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Field-Emission Studies of the Interaction of Hydrogen Sulfide and Sulfur with Tungsten

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The interaction of hydrogen sulfide and sulfur vapor with tungsten has been studied by field-emission microscopy. Adsorption of hydrogen sulfide at 22°C begins along the [111] zones and at a pressure of about 5×10^{-8} mm the adsorption appears to be complete within 4 min. An increase in the average work function of 0.3 volt has been estimated for the process. On heating a surface saturated with hydrogen sulfide, surface migration begins at about 1150°C, leading to a concentration of sulfur along the [111] zones from which desorption takes place, i.e., the desorption processes are the reverse of the adsorption sequence. The activation energy for desorption is about 80 to 90 kcal/mole and complete removal of sulfur is observed at about 1600°C.

Sulfur adsorption at 10^{-7} mm and 22°C results in a large number of brightly emitting spots which move continually. These are mainly observed around the (111) and (011) planes. A field-induced process resulting in a sudden enlargement of the emitting area and consequent mechanical failure of the tip occurs at 22°C. This is attributed to the growth of a sulfide whisker. Presorbed hydrogen has an inhibiting effect on this nucleation phenomenon.

INTRODUCTION

In a previous paper (*1*) we investigated the mechanism of the interaction of hydrogen sulfide with tungsten films. Adsorption was undoubtedly dissociative at room temperature but we had no evidence for incorporation of sulfur into the tungsten lattice. No information concerning any crystallographic specificity of the adsorption process was obtainable.

There is no field-emission data for the interaction of hydrogen sulfide with tungsten but Müller (*2*) has reported very briefly the appearance of a number of brightly emitting areas which are granular in appearance when sulfur is adsorbed on tungsten. In view of the dissociative character of the hydrogen sulfide adsorption it was important that we should not only investigate the adsorption and desorption of hydrogen sulfide but also study the adsorption and desorption of both sulfur and hydrogen and the influence of one on the other. In particular, we were interested in specific effects associated with different crystallographic regions.

EXPERIMENTAL

The apparatus is shown schematically in Fig. 1. It consisted of two main sections, the first incorporating the field-emission tube (F) which was enclosed in an electrically heated oven (shown by a dotted line) and the second for gas preparation. The general procedure for obtaining a pressure of 10^{-9} mm has been described (*3*). The tungsten tips were prepared by electrolytic etching of a 0.1-mm tungsten wire as described by Lodge (*4*). The fluorescent screen was prepared by a method based on that described by Friedman (*5*).

Hydrogen sulfide was prepared and purified as previously described (*1*). It was transferred in a sealed-off tube, one end of

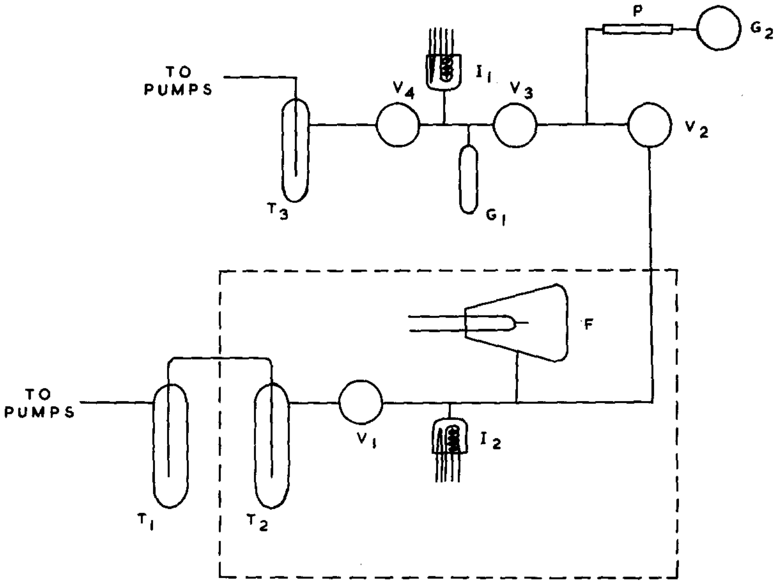

FIG. 1. Schematic representation of the apparatus: T_1, T_2, T_3, traps cooled in liquid nitrogen; I_1, I_2 Alpert-type ion gauges; V_1, V_2, V_3, V_4, ball and socket valves; G_1, G_2, gas storage vessels; P, palladium thimble; F, field-emission tube. Dotted line represents the oven.

which had been drawn down to a fine point, and placed in G_1 which was then evacuated to about 10^{-7} mm. G_1 was cooled in liquid nitrogen before the fine point of the tube was broken to provide a convenient source of hydrogen sulfide since the vapor pressure is about 10^{-4} mm at —195°C.

Recrystallized sulfur was obtained from Hopkin & Williams Ltd., stored in G_1, and degassed thoroughly by flaming. Since the vapor pressure is about 10^{-5} mm at room temperature it was not necessary to cool G_1 when a supply of vapor was required. Pure hydrogen was obtained in sealed bulbs, G_2, from B.O.C. Ltd. and further purified by diffusion through the palladium thimble P.

The field-emission patterns were photographed by means of a Nikon (4F) camera with a Nikkor f.2 lens at a distance of 2 ft (about 60 cm) with an exposure time of 1 sec. The applied voltage was always adjusted to give an electron current of about 0.5 μamp which was measured on a "Scalamp" galvanometer of sensitivity 160 mm/μamp. The temperature of the tungsten tip was measured by means of an optical pyrometer. The pressures were measured by means of Alpert-type ionization gauges which had been calibrated for hydrogen and air. Thus, pressures quoted for hydrogen sulfide and sulfur vapor are only approximate. The ion gauges were not kept on during an experiment any longer than was necessary to measure the pressure, i.e., about 10 sec.

The main crystallographic planes of tungsten which are relevant to the field-emission patterns are shown in Fig. 2.

RESULTS

Hydrogen Sulfide

1. Low Pressure Experiments

Adsorption at 22°C. After ensuring that the tungsten surface had been thoroughly cleaned, that the emission observed was characteristic of clean tungsten, and that it could be maintained in this state for some time, hydrogen sulfide was allowed to flow over the tip at a pressure of about 5×10^{-8} mm. A steady flow of hydrogen sulfide could be maintained by keeping G_1 in liquid nitrogen and continuously pumping through V_3, V_2, and V_1 with V_4 closed.

Pattern 1 shows the emission characteristics of clean tungsten and patterns 2 to 8 indicate changes occurring after various times for which the gas has been flowing. The field was applied continuously during this time. After a period of adsorption of 210 sec the emission characteristics remained the same and, therefore, pattern 8 represents saturation of the surface. This pattern did not change on evacuating to $\sim 10^{-9}$ mm or on increasing the pressure to 10^{-4} mm. The voltage had to be increased steadily as adsorption progressed in order to maintain an electron emission of 0.5 μamp, as indicated in Table 1(a). Patterns 2 to 4 show that adsorption occurs most readily along the [111] zones, but at longer times (patterns 6 to 8) the surface gives more uniform emission.

Desorption from the surface saturated at 22°C. The standard procedure for studying desorption was to heat the tungsten tip for a period of 2 min to a measured temperature at a pressure of $\sim 10^{-9}$ mm (V_2 closed), cool to room temperature, and examine the emission pattern by applying a field to give an electron current of 0.5 μamp. The applied voltage and temperature of heating are shown in Table 1(b).

The pattern characteristic of saturation at 22°C (number 8) was unchanged on heating to 750°C but at 950° a slight darkening was noticeable around the (112) planes (pattern 9). With increasing temperature, emission decreased in the region of the (112) and the (011) planes (pattern 10) and eventually at a temperature of

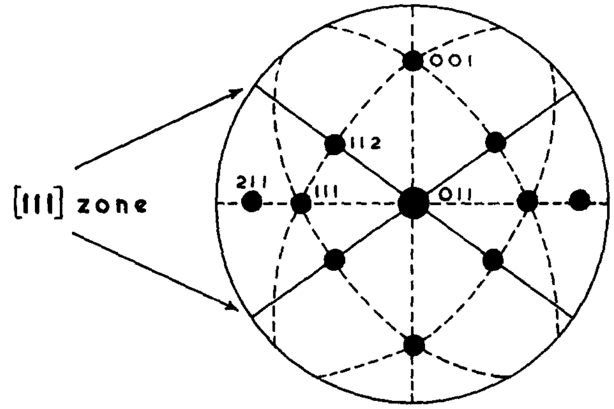

FIG. 2. Orthographic projection of a cubic crystal showing the main planes relevant to this work and the [111] zones.

TABLE 1

ADSORPTION OF H_2S AT 5×10^{-8} MM AND 22°C AND SUBSEQUENT DESORPTION BY HEATING FOR 2 MIN AT SUCCESSIVELY HIGHER TEMPERATURES

(a) Adsorption			(b) Desorption		
Pattern number	Voltage (kv)	Time (sec)	Pattern number	Voltage (kv)	Temperature (°C)
1	8.5	clean tip	8	9.4	22 to 750
2	8.6	15	9	9.4	950
3	8.6	30	10	9.4	1150
4	8.9	60	11	9.0	1200
5	9.0	120	12	8.8	1310
6	9.4	180	13	8.8	1380
7	9.4	210	14	8.6	1500
8	9.4	>240	15	8.6	1580

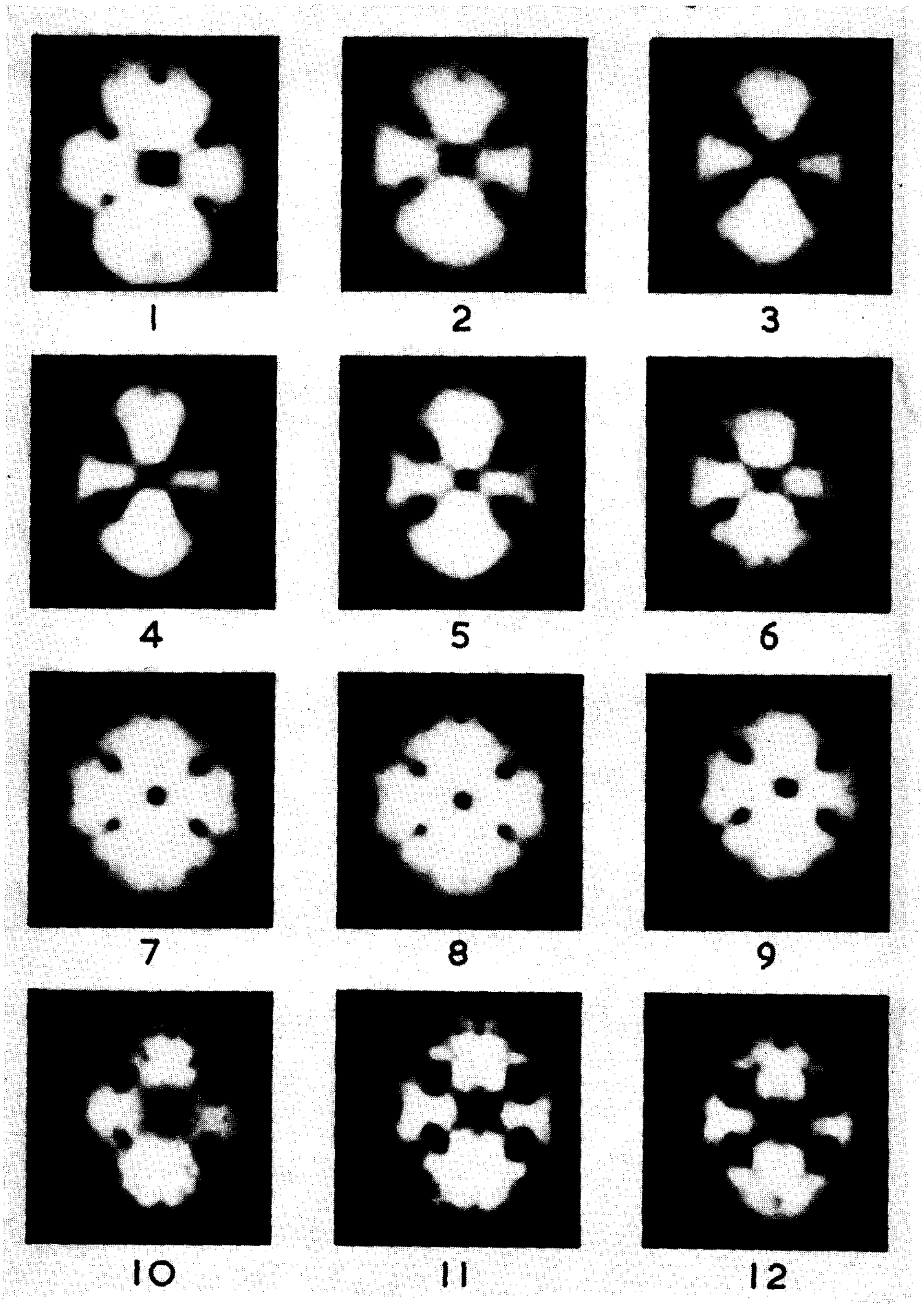

FIG. 3. Patterns 1 to 12.

1310°C (pattern 12) the [111] zones became nonemissive. On further heating, emission increased along the [111] zones and around the (112) planes so that at 1580°C (pattern 15) the surface characteristics were nearly those of clean tungsten (cf. patterns 15 and 2). The applied voltage decreased fairly steadily with increasing temperature of desorption [Table 1(b)]. If desorption was studied with a surface which had not attained saturation at room temperature (e.g., pattern 6) then patterns 10, 11, and 12 were not observed and we only obtained patterns like 13, 14, 15, and finally 1. It was also possible to obtain patterns 10 to 14 by adsorbing hydrogen sulfide at $\sim 10^{-7}$ mm at the temperatures corresponding to the particular desorption experiments. This means that the patterns represent conditions of surface equilibrium.

By measuring the time required to attain a particular emission pattern at some temperature T_1 and comparing it with the time required at a higher temperature T_2 it was possible to estimate the activation energy of the desorption process. For example in one experiment at 1150°C pattern 10 was attained in 90 sec while at 1250°C it was attained in 12 sec. This gave an activation energy of about 90 kcal/mole. In two other similar experiments values of about 85 and 80 kcal/mole.

2. High Pressure Experiments

It was not possible to observe progressive changes in emission during adsorption at room temperature since the pressure was so high ($\sim 10^{-4}$ mm) and, therefore, the process was complete within a few seconds of opening the valve V_2. Therefore, pattern 16 reflects the final surface condition at room temperature at a pressure of 10^{-4} mm. After evacuating to a pressure of $\sim 10^{-7}$ mm the tip was heated for 2 min intervals, recooled, and the emission examined. It should be noted that in this series of experiments the system could only be evacuated to about 10^{-7} mm (cf. 10^{-9} mm after the low pressure experiments) so that desorption was being studied in the presence of a small pressure, probably of hydrogen sulfide. Patterns 17 to 24 represent emission photographs up to 1650°C; a clean pattern could only be obtained after rebaking the apparatus for a few hours at 400° and flashing to 1600°C. There were a number of significant features in these experiments. Pattern 16 was stable up to 750°C and the voltage was 8.5 kv (Table 2) which was the same as that for clean tungsten. On heating to 1010°C pattern 17 was obtained but with a reduced voltage of only 8.2 kv. Electron emission only occurred around the (111) region, which consisted of intensely bright units gathered into clusters. On heating to a slightly higher temperature (1100°C) emission was still intense from the (111) region but the cluster-type pattern became smooth in appearance (pattern 18). A marked increase in applied voltage was required between 1150° and 1200°C to maintain constant emission. The following patterns (21 to 24) showed surface changes on heating, in stages, to 1650°C. Some similarity between patterns 24 and 13, and 23 and 11 should be noted, but the large difference in the applied voltage indicated that the surface was somewhat different in character. This was undoubtedly connected with the rather high pressure of hydrogen sulfide ($\sim 10^{-7}$ mm) present, which would have caused some further adsorption to occur as the tip was cooled to room temperature.

TABLE 2
ADSORPTION AND SUBSEQUENT DESORPTION FROM A SURFACE WHICH HAS ADSORBED H_2S AT $\sim 10^{-4}$ MM AND 22°C

Pattern number	Voltage (kv)	Temperature (°C)
16	8.5	23 to 750
17	8.2	1010
18	8.2	1100
19	8.2	1150
20	10.2	1200
21	9.9	1310
22	9.9	1400
23	9.7	1500
24	9.6	1650

Sulfur

By maintaining the source of sulfur at room temperature and keeping V_1, V_2, and V_3 open and V_4 closed, a stream of sulfur vapor at a pressure of $\sim 10^{-7}$ mm was passed over the tungsten tip. The sequence of patterns 25 to 28 represents changes in the surface characteristics at 22°C as a function of time with the field applied. The

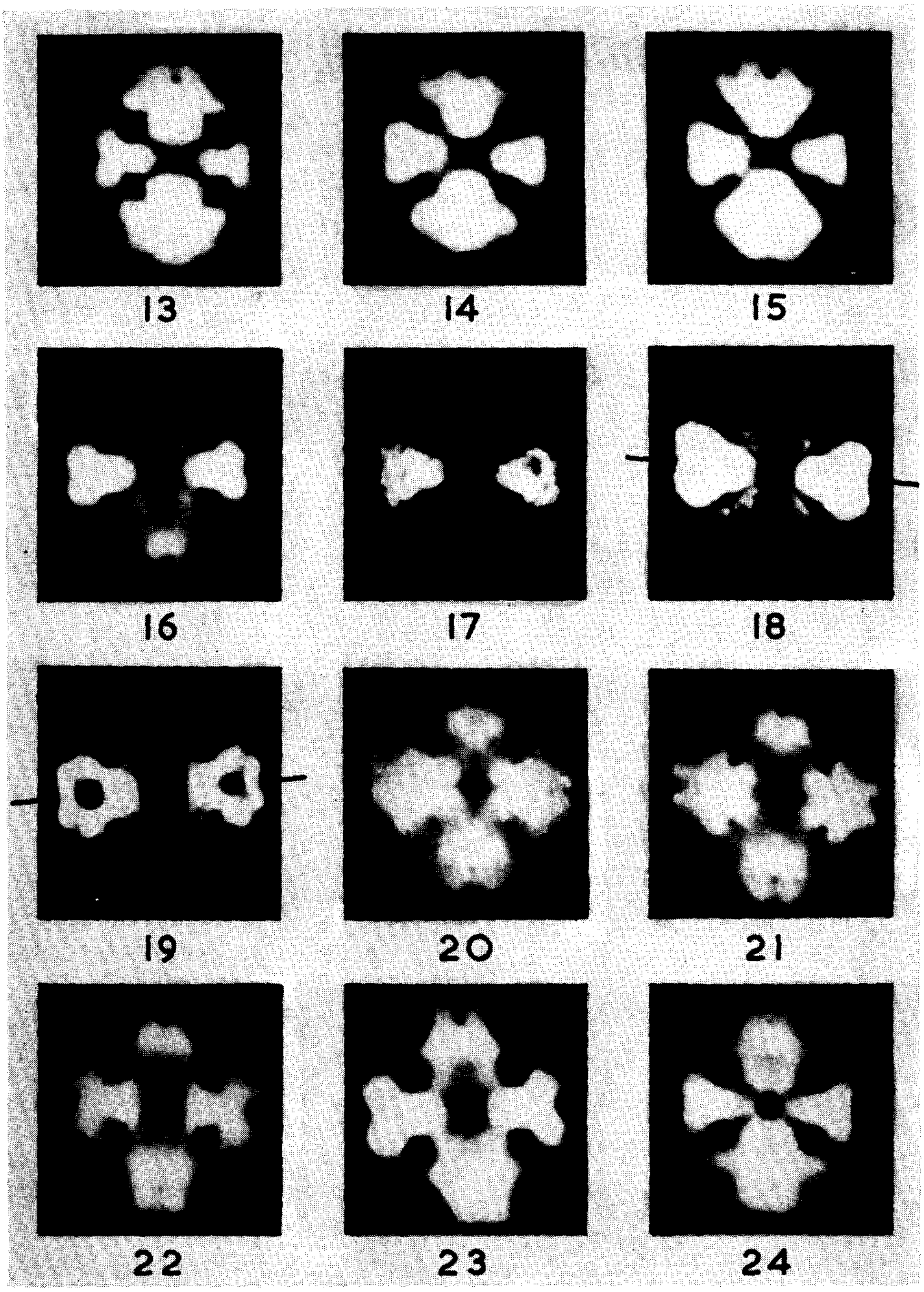

FIG. 4. Patterns 13 to 24; the orientation of most patterns is obvious but, in some cases, lines are added at the side to show the direction of the [110] zones.

emitting region (patterns 25 and 26) was concentrated around the (011) plane and consisted of a large number of small discrete clusters. These clusters were in continual motion and sometimes two or more would coalesce to form a larger cluster. The type of emission observed in pattern 26 sometimes persisted for 30 min or longer

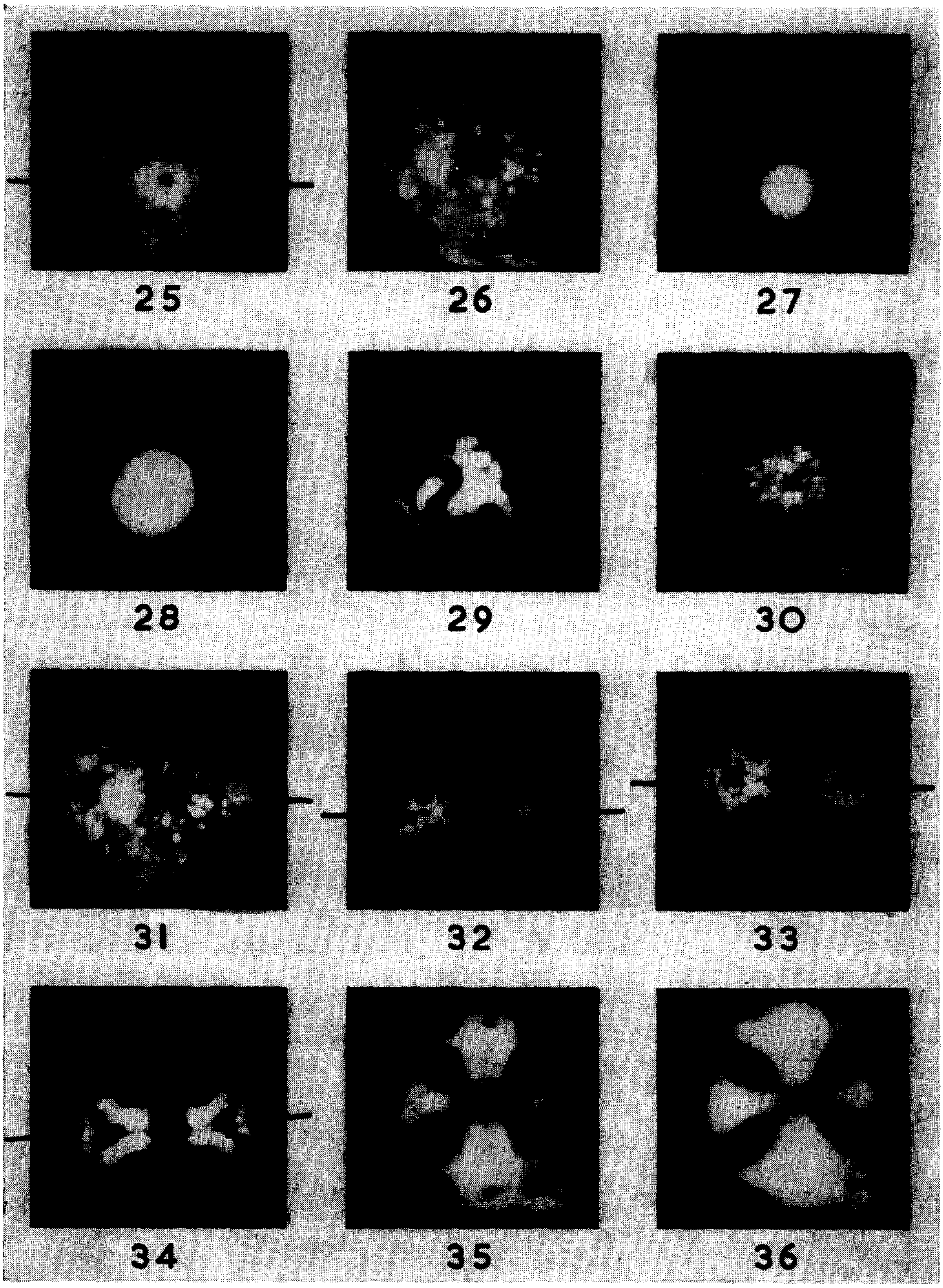

FIG. 5. Patterns 25 to 36; lines indicate the direction of the [110] zones.

but in this particular experiment after 15 min [see Table 3(a)] it suddenly changed, the emission being concentrated in one area which suddenly enlarged (pattern 28), and then electron emission ceased. On examining the tip with a microscope, it was observed to be deformed. If, however, the tip was quickly heated at the stage shown in pattern 27 or 28, i.e., before sufficient time had been allowed for mechanical failure to occur, the ball-shaped pattern was seen to break up (pattern 29). Mechanical

TABLE 3

Adsorption of Sulfur Vapor at ~10^{-7} mm and 22°C with Applied Field and Desorption from a Surface Exposed to Sulfur Vapor for about 2 min

(a) Adsorption			(b) Desorption		
Pattern number	Voltage (kv)	Time (min)	Pattern number	Voltage (kv)	Temperature (°C)
25	10.2	1	30	10.5	22 to 750
26	10.5	6	31	10.4	950
27	10.5	15	32	8.6	1000
28	10.6	15.1	33	8.7	1150
29[a]			34	8.7	Influence of field at 22°C
			35	9.6	1200
			36	9.2	1450

[a] Obtained after removal of applied field and heating tip to 1400°C for 2 min.

rupture of the tip only occurred in the presence of the applied field; patterns like 28 were stable in the absence of field and could be observed again after an interval of 30 to 40 min.

When sulfur vapor was allowed to interact at a pressure of about 10^{-7} mm for 2 min at room temperature (pattern 30), the system evacuated, and the tip heated in stages to 1500°C, the sequence of patterns was 31 to 36. The relevant voltages and temperatures are given in Table 3(b). There was a gradual decrease in voltage up to 1150°C but this was followed by a sudden increase (pattern 35). There was a general similarity between patterns 32 to 36 and the corresponding results shown in patterns 17 to 24 for desorption from a tip which had been treated with a high pressure of hydrogen sulfide; this was particularly evident for 34 and 19, and for 36 and 24.

Hydrogen

The interaction of hydrogen with tungsten has already been studied thoroughly (*6, 7*). The purpose of our experiments was to investigate the influence of presorbed hydrogen on the subsequent interaction of sulfur and to see whether the emission pattern produced by adsorbing hydrogen sulfide was changed on subsequent addition of hydrogen. We also confirmed that complete desorption of hydrogen occurred below 950°C.

Addition of hydrogen to a pressure of 10^{-4} mm had no influence on the emission characteristics of a surface which had adsorbed hydrogen sulfide at 22° and subsequently was heated to any temperature up to 1400°C. If hydrogen was first adsorbed at 22°C followed by sulfur at the same temperature the number of clusters (cf. pattern 26) was reduced considerably and no tendency for growth of the clusters was observed even when the applied voltage was increased to 12.5 kv.

Discussion

The main advantage of the field-emission microscope is that it enables one to ascertain whether crystallographic heterogeneity is an important aspect of a surface process. It is, however, not always a diagnostic tool since, for example, the (011) plane has a very high work function (~6 ev) so that it is likely to remain nonemitting even if it is active in adsorption. There is also the added complication that electron emission may be enhanced if a buildup of surface complexes occurs. However, if a particular region is becoming progressively less emitting during adsorption we are justified in concluding that adsorbed species are concentrating in that region.

Approximate estimates can be made of the changes in the average work function during interaction by comparing the voltages required to maintain a fixed emission current (0.5 μamp in our case) from a surface with adsorbed gas and from a clean surface. The procedure, which ignores any changes in the temperature-independent factor in the equation for electron emission, is similar to that used by Arthur and Hansen (*8*) and originally by Klein (*9*). Thus, using Eq. (1)

$$\frac{\phi_{\text{ads}}}{\phi_{\text{clean}}} = \left(\frac{V_{\text{ads}}}{V_{\text{clean}}}\right)^{2/3} \tag{1}$$

where ϕ_{ads} is the work function of the surface with adsorbed atoms, V_{ads} and V_{clean} are the respective voltages to obtain 0.5 μamp emission from the reacted and clean surfaces. Then using the value 4.5 ev (*10*) for the work function of clean tungsten (ϕ_{clean}) we can estimate ϕ_{ads}. Table 4 shows the work functions of some of the surfaces whose emission patterns have been characterized.

TABLE 4

AVERAGE WORK FUNCTIONS FOR SOME OF THE EMISSION PATTERNS

Pattern number	Work function (ev)
1, 32	4.5
4	4.7
6	4.8
12	4.6
17	4.4
20	5.1
24, 35, 36	4.9

When hydrogen sulfide is adsorbed at a pressure of about 10^{-7} mm at room temperature preferential interaction occurs along the [111] zones. After a time of adsorption of 60 sec (pattern 4) the change in work function is 0.2 volt while at saturation the value is 0.3 volt (pattern 6). These values are composite since they include contributions from adsorbed hydrogen and sulfur. They may, however, be compared with 0.15 volt for the surface potential derived by applying the Mott-Cabrera theory to the interaction of hydrogen sulfide with nickel films (*1*).

We believe that the sequence of events during the heating of a surface after adsorption of low pressures of hydrogen sulfide is as follows: (*i*) desorption of hydrogen around 1000°C; (*ii*) migration of sulfur atoms (patterns 10, 11, and 12); and (*iii*) desorption of sulfur (patterns 12 to 15). The final result of the migration of sulfur is a suppression of emission along the [111] zones but the process starts with enlargement of the dark areas around the (112) and (011) planes, presumably due to a concentration of sulfur around these planes. Pattern 11 shows a characteristic six-pointed dark area around the (011) plane and also the darkening of various planes situated around the (001) planes. The fact that the final stages of the desorption process involve removal of sulfur from the [111] zones is consistent with the initial adsorption on the same zones.

The vapor pressure of tungsten sulfide is about 10^{-4} mm at 1200°K (*11*) so that if the chemisorbed layer behaves like bulk sulfide we would expect to observe desorption at this temperature. It has been shown by Roberts (*12*) that an empirical relationship exists between the initial heat of chemisorption of simple molecules on metals and the heat of formation of the corresponding bulk compound. Since the heat of formation of WS_2 is —75.9 kcal/mole (*13, 18*) then according to this relationship the initial heat of chemisorption of sulfur on tungsten is about 120 kcal/mole. Our experimental kinetic data for an undefined (but probably high) surface coverage (pattern 10) give a value of between 80 and 90 kcal/mole for the activation energy of a process which is most likely to be sulfur removal. Confirmation that some desorption is likely to occur at 1200°C can be obtained from the equation

$$\tau = (h/kT) \exp (E/RT) \tag{2}$$

relating the lifetime of an adsorbed atom to the activation energy of desorption. If E is 90 kcal/mole then τ at 1200°C is just under 1 sec. A higher temperature will be needed to remove all the adsorbed sulfur if the initial heat of adsorption is about 120 kcal/mole and this is borne out by the desorption data shown in Table 1.

The most significant features of the desorption experiments from a surface exposed to a high pressure of hydrogen sulfide are the low apparent work functions associated with patterns 17, 18, and 19 which indicate that emission is occurring mainly from areas of threefold symmetry around the (111) planes, and the sudden increase of work function at 1200°C leading to emission over a wider area of the tip (pattern 20). It seems likely that some buildup of tungsten sulfide has occurred around the (111) planes and that the enhanced emission is the result of intensification of the electric field around these structures. An alternative way of describing the phenomena is that some sulfide is incorporated in the tungsten lattice [cf. the oxidation of metals (*14*) or the interaction of chlorine with nickel (*15*)]. The marked changes at 1200°C must correspond to the breakup of such tungsten sulfide structures and pattern 20 and the subsequent patterns must be associated with adsorption limited to a single layer over the surface. The comparatively slow desorption at higher temperatures is undoubtedly a consequence of the relatively poor vacua in this set of experiments.

The marked similarity between the desorption patterns 32 to 36 on heating a tip exposed to sulfur and the results just described is interesting. The voltages do not correspond very closely in the two experiments but there is the same change from a localized structure giving fairly good emission to monolayer-type adsorption at 1200°C requiring a higher applied voltage to achieve an emission current of 0.5 μamp.

Sulfur adsorption occurs predominantly around the (111) and (011) planes, and the nature of the emission is quite different from that observed at any stage with hydrogen sulfide, the emission apparently coming from discrete particles. We have definite evidence for a field-induced surface process, [cf. ref. (*16*)], for the interaction of sulfur with tungsten since, if the field is turned off at the stage shown in pattern 28, the same pattern can be obtained 30 min later. In the presence of the field, emission would have ceased within a few seconds after the formation of the ball-shaped pattern of 28. It is likely that patterns 27 and 28 reflect a nucleation process, possibly the growth of a sulfide whisker, which would account for the mechanical failure due to an increase in field strength. Needle-like growths have been observed, with the electron microscope, to form when a thin oxide layer on aluminum is heated in vacuum at 600°C (*17*). Moreover, pattern 29 shows that by rapid heating to 1400°C in the absence of the field the structure responsible for 28 disintegrates into a number of distinct parts.

The fact that the emission patterns produced on adsorbing sulfur bear no resemblance to the hydrogen sulfide patterns indicates the significant role played by the hydrogen adatoms produced on dissociation of hydrogen sulfide. This is also borne out by adsorbing hydrogen at room temperature before admitting sulfur vapor when no nucleation effects (cf. patterns 26 to 28) were observed.

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