FIELD-EMISSION INVESTIGATION OF COMPOSITE ADSORPTION LAYERS OF HYDROGEN AND HYDROGEN SULPHIDE ON TUNGSTEN

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Abstract

The interaction of H_2 and H_2S with tungsten, and of H_2S with hydrogen-covered tungsten, has bean investigated in the field emission microscope. A number of chemisorbed states with varying heats of adsorption have been identified throughout H_2 adsorption at a pressure of $10^{-5}Nm^{-2}$ and 78K on tungsten. When H_2S was adsorbed at 295K and gas pressure of $10^{-5}Nm^{-2}$ on clean tungsten surface a preferential interaction occurred along the (111) zones. An increase in the average work function of 0.3V has been found for the process. Desorption of hydrogen, resulting from H_2S adsorption, began at 1270K. Migration of the remaining sulphur began at 1400K while desorption occurred above 1500K and was complete at 1870K. Activation energies for the desorption of hydrogen and sulphur have been estimated. The effect of increasing H_2S pressure on the emission patterns of tungsten has also been studies. Addition of H2 had no influence on the emission characteristics and subsequently was heated at 1700K.

دراسة الانبعاث الالكتروني المجالي للامتزاز المزدوج للهدروجين وكبريتيد الهيدروجين على سطح التنكستن

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الخلاصة

تمت دراسة تفاعل كل من غازي H_2 و H_2S مع سطح البلورة المنفردة لفلز التنكستن، وتمت كذلك دراسة تفاعل غاز H_2S مع سطح التنكستن المغطى بالهيدروجين وذلك باستخدام تقنية مجهر الانبعاث الاكتروني المجالي. تم تشخيص حالات امتزاز كيميائي متعددة التي تتمتع بحرارات امتزاز متباينة وذلك بالنسبة لامتزاز الهيدروجين على التنكستن بدرجة حرارة 295K وضغط $^{5}Nm^{-2-}$ 10 $10^{-5}Nm^{-2}$ على سطح التنكستن النظيف حدث تفاعل تفضيلي للغاز على امتداد مناطق (111) البلورية للسطح الفلزي. وحدث ازدياد في معدل قيمة دالة الشغل بمقدار 0.3 فولت في عملية الامتزاز. إن desorption الهيدروجين الناجم عن امتزاز H_2S على السطح المغطى به، بدأ بدرجة 1270 K. وبدأت هجرة ذرات الكبريت المتبقية على السطح بدرجة 1400 K في حين بدأ desorption بدرجة 1500 K واكتمل بدرجة 1870 K. وتمت كذلك دراسة تأثير زيادة ضغط غاز H_2S على انماط الامتزاز من سطح التنكستن. ولم يكن هناك أي تأثير لإضافة الهيدروجين على الخصائص الانبعاثية لسطح التنكستن الذي امتز غاز H_2S بدرجة 295K والذي تم تسخينه فيما بعد الى درجات الحرارة التي بلغت حدها الاقصى في 1700 K

Introduction

The occurrence of composite layers on a surface indicates that the adsorbed molecules can react in various ways with the adsorbing surface. This may result in the formation of different types of adsorbed species, or adsorption complexes, on the surface [1-3]

In view of the dissociative character of the hydrogen sulphide adsorption on tungsten [4], It is important not only to investigate the adsorption and desorption of H_2S but also of hydrogen and to find out the influence of pre-adsorbed H_2 on the subsequent adsorption of H_2S. In the present paper a study of the adsorption of H_2 , at 78K, and of H_2S at 295K, on tungsten has been described. Composite adsorption layers of these gases on tungsten surface have been carefully analyzed by means of field–emission microscopy. The investigation covered other aspects which have been disregarded in previous publications [5].

Experimental

The operation technique and the experimental set-up have been described in previous papers [5-7]. The apparatus (Figure1). Was thoroughly degassed and the pressure was lowered to $10^{-8}Nm^{-2}$ prior to gas adsorption.

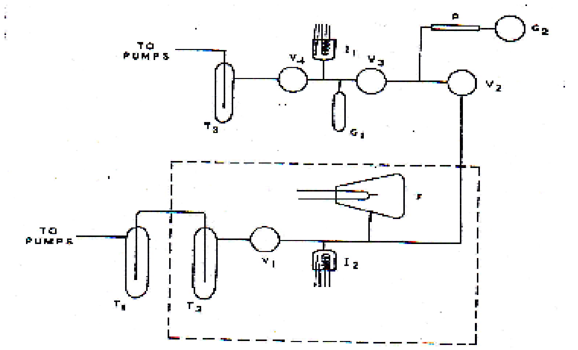


Figure 1: Schematic representation of the apparatus: T1, T2, T3, traps cooled in liquid nitrogen: I_1 I_2 Alpert-type ion gauges; V1, V2, V39 V49 ball and socket valves; G1, G2, gas storage vessels; palladium thimble; F, field-emission tube. Dotted line represents the oven

The electroanalytically etched tungsten tipe were cleaned thermally above 2800K. Hydrogen and hydrogen sulphide were prepared, purified and used as presented in early papers [4 , 5]

The work functions were derived from the current voltage characteristics which obeyed the Flower - Nordheim equation [8 , 9].

The surface potential (v), characterizing any adsorption state is given by the definition [6]:

$v = Ø_{\circ} - Ø$

Where $Ø_{\circ}$ is the work function of clean tungsten surface (0.8 ev) and Ø is the work function of the same surface after gas adsorption. A positive value of v indicates a positive charge on the adsorbate with respect to the adsorbing surface [9].

Activation energies of desorption (E_d) were derived from the observed desorption rates. As adsorption was little, or not, activated in the cases studied, E_d was considered to be nearly equal to the heat of adsorption [5-7].

Results and discussion

Adsorption of hydrogen: In a series of experiments a bare tungsten tip (Figure 2) [10].

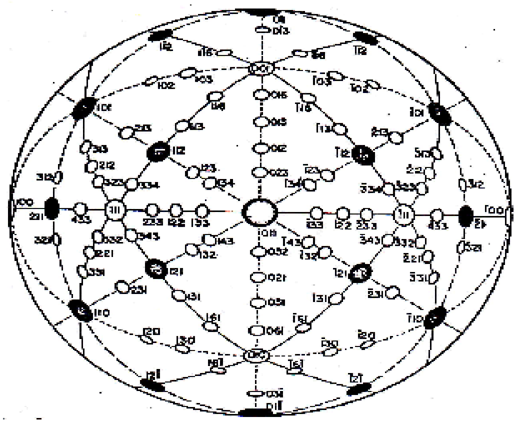


Figure 2: Orthographic projection of hemispherical cubic crystal with (011) in the axis. Emphasis is on the planes predominating on b. c. c. crystals; (110) zone lines solid, (111) zones long dashed, (100) zones short dashed.

Was the first kept at 78K under a pressure of $10^{-8}Nm^{-2}$. It was then exposed to hydrogen under a pressure of $10^{-5}Nm^{-2}$ and the adsorption pattern for the hydrogen-saturated surface was observed. The temperature of the tip was then raised in successive stage to 1300K. The pattern of the tungsten surface was recorded at a number of temperatures and the corresponding work functions were estimated. (Figure 3) shows a plot of surface potential (-v) versus the temperature (T) to which the tip was heated. The coverage (n_H) of the tungsten surface by hydrogen atoms. in atoms/cm^2, could be calculated from the temperature and pressure. Since the function n_H (P, T) is known from Hickmott's data [8]. In (Figure 3) the n_H scale is shown below the temperature scale. The n_H scale tends only to provide a rough orientation as Hickmott's data were measured on macroscopic wires, the surface of which differ in crystalline composition from hemispherical tips.

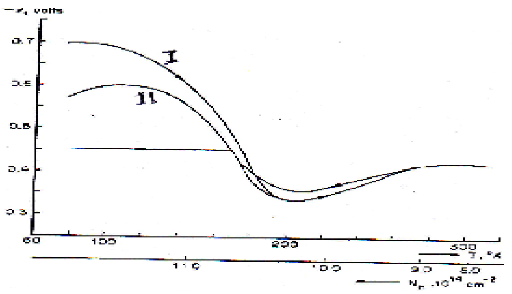


Figure 3: Surface potential of hydrogen on tungsten versus temperature and coverage.

I) Adsorption at 259K, then cooling to 78K.

II) Adsorption at 78K, then warming to 295K.

Adsorption of hydrogen on tungsten at 78K has an overall v=0.95V. The emission pattern at this temperature showed bright areas on (411), (320), (111) planes and on (111) zone. The (112) planes remained non-emissive. When the tip at this stage was heated to 150K, the work function increased and the decrease of emission was pronounced from (111), (411) and (320) planes. Almost a similar behavior could be detected on pumping a hydrogen-saturated tungsten tip at 78K. This may be attributed to the desorption of "Positive" hydrogen with:

$$E_d = 40\ KJmol^{-1}.$$

On heating the W tip to 150-200K further desorption of hydrogen, with E_d=60KJmol^{-1}, occurred. The work function decreased considerably due probably to negatively polarized hydrogen atoms. Between 200-295K a slight increase in work function took place as a consequence of the desorption of positively polarized H species from (411) plane and (111) zone. E_d for such species was 80KJmol^{-1}. the surface potential (v) of the tip at ≥ 295K became -0.4V and less negative. The remaining strongly bound H atoms gradually removed by further heating to temperature much higher than 295K. Complete removal of hydrogen, of E_d=180KJmol^{-1}, occurred only at 1200K.

Path (1) in (Figure 3) gives the changes in surface potential (v) with the temperature of the tip. The curve (1) shows the behavior of v on heating the tungsten surface from 78K to 295K, while curve (II) presents variation of v values to 78K. Values of v differed considerably below 150K.

On cooling from 295K (Curve II), values of v attained much lower surface potentials as compared with the case when H_2 adsorption on the tungsten surface occurred at 78K and the surface was thereafter heated in successive stages to 295K. The difference in behavior is thus reflects the difference in the strengths of hydrogen adsorption [9].

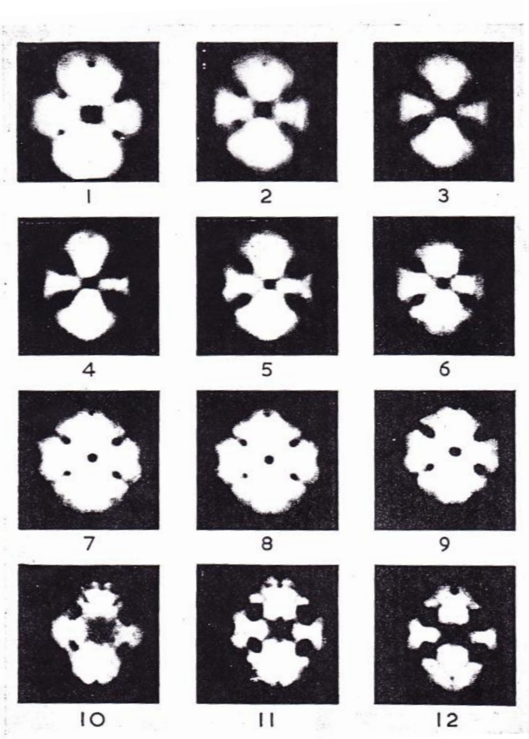
Adsorption of hydrogen at 78K (curve 1) gives rise to weaker surface attachment and consequently to less negative values of v as compared with the case when the covered surface with the strongly adsorbed hydrogen was cooled to 78K (curve II).

<u>Hydrogen Sulphide Adsorption:</u> When H_2S was adsorbed at 295K and a gas pressure of $10^{-5}Nm^{-2}$ preferential interaction occurred along the (111) zones as shown in patterns (1-8) in (Figure 4). After 60s (Pattern 4) the change in work function was 0.2V while at saturation the value became 0.3V (Pattern 6). These values are composite since they include contributions from adsorbed hydrogen and sulphide species.

The sequence of events during the heating of a tungsten surface after adsorption of H_2S in patterns (7-16) in (Figure 4)[10]involved: (i) desorption of hydrogen around 1270K; (ii) migration of sulphur atoms (Patterns 10,11 and 12); and (iii) desorption of sulphur (Patterns 12 to 15). The final result of sulphur migration was a suppression of emission along the (111) zones but the process started with the enlargement of the dark areas around the (112) and (011) planes, presumably due to a concentration of sulphur around these planes. Pattern (11) shows a characteristics 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 involves removal of sulphur from the [111] zones is consistent with the initial adsorption on the same zones. E_d for a stage corresponding to pattern (10) of (Figure 4) [10] was 380 kJmol^{-1} which is most likely to be sulphur removal from tungsten. Confirmation that some desorption is likely to occur at 1470K (Pattern 10) can be obtained from the equation [5].

$$\tau=(h/KT)\exp(E_d/RT)$$

relating the lifetime (τ) of an adsorbed atom to the activation energy of desorption (E_d). If Ed= 380 kJmol^{-1} then τ at 1470K is just under 1s. A higher temperature will be needed to remove all the adsorbed sulphur if the initial heat of adsorption as 500 kJmol^{-1}.



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

Figure 4: Patterns 1 to 12 for H_2S adsorption on tungsten

The most significant features of the desorption experiments from a surface exposed to a higher pressure of H_2S are the low apparent work functions associated with patterns (17 , 18) and (19) which indicates that emission is occurring mainly from areas of threefold symmetry around the (111) planes, and a sudden increase of work function at 1470K leading to emission over a wider area of the tip (Pattern 20 to 24 of Figure 5) [10]. It seems likely that some build-up of tungsten sulphide has occurred around the (111) planes and that the enhanced emission is a result of intensification of the electric field around these structures. The marked changes qt 1470K must correspond to the breakup of such structures and pattern (20) and the subsequent patterns must be associated with adsorption limited to a single layer over the surface.

Addition of hydrogen at a pressure of $10^{-5}Nm^{-2}$ had no influence on the emission characteristics of a surface which had adsorbed H_2S at 295K and subsequently was heated to any temperature up to 1673K. If hydrogen was first adsorbed at 78K or 295K followed by H_2S adsorption at the same temperature the build-up of tungsten sulphid structure considerably diminished. Adsorption of H_2S on a tungsten surface which had been saturated with hydrogen at 295K gave rise to a relatively more stable adsorbed layer and raised the temperature of surface migration and desorption [11]

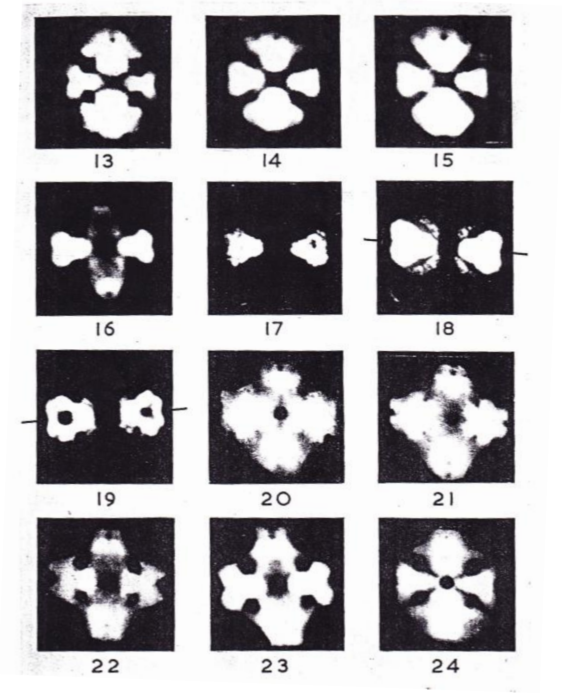


Figure 5: Patterns 13 to 24 for H_2S adsorption on tungsten

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