

CHEMICAL ADSORPTION OF OXYGEN ON THE (110) PLANE OF TUNGSTEN

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الخلاصة :

في مختبر السطوح في دائرة الفيزياء استعملنا حيود الالكترونات ذات الطاقة المنخفضة ومطيافية أوجيه لدراسة حركية امتزاز الاكسجين على سطوح (١١٠) لفلز التنجستون وعلى درجة حرارة ٣٠٠° مطلقاً . لاحظنا تكوّن حالتين امتزاز كيميائيتين الاولى مرتبطة بقوة بسطح الفلز ومعامل التصاقها يقارب ٠,٢٥، اما الثانية فتبدأ بالتكون على ما يقارب نصف مدمالك ، ولها معامل التصاق اقل بكثير من الحالة الاولى ، وتعتمد على الضغط في استقرارها . وعندما يكون اقل من نصف سطح التنجستون مغطى بالاكسجين يمكن وصف امتزازية السطح بدالة جبرية بسيطة .

ABSTRACT

Low energy electron diffraction (LEED) and Auger electron spectroscopy have been used to follow the kinetics of adsorption of oxygen on the (110) surface of tungsten at 300 K. Two chemisorbed states are formed. The first of these is a tightly-bound state with an average sticking coefficient of approximately 0.25. The second state which begins to form at a coverage of half a monolayer, has a much lower sticking coefficient and appears to be pressure dependent. For $\theta < 0.5$ the rate of adsorption is found to obey a simple probability function.

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1. INTRODUCTION

The LEED patterns and their interpretation for oxygen adsorption on (110) tungsten over a wide range of temperatures have been well established [1-4]. The associated work function changes have also been measured [4-6]. The object of the present work is to report some interesting features in the kinetics of adsorption at 300 K which have been observed using combined LEED/Auger measurements.

2. EXPERIMENTAL

Both the LEED and Auger measurements were carried out in a standard Varian 'FC 12E' stainless steel vacuum system. In this system, pressures of the order of 10^{-10} Torr were obtained without undue effort by combining a 240 l/sec ion getter pump with a titanium sublimation pump. The roughing system was provided by twin vac-sorption pumps.

The LEED system consisted of a four-grid display optics combined with a movable Faraday-cup for spot intensity measurements. Auger measurements were made using a single pass cylindrical mirror analyzer (CMA) backed by a multiplex and lock-in amplifier. With the CMA a complete spectrum between 0 and 2000 eV was recorded fast enough to be displayed on an oscilloscope. By use of the multiplex, individual peaks in the Auger spectrum were monitored. This fast scan rate was particularly suitable for following the kinetics of adsorption. The ultimate sensitivity of the CMA was better than 0.1% of a monolayer. The electron gun, mounted inside the analyzer, was capable of producing electron beams of either a fixed energy of 2000 eV or variable energies in the 0-10 000 eV range. With this instrument a magnified image of the surface was displayed on a monitor screen using the total current collected by the sample which was modified by the local variations of the secondary emission coefficient on the surface. The purpose of this display was to enable a particular area on the surface to be identified and returned to quickly and repeatedly. The lateral distribution of elements on the crystal surface was achieved by scanning the primary beam across the sample surface whilst simultaneously monitoring the Auger spectrum.

The 6 mm diameter single crystal was supplied by

Metals Research Ltd. (Cambridge). The crystal was polished by rubbing with successive grades of emery paper and finally lapped with aluminum oxide (Al_2O_3) powder down to the 0.5μ grade. After this preliminary grinding and polishing the crystal was electropolished in 0.5N sodium hydroxide solution for about ten minutes at 9V with a stainless steel cathode. After electropolishing, there was no overall surface structure as observed with an optical microscope.

The sample was mounted on a Varian manipulator which provided facility for rotation on the axis of the manipulator as well as horizontal and vertical shifts. A 'flip-mechanism' allowed the crystal to be rotated through 100° about a horizontal axis. Provision was also made for cooling the sample with liquid nitrogen and for indirect heating up to $1200^\circ C$.

Oxygen was admitted to the experimental chamber via a variable leak valve. Pumping of the 'dead-space' between the gas flushing valve and the variable leak valve was achieved by means of an 8 l/s^{-1} sputter-ion pump. Gas purity was checked using a Varian quadrupole residual gas analyzer while total pressure was monitored using a dual range ionization gauge.

Following the usual bake-out of the system the crystal was outgassed by conduction from the resistive heater for several hours. In addition, in the hope of removing all the carbon the hot crystal was exposed to oxygen at about 1×10^{-7} Torr for about ten hours. At the completion of the outgassing and with the crystal still hot the pressure in the chamber was below 1×10^{-9} Torr. On cooling, the pressure rapidly fell below an indicated 2×10^{-10} Torr and it was possible to heat the crystal for short periods without the pressure exceeding 5×10^{-10} Torr. The resulting well-defined LEED spot pattern is shown in Figure 1. The Auger spectrum at this point was characteristic of pure tungsten and indicated that the relative amount of carbon contaminant in the surface was negligible.

Oxygen was then introduced into the system in controlled doses of 0.1 monolayers (2×10^{-8} Torr for 10 s) records being made of the diffraction pattern and Auger spectrum for each dose. This process was continued until no further changes in either the diffraction pattern or Auger spectrum were observed. Gas purity was checked several times during the experiment.



Figure 1. LEED Pattern at 172 eV for the Clean W(110) Surface

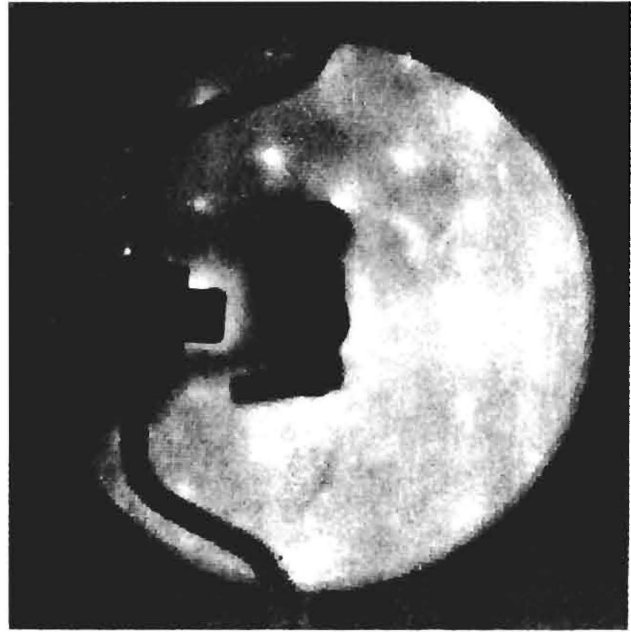


Figure 2. LEED Pattern at 172 eV for Oxygen Adsorbed on the W(110) Surface for 0.5 Monolayers

3. RESULTS

Ten independent sets of measurements were made. For each Auger spectrum the peak-to-peak amplitude of the oxygen KLL line was measured. From these amplitudes the relative amount of a species on the surface is fairly simple to determine because the emission current of Auger electrons is proportional to the number of excited atoms, n_a . If the Auger peak in the $N(E)$ curve is Gaussian then the peak-to-peak height of the differentiated Auger line is proportional to n_a , and this quantity has been used in the present work as a measure of relative surface concentrations. The determination of absolute surface concentrations (i.e. number of particles per cm^2) from the Auger peak heights should in principle be possible on the basis of a knowledge of all factors which contribute to the emitted current. This problem is very complex and is not yet completely solved. Consequently the use of reference data from independent calibrations is necessary for determining absolute concentrations. In this experiment such independent calibration points were obtained from two techniques. From the LEED pattern evidence of 0.5 monolayers of oxygen atoms was provided by a maximum in intensity of the $p(2 \times 1)$ pattern of Figure 2. At higher exposures (10^{18} molecules cm^{-2}) a monolayer was assumed present when with continued oxygen exposure there was no detectable change in the diffraction pattern. Further in-

dication of the monolayer point was obtained from observation of the rate of change of Auger peak height with exposure. Since chemisorption ceases when the adsorbate can no longer make direct contact with the surface then increasing exposure after a monolayer has been adsorbed causes no further increase in the Auger amplitude. Using these calibration points the Auger amplitudes were converted to coverage, θ_a , measured in monolayers (for the (110) surface of the tungsten one monolayer corresponds to 1.4×10^{15} atoms cm^{-2}).

The exposure was determined from the expression:

$$n = 2 \times 3.5 \times 10^{22} \times \frac{P_{\text{Torr}}}{(MT)^{1/2}} \text{cm}^{-2} \text{s}^{-1}$$

based on the kinetic theory of gases: n is the number of gas atoms incident on one square centimeter per second, M is the molecular weight, T is the temperature and P_{Torr} is the gas pressure. Exposure, θ_i , was converted to units of a monolayer by dividing by the surface concentration of tungsten atoms.

The LEED observations were essentially the same as those already established. The coverage versus exposure curve is shown in Figure 3 and exhibits two clear and distinct regions. Over the first stage of adsorption the coverage increased steadily with exposure up to $\theta_a \cong 0.5$. Figure 2 shows the $p(2 \times 1)$ diffraction pattern characteristic of this coverage. The average sticking coefficient for this phase was of the

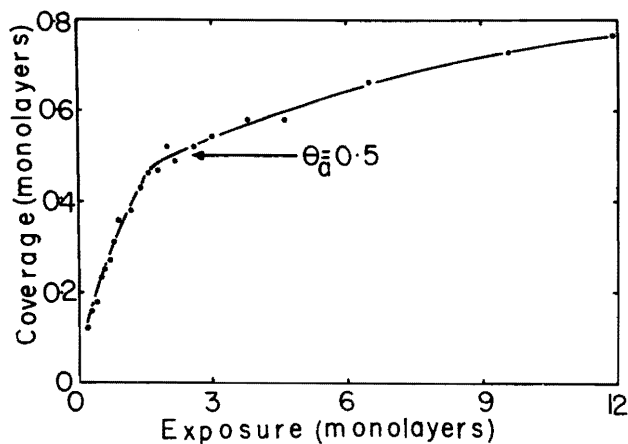


Figure 3. Concentration of Oxygen Atoms Absorbed, Coverage, as a Function of Exposure

order of 0.25. At approximately half a monolayer an abrupt change occurred in the rate of adsorption with the sticking coefficient for the next quarter monolayer falling to about 0.03. Thereafter the sticking coefficient fell steadily until saturation.

Up to a coverage of 0.5 monolayers the curve was dependent only on exposure but beyond this point was extremely pressure dependent. A burst of relatively high pressure oxygen caused a sharp increase in the Auger amplitude which decreased again on re-evacuation of the chamber. In experiments to study this second stage of adsorption more closely the effects of heating were examined. When saturation with oxygen had occurred the surface was gradually warmed up and the Auger amplitude followed continually. This decreased steadily towards the value corresponding to $\theta_a \cong 0.5$ and then remained constant. Only after heating the crystal to much higher temperatures for several hours was the first stage of adsorption removed.

4. DISCUSSION

The coverage versus exposure curve of Figure 3 shows clearly that the adsorption of oxygen on the (110) face of tungsten takes place in two quite distinct phases. The initial phase has been examined in some detail by Tracy and Blakely (1) using the Kelvin work function technique. By making the assumption that for coverage up to 0.2 monolayers the work function change is directly proportional to the coverage, Tracy and Blakely show the functional dependence of the coverage on exposure to be $\theta_a \propto \theta_i^2$ in agreement with a model in which island growth is surface diffusion limited.

For simple activated adsorption the sticking probability, S , may be written as

$$S = \sigma f(\theta_a) e^{-E/RT}$$

In this equation σ is the condensation coefficient. It is the probability that a molecule is adsorbed, provided it possesses the necessary activation energy, E , and collides with a vacant site. $f(\theta_a)$ is a function of the surface coverage θ_a and represents the probability that a collision will take place at an available site. If the adsorption takes place on a single site, $f(\theta_a) = 1 - \theta_a$ and represents the fraction of vacant sites, whether the adsorbed layer is mobile or not. Using both the retarding field work function technique and the electron-stimulated desorption method, Zingerman and Ishchuk [7, 8] found that $f(\theta_a)$ could be represented by $f(\theta_a) = (1 - \theta_a)$ if they assumed a sharp change in the condensation coefficient at a coverage of 0.5. They suggest that in the region $\theta_a > 0.5$, the chemisorption becomes activated.

If the adsorption requires two sites, and if the adsorbed layer is mobile, $f(\theta_a) = (1 - \theta_a)^2$, which is the possibility of finding two free adjacent sites. Using this expression for $f(\theta_a)$ and writing S as $d\theta_a/d\theta_i$, the solution of the above equation is:

$$\frac{1}{(1 - \theta_a)} = \sigma e^{-E/RT} \theta_i + 1$$

Using results for θ_a and θ_i obtained in the present work a plot of $1/(1 - \theta_a)$ against θ_i (Figure 4) gives two straight lines, joined at a position corresponding to a value of θ_a of approximately 0.5. In the region $\theta_a < 0.5$ it appears that the probability that oxygen molecules meet vacant adsorption sites can be fairly represented by:

$$f(\theta_a) = (1 - \theta_a)^2$$

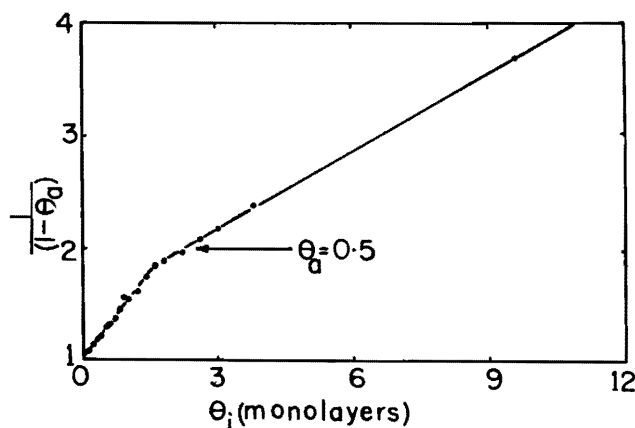


Figure 4. Dependence of $1/(1 - \theta_a)$ on θ_i

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