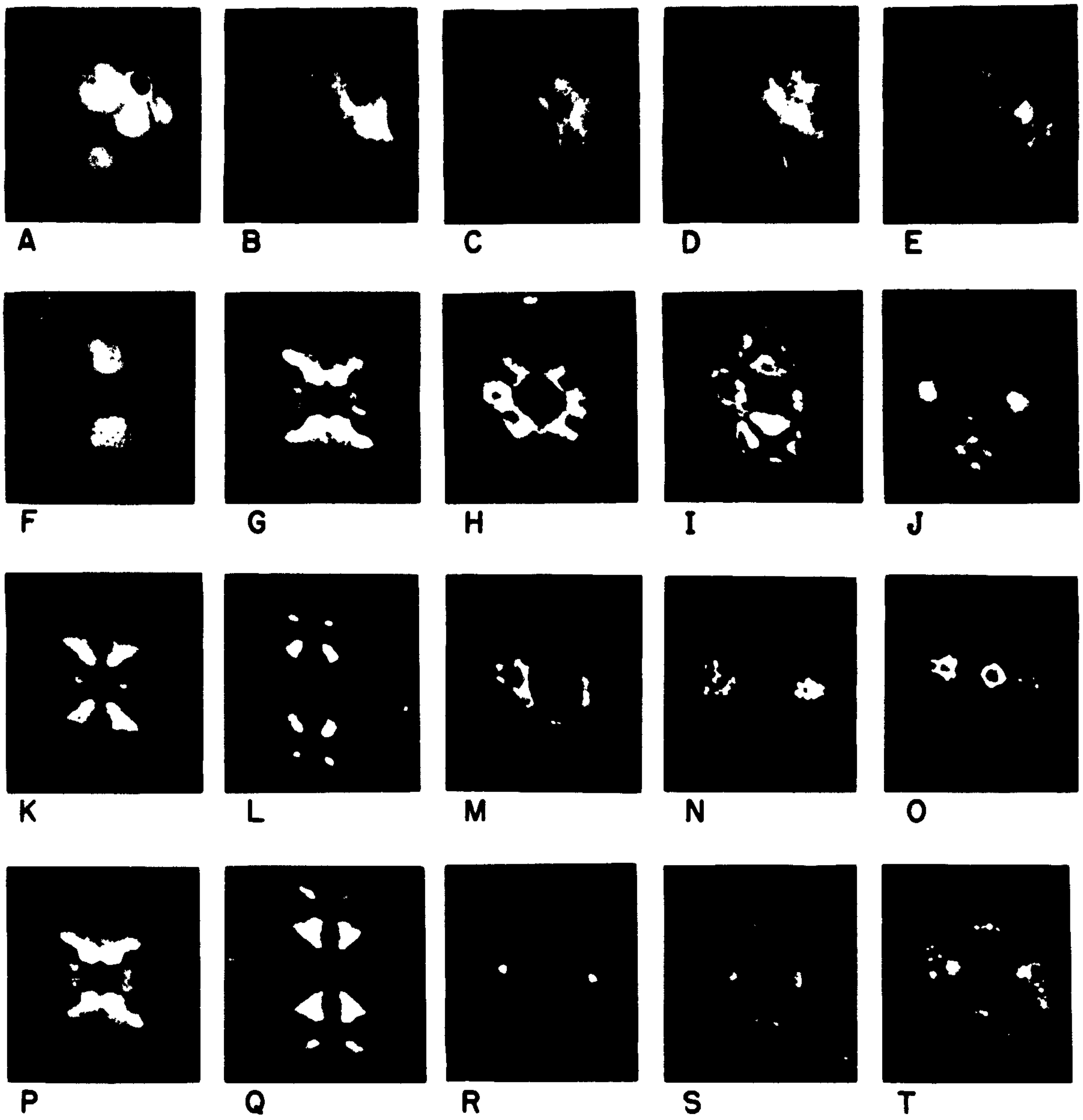
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Figure 10

FEM patterns observed during deposition of SrO at several tip temperatures.

T_r = room temperature

Pattern	A	B	C	D	E
Time (min)	0.5	4	20	60	120
ϕ (ev)	4.36	2.50	2.37	2.25	1.88

$T_r = 950^\circ K$

Pattern	F	G	H	I	J
Time (min)	0	1	35	50	260
ϕ (ev)	4.5	4.10	2.69	2.54	2.70

$T_r = 1155^\circ K$

Pattern	K	L	M	N	O
Time (min)	5	10	65	165	300
ϕ (ev)	4.31	3.81	2.33	5.60	5.49

$T_r = 1250^\circ K$

Pattern	P	Q	R	S	T
Time (min)	1	7	55	111	205
ϕ (ev)	4.40	4.26	2.89	2.38	3.96

symmetry of the W pattern. A sharp leading edge of the deposit could be observed after 60 minutes, and most of the symmetry was gone. Sixty minutes later the grainy bright region extended over most of the side of the tip. Further deposition beyond 120 minutes caused no apparent change in the pattern. These data show that SrO, like Sr, was immobile at 300^{o}K, but, unlike Sr, an optimum quantity of SrO leading to maximum emission could not be found. The sharp line between bright and dark seen in pattern D merely delineated the edge of the deposit.

The second deposition sequence was made at a temperature T_r equal to 950^{o}K. The patterns observed during the initial part of this sequence were symmetric, indicating a migration more rapid than the arrival rate. Pattern G shows a marked resemblence to a light coverage of Sr such as pattern O, row IV of Figure 1. The work function during this deposition decreased smoothly to a minimum for pattern I; thereafter, the measured work function was not reliable due to the formation of clusters. Continued deposition increased the size and number of the clusters.

At T_r equal to 1155^{o}K the pattern remained symmetric at all times during deposition, and the work function went through a minimum. After the minimum in the work function the pattern consisted of clusters on the $\{111\}$ planes and the $\{110\}$ plane edges. Depositing more SrO caused no changes in the pattern.

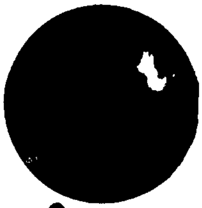
The final deposition was made at T_r equal to 1250^{o}K. Here again the pattern remained symmetric at all times; the initial stages were similar to Sr on W or like the deposition of SrO at 1155^{o}K. The work function decreased to a minimum, and then increased with equal speed. No clusters were observed on the 110 plane edges in this case. The final pattern was stable, and further deposition did not change its main features.

The stable condition of the patterns reached when the tip temperatures were 950°K and above was probably due to the steady state attained between the rate of evaporation and the rate of deposition.

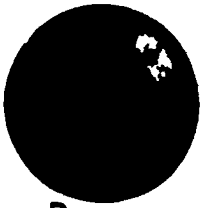
SrO was deposited on the W tip held at room temperature and then the deposit was activated at some higher temperature. Patterns obtained in this way were compared with those obtained by deposition on the tip held above room temperature. These are shown in Figure 11. Pattern B shows the distribution after a 25 minute deposit, which is the same as pattern C of Figure 10 row 1. When the tip was heated to an activation temperature of 700°K the grainy bright region nearest the source become smaller, but maintained its grainy appearance as in patterns C to E. In pattern E, individual emitting centers could be distinguished in this region. No other emission could be observed even though very large electron currents were drawn from the tip. The emitting centers appeared to be in a continuous state of agitation similar to the clusters observed with Sr on W. In pattern F bright regions appeared in the center of the pattern at the $\{110\}$ plane edges. These regions increased in intensity with time until a symmetric distribution became visible in pattern H, however, the grainy region associated with the pile up of SrO was still evident in the upper right. A completely symmetric pattern I with no traces of the accumulation evolved from H only after a long time compared with the time required to arrive at H. This final pattern was stable, and the emitter had a work function of 2.0 ev as determined from the Fowler-Nordheim plot of Figure 5. This pattern and work function may be used to identify the final state of the activation process. Further heating at a temperature of 1400°K resulted in the stable patterns and characteristic work function minimum observed by Cape (1) in the temperature range 1150-1525°K

A

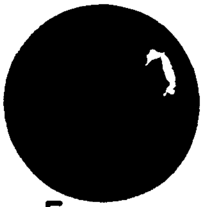
B



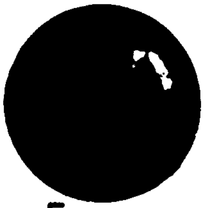
C



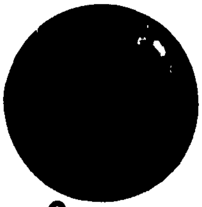
D



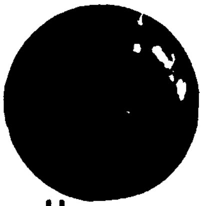
E



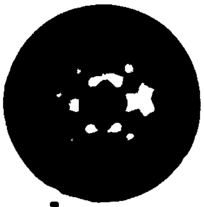
F



G



H



I

Figure 11

Sequence of patterns observed during the migration of SrO on W. $T_a = 700^{\circ}K$. T_r = room temperature.

Pattern	A	B	C
Time (min)		0	13
I(μ a) V(kv)	5 10.20	30 4.10	50 3.10
ϕ (ev)	4.5	2.2	1.8

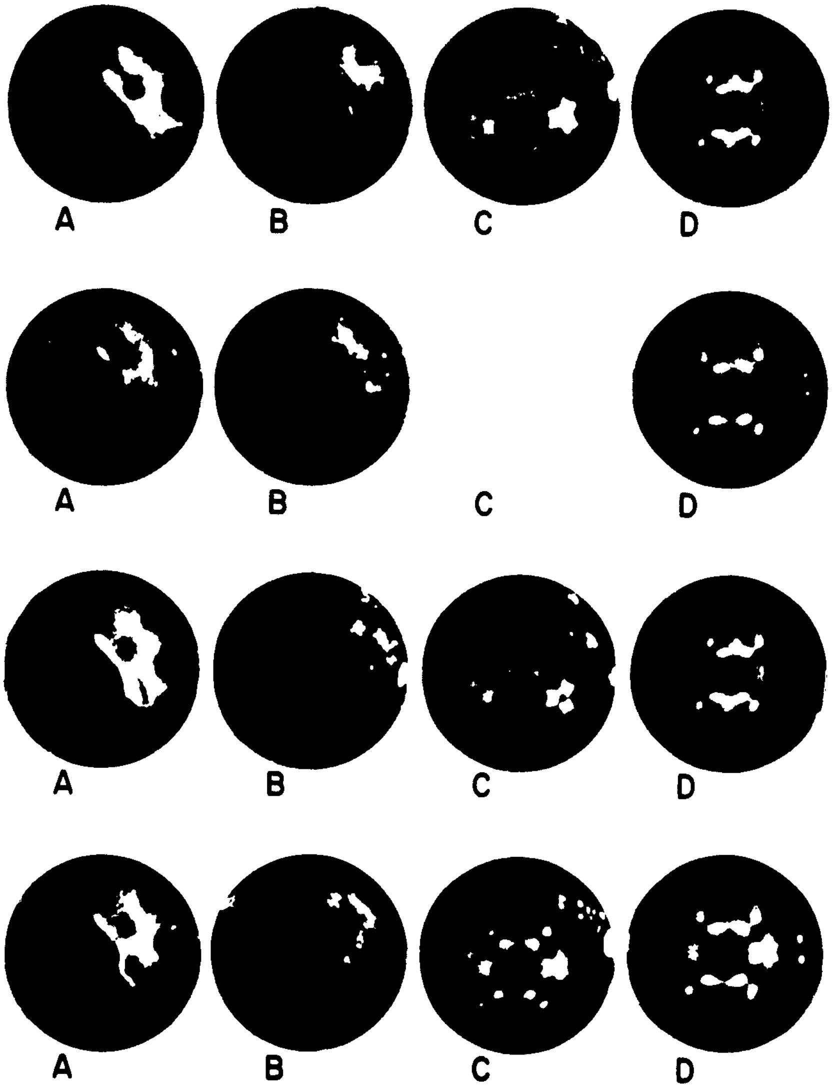
Pattern	D	E	F
Time (min)	25	40	50
I (μ a) V(kv)	50 3.00	50 3.05	50 3.10
ϕ (ev)	1.7	1.8	1.8

Pattern	G	H	I
Time (min)	65	75	490
I (μ a) V(kv)	50 3.20	50 3.30	5 2.95
ϕ (ev)	1.8	1.8	2.0

Figure 12 shows the sequence of patterns observed at four different activation temperatures in the range 670-790°K after identical depositions at 300°K. The second pattern in each sequence shows that the grainy region associated with the accumulation of SrO becomes smaller with time, and the third pattern shows that a symmetric pattern appears while this region is still visible. An Arrhenius plot of these data is given in Figure 7. A least squares fit of the experimental points yields an activation energy of 44 kcal/mole, or 1.9 ev/molecule, to an estimated accuracy of 8 kcal/mole.

Boundary free migration can account for the decrease in size of the grainy region and the appearance of the symmetric pattern. Another possibility is that SrO may dissociate at these temperatures on the W surface and the components then migrate at different rates. The overall rate then should be determined by the slowest process.

Cape and Coomes showed that the sequence of patterns observed for SrO on W, in the temperature range 1150°-1550°K, could be reversed by the deposition of SrO at a temperature below 1150°K. This sequence of patterns is shown in Figure 9 Row III. The first pattern in this sequence was referred to as the X pattern and the last was called Z. After going through the sequence at T_a equal to 1435°K to the Z pattern, a deposit of SrO at T_r equal to 1050°K brought back the Z pattern and the sequence at T_a equal to 1430°K could be repeated. This procedure was used in an attempt to identify the role of Sr in this process. The FEM patterns are shown in Figure 13. Pattern A of Row I is the Z patterns, the terminal point of activation at T_a equal to 1483°K after deposition of SrO at T_r equal to 1075°K. The tip temperature was reduced to 635°K and Sr deposited from the lower left for a period of two hours at which time pattern B was observed. The tip was then heated to T_a equal to 1418°K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D

Figure 12

FEM Patterns observed during migration of SrO on W at different temperatures T_a. T_r = room temperature.

$T_a = 790^oK$

Pattern	A	B	C	D
Time (min)	0	2	10	15
I (μa) V(kv)	50 4.30	50 3.45	50 3.65	50 3.65
φ (ev)	2.2	1.8	1.9	2.0

$T_a = 750^oK$

Pattern	A	B		D
Time (min)	0	2		72
I (μ a) V (kv)	50 4.30	50 3.10		90 3.18
φ (ev)	2.2	1.7		1.9

$T_a = 700^oK$

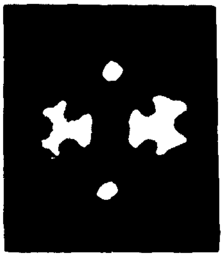
Pattern	A	B	C	D
Time (min)	0	40	100	460
I (μa) V(kv)	40 4.30	50 3.45	50 3.65	50 3.65
φ (ev)	2.3	1.8	1.9	2.0

$T_a = 670^oK$

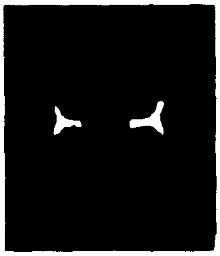
Pattern	A	B	C	D
Time (min)	0	30	1015	2425
I (μ a) V (kv)	50 4.55	50 3.00	50 3.65	50 3.70
φ (ev)	2.3	1.8	1.9	2.0

and patterns C to E observed at the times indicated. Pattern E can be identified as the pattern Z but none of the other patterns resemble the X to Z sequence. The work function does not show the minimum, instead the work function starts at a value considerably less than that normally observed for X and gradually increases to that of the Z. The procedure was repeated at a number of different receiver temperatures from 500^{o}K to 1163^{o}K but the X pattern was never observed nor could the X to Z sequence be reproduced. Low work functions were always observed following the Sr deposition but the pattern depended on the receiver temperature. One point was significant; sufficient Sr could be adsorbed on the point to lower the work function considerably even at 1163^{o}K, whereas clean W could not adsorb much Sr at this temperature and the work function decreased only slightly.

The role of Sr in the formation of the X pattern was also investigated. The FEM patterns are shown in Figure 13, Row 11. SrO was deposited for 5 hours with T_r' equal to 1155^{o}K giving pattern F, the end point pattern for deposition at this temperature. Activation for 35 minutes at T_a equal to 1410^{o}K resulted in the X pattern as shown by G. At this point the temperature was reduced to 1155^{o}K and Sr deposited for 160 minutes. The pattern is not symmetric after this deposition and the apparent work function is low. The part of the pattern which is bright is symmetric and not very different from the X pattern. Continued deposition at T_r' equal to 300^{o}K for one hour reverses the emitting part of the pattern as in I but does not otherwise change the appearance. This second deposition was made to be sure that Sr was actually being adsorbed. The tip was heated to T_a equal to 525^{o}K in order to bring about a symmetric distribution of Sr. After 20 minutes pattern J was obtained with the general features of the X pattern but a slightly lower work function. The starting point



A



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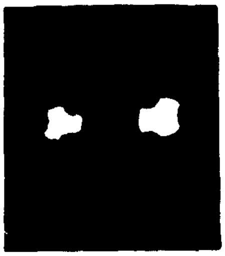

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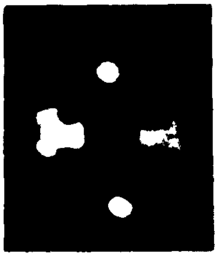

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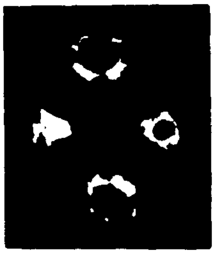

G

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Figure 13

Sr - SrO on W

$T_r = 635^\circ K$, deposition time of Sr = 120 min., $T_a = 1418^\circ K$

Pattern	A	B	C	D	E
Time (min)		0	5	25	147
ϕ (ev)	4.23	1.95	3.05	2.90	3.38

Pattern	F	G	H	I	J
Temperature ($^\circ K$)	$T_r = 1155$	$T_a = 1410$	$T_r = 1155$	$T_r = 300$	$T_a = 525$
Time (min)	300	35	160	60	20
ϕ (ev)	4.0	4.4	3.5	3.39	3.9

of pattern F was never achieved but activation always terminated in what appears to be pattern X.

These experiments failed to show the specific role of Sr in transition from one Sr-O-W complex to another. They did show that Sr can be adsorbed on the Sr-O-W complex in larger quantities than it can on clean W in the temperature region between 1000 - 1200° K.