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FIELD EMISSION MICROSCOPIC OBSERVATION OF THE ADSORPTION OF OXYGEN, NITROGEN, HYDROGEN, CARBON MONOXIDE AND XENON ON RHENIUM

By

Kazuhiko ISHIZUKA*)

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Abstract

The behaviors of adsorbed oxygen, nitrogen, hydrogen, carbon monoxide and xenon on rhenium were observed with a field-emission microscope. At 77°K changes in the emission patterns and average work function of rhenium resulting from the adsorption of these gases were observed, and by raising temperature stepwise up to 2000°K their subsequent changes due to desorption (or surface reaction) were pursued.

The following changes in emission patterns were obsrved. Oxygen adsorption at $\sim 10^{-8}$ mmHg darkened the $(11\bar{2}3)$ and $(11\bar{2}1)$ regions of rhenium. On heating up to 800°~1300°K most of oxygen was removed from the surface and the pattern changed drastically to give a build-up pattern. Above 1400°K the emitting regions gradually broadened out, and finally at 2000°K a pattern regarded as that of clean rhenium was obtained. Nitrogen, hydrogen, carbon monoxide and xenon adsorptions resulted in a pattern insensitive to the surface topography, that with relatively bright arcs and ovals bounded by the $[1\bar{2}10]$, $[1\bar{1}00]$, $[11\bar{2}3]$ zone lines, that of a mottled appearance, and that with prominently bright regions along the $[1\bar{1}00]$ zone, respectively.

Adsorbed xenon, hydrogen, nitrogen and carbon monoxide were thoroughly removed by raising temperature up to room temperature, 900°, 1000° and 1100°K respectively, although even at 77°K xenon was partially removed by evacuating down to 2×10^{-9} mm Hg.

The increase in the average work function of rhenium caused by the adsorption of oxygen, nitrogen, hydrogen, carbon monoxide or xenon was 1.9 eV, −0.41 eV, 0.55 eV, 0.72 eV or −1.1 eV, respectively, at 77°K.

Introduction

Although the field emission microscopic (FEM) study of gas adsorption on a tungsten emitter has been carried out extensively, relatively few investigations have been done with other emitters such as nickel, platinum, iridium, tantalum, niobium and molybdenum.[1)~6)] Rheninm is interesting metal as an emitter since it has hexagonal closed packed crystal structure in contradistinction to the cubic lattice structure of the above metals. So far the FEM studies of adsorp-

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tion on rhenium have been scanty; BARNES[7] has first observed the field emission pattern of clean rhenium and examined the influence of residual gas upon the emission pattern.

It is to be noted that rhenium is useful as emitter material for vacuum tubes as some of its physical properties are superior to those of more commonly used metals such as tungsten. A rhenium filament is sometimes used as an electron emitter in a mass spectrometer in place of tungsten for the reason that carbiding of the emitter does not occur, no conditioning process is required and the life of the emitter is sufficiently long.[8]

The catalytic properties of rhenium, particularly for certain hydrogenation and dehydrogenation reactions and for reforming of naphthas, are also excellent[9] in terms of selectivity and resistance to poisoning. At present, however, rhenium catalysts are not being used for a practical purpose, but they seem to be promising because its chemical and metallurgical properties are very much like those of noble metals in some respects and those of refractory transition metals in other respects.

It is therefore desirable to have more information about the catalytic properties and surface properties of rhenium. Thus we have undertaken to study, as the first step, the behavior of some simple gases, namely, oxygen, nitrogen, hydrogen, carbon monoxide and xenon on rhenium by means of a FEM.

Experimental

Oxygen, nitrogen, hydrogen, carbon monoxide and xenon were obtained commercially (the "Extra Pure Gas" provided by Takachiho Kagaku Co.) in one-liter glass flasks provided with breakseals. These gases were, through a liquid nitrogen trap, filled individually in differenet reservoirs, each of about 2 cc capacity and provided with a breakseal, at about 10^{-3} mmHg. These reservoirs had previously been outgassed down to about 10^{-8} mmHg at 400°C for about 10 hours or more.

The experimental arrangement was similar to that of AZUMA[10] except that gas reservoirs were put outside the furnace to prevent possible contamination by gases released from glass-walls during bake-out. The apparatus is shown schematically in Fig. 1. The FEM-cell in our study was made of molybdenum glass flask with a nearly flat bottom. The bottom was coated with willemite phosphor by the nitrocellulose method[11] and backed with an evaporated aluminum film, which was connected by means of platinum foil to a molybdenum rod sealed through the side of the cell as seen in Fig. 1. The tip was prepared by electrolytically etching a 0.175 mm diameter rhenium wire in conc. HNO_3 with 12 volt ac and spot-welded to a 0.3 mm diameter tungsten loop

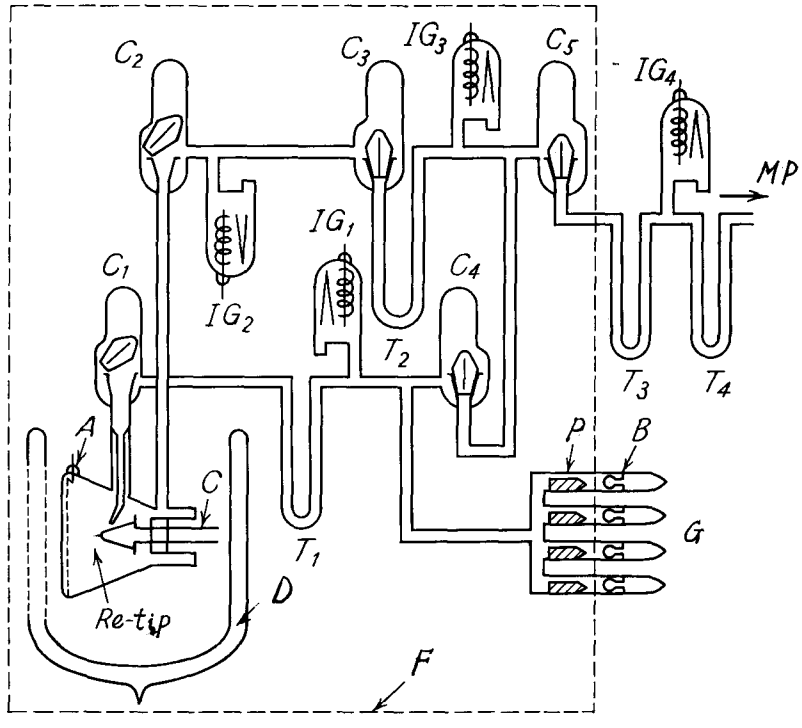


Fig. 1. Vacuum apparatus.
MP: mercury-diffusion pump. T_1, T_2, T_3 and T_4: traps. C_1, C_2, C_3, C_4 and C_5: greaseless stop-cocks. IG_1, IG_2, IG_3 and IG_4: B-A type ionization gauges. A: anode lead. C: cathode lead. B: breakseal. P: pellets. G: gas-reservoirs. D: Dewar vessel. F: furnace.

of about 4 cm half length, which in turn was welded to the ends of two molybdenum rods. The cell thus constructed was connected to a high vacuum system, as shown in Fig. 1.

The cell, B–A gauges, liquid nitrogen traps and exhausting pipes of the high vacuum system in the furnace were baked out at about 400°C for 10 hours or more. After the bake-out all metal parts of the cell and B–A gauges were further outgassed by electric heating or by electron bombardment. The above treatments were repeated until a pressure of the order of 10^{-9} mmHg was attained in the high vacuum system; the greaseless stop-cock C_5 was now closed to cut off the mercury diffusion pump and then the pressure was reduced to the order of 10^{-10} mmHg by the operation of the B–A gauges while the emitter was kept at red heat and flashed intermittently at about 2500°K.

The emission pattern was then observed at a room temperature in order

to check cleanness of the tip and stability of the emission pattern. When a stable pattern of clean rhenium surface identical with that observed by BARNES[7] was obtained, the whole cell was immersed in liquid nitrogen and the emission pattern was rechecked for cleanness.

Gas was admitted to the cell from its reservoir through a greaseless stopcock C_1 and a capillary of 0.3 cm inside diameter, the end of the latter being about 1 cm apart from the tip. Changes in emission pattern, emission current, applied voltage and gas pressure were now followed simultaneously. After a stable emission pattern was obtained, the tip was subjected to intermittent heat treatments for different periods of time at different temperatures at a pressure of about 10^{-9} mmHg or less by heating the tungsten loop electrically without applying electric field, each treatment being followed by observation of emission pattern, emission current, applied voltage and pressure while the cell was kept at 77°K.

Emission pattern were observed through an unsilvered window of the Dewar vessel and photographed continuously by means of motor-driven Nikon F camera with a Nikkor f : 1.4 lens and Fuji Neopan-SSS film. The applied voltage was usually adjusted to give a constant emission current of 0.5 μA and recorded automatically with a recorder (Yokogawa Electric Works, Inc., Model ER–10). The emission current was measured by an electronic micro-micro ammeter (Takeda Riken Co. Model TR–6) and recorded with another recorder of the same type.

The pressure was measured with the B–A gauge IG_2 and/or IG_1 (see Fig. 1). The temperature of the tip was determined by measuring the heating current through the tungsten loop; the temperature-current relation was preliminary calibrated by means of an optical pyrometer or by measuring the resistance of the tungsten loop according as temperature was higher or lower than 800°K.

The average work function increase, $\Delta\phi$, cused by adsorption was derived from the approximate form of the Fowler-Nordheim equation,

$$I = AV^2 \exp(-B\phi^{3/2}/V),$$

where I is the emission current, V the applied voltage, ϕ the average work function, and A and B constants. Comparing the slope of the Fowler-Nordheim plot, $\log(1/V^2)$ *vs.* $1/V$, with that of the clean surface and assuming the value $\phi = 4.9$ eV[12] for the clean surface, one can estimate $\Delta\phi$. The change of log A due to adsorption was determined in a similar way, and was taken to be a measure of the change of the emitting area.[13]

Results and Discussion*)

Clean Rhenium

Fig. 2 (a) shows an emission pattern characteristic of a clean, $(10\bar{1}0)$ oriented rhenium surface. It is to be noted that the c-axis of six-fold symmetry is nearly perpendicular to the emitter axis.**) The main crystallographic planes of low Miller indices were identified by angular separation.[7] Planes thus identified are shown in Fig. 2 (b), in which the crystallographic zone lines are also shown with broken lines.

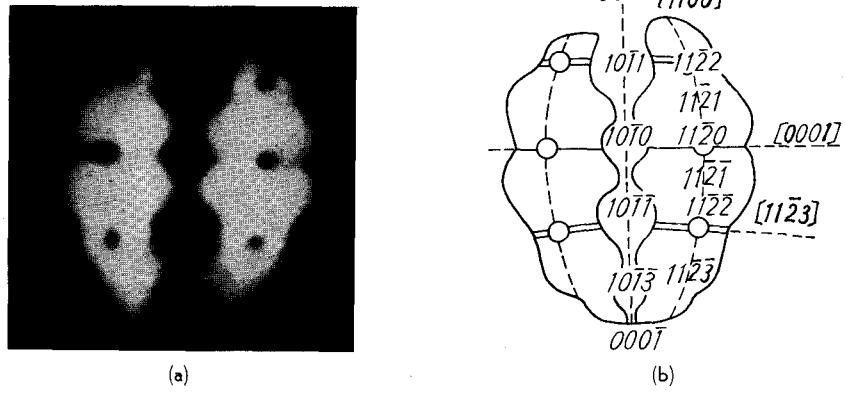


Fig. 2. Clean rhenium.
(a) field emission pattern at $I=5\times10^{-7}$ amp and $V=11.4$ kV.
(b) orientation diagram of the emitter in (a).

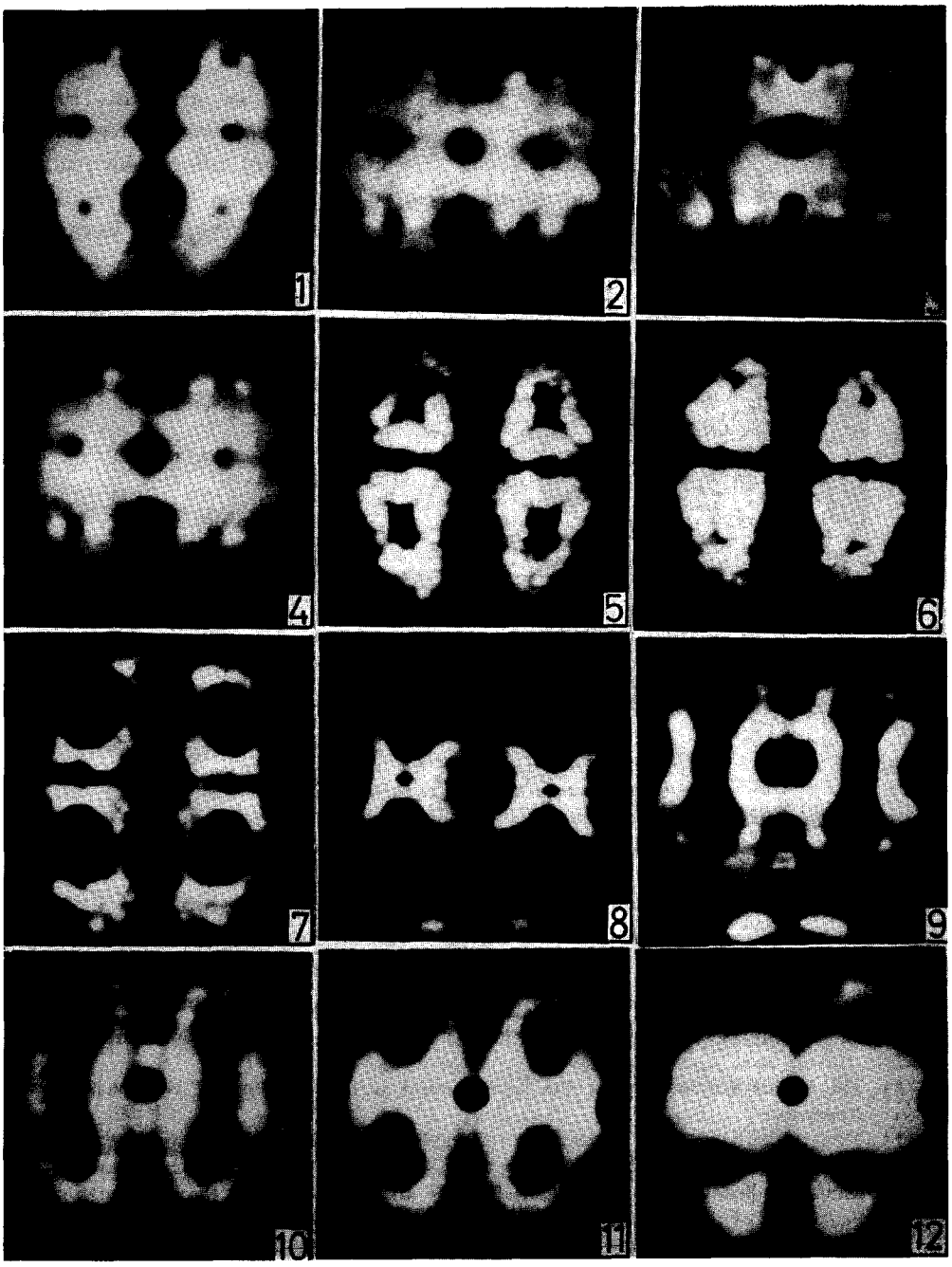
Oxygen

A sequence of emission patterns for adsorption and desorption of oxygen are ahown in Fig. 3. As soon as oxygen was allowed to flow over the tip at a pressure of about 2×10^{-8} mmHg, a minor change in the pattern occurred: the $(11\bar{2}3)$***) regions around the (0001) planes were darkened and the brightly emitting region became granular (Plate 2 of Fig. 3). At the same time the

*) The atomic arrangement of the hemispherical surface of rhenium is explained in Appendix.

**) This tendency was first noticed by BARNES[7] who observed the patterns of several rhenium emitters.

***) MILLER indices of physically identical planes are represented by the index of a particular one of them throughout this paper; *e.g.*, the $(1\bar{1}00)$, $(10\bar{1}0)$, $(01\bar{1}0)$, *etc.* planes are called the $(10\bar{1}0)$ plane. Similarly, physically identical crystallographic zones are indicated by one representative index.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average work function increased steadily with time to 6.2 eV ($\Delta\phi=1.3$ eV). This seems to indicate that the surface is initially covered by uniformly distributed oxygen, whose coverage is roughly estimated to be about 0.7 by comparing the average work function increment with that of saturated one (see below). After 15 minutes the pattern showed characteristic fatures having the dark $(11\bar{2}3)$ and $(11\bar{2}0)$ regions, exceedingly bright rings around the $(10\bar{1}1)$ plnes and bright lines along the $[11\bar{2}3]$ zones (Plate 3). The pattern did not change significantly during subsequent exposure to oxygen and therefore the pattern of Plate 3 can be interpreted as indicating saturation of the surface. The average work function increased steadily as adsorption progressed, finally reaching a saturation value 6.8 eV, *i.e.*, $\Delta\phi=1.9$ eV, which is nearly equal to the value, 1.7~1.9 eV reported for oxygen on tungsten.[13),14)] The darkening of the $(11\bar{2}0)$ and $(11\bar{2}3)$ regions indicates that some preferential interaction occured more strongly in these regions. The bright regions around the $(10\bar{1}1)$ planes can be interpreted as due to physisorption because they easily disappeared and became dark by warming to room temperature. The pattern of Plate 3 remained unchanged otherwise on heating the tip up to 500°K.

On heating to 600°K the pattern became rather uniform (Plate 4) while the average work function remained nearly the same. This can be attributed to rearrangement of adsorbed oxygen by surface diffusion. At 800°K the pattern changed drastically and the average work function reduced to 5.3 eV ($\Delta\phi=0.4$ eV). The emitting region concentrated around the $(11\bar{2}2)$ planes forming bright triangular frames bounded by the dark [0001] and $[1\bar{2}10]$ zones (Plate 5). On heating to a slightly higher temperature, the dark $(11\bar{2}2)$ regions in the triangles were covered with the bright spots (Plate 6). At 1100°K the $(11\bar{2}2)$ regions were darkened and enlarged (Plate 7), the average work function reducing to 4.6 eV ($\Delta\phi=-0.3$ eV). At 1250°K a couple of bright H-shaped

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Fig. 3. Field emission patterns for oxygen on rhenium.

1: clean rhenium; $V=11.4$ kV ($I=5\times10^{-7}$ amp).
2: adsorption of 2×10^{-8} mmHg oxygen for 10 sec at 77°K; $V=13.8$ kV ($I=5\times10^{-7}$ amp).
3: after 15 min; $V=18.3$ kV ($I=2\times10^{-7}$ amp). $\Delta\phi=1.8$ eV, $\Delta\log A=1.66$.
4: oxygen desorbed by heating for 2 min at 600°K; $V=18.5$ kV ($I=2\times10^{-7}$ amp), $\Delta\phi=1.80$ eV, $\Delta\log A=1.66$.
5: heating for 2 min at 800°K; $V=15.4$ kV ($I=5\times10^{-7}$ amp), $\Delta\phi=0.4$ eV, $\Delta\log A=1.60$.
6: heating for 2 min at 900°K; $V=13.4$ kV ($I=5\times10^{-7}$ amp).
7: heating for 2 min at 1100°K; $V=13.8$ kV ($I=5\times10^{-7}$ amp), $\Delta\phi=-0.30$ eV, $\Delta\log A=2.17$.
8: heating for 2 min at 1250°K; $V=14.2$ kV ($I=5\times10^{-7}$ amp), $\Delta\phi=-0.32$ eV, $\Delta\log A=2.22$.
9: heating for 2 min at 1400°K; $V=16.6$ kV ($I=2\times10^{-7}$ amp), $\Delta\phi=0.66$ eV, $\Delta\log A=1.40$.
10: heating for 2 min at 1500°K; $V=13.0$ kV ($I=5\times10^{-7}$ amp), $\Delta\phi=0.54$ eV, $\Delta\log A=0.94$.
11: heating for 2 min at 1700°K; $V=13.1$ kV ($I=5\times10^{-7}$ amp), $\Delta\phi=0.48$ eV, $\Delta\log A=0.80$.
12: heating for 2 min at 1900°K; $V=12.0$ kV ($I=5\times10^{-7}$ amp), $\Delta\phi=0.31$ eV, $\Delta\log A=0.40$.

buildup regions around the $(11\bar{2}0)$ planes appeared (Plate 8). The average work function further reduced to the minimum value of 4.58 eV ($\Delta\phi = -0.32$ eV). At 1400°K the bright crescent ridges around the $(10\bar{1}0)$ planes elongated to form a bright ring and the $(11\bar{2}3)$ regions became visible (Plate 9). The average work function increased again to 5.56 eV ($\Delta\phi = 0.66$ eV). These drastic pattern changes at 800° to 1400°K were possibly caused by partial desorption and redistribution of oxygen. However, in order to explain the observed lowering of the average work function below the clean value (*i.e.*, $\Delta\phi < 0$), one has to assume that there occurred also oriented overgrowth of oxide layer and/or rearrangement of rhenium atoms, which gave rise to local field enhancement and diminished the effective emitting area. Further heating up to 1900°K lead to gradual spreading of the emitting regions around the $(10\bar{1}0)$ and $(11\bar{2}0)$ planes, the average work function decreasing to 5.21 eV ($\Delta\phi = 0.31$ eV) (Plate 10 to 12). These behavior may be interpreted as arising from the evaporation of oxide and redistribution of adsorbed oxygen over the surface. It is to be noted that the pattern obtained by heat treatment at about 1900°K or higher have the dark lines of the $[1\bar{2}10]$ and $[11\bar{2}3]$ zones, which is similar to the dark "cross bone" formed by the [111] zones for oxygen-tungsten system. A clean pattern could only be obtained by flashing to 2500°K or prolonged heating at 1900°K in a high vacuum of $10^{-9}\sim10^{-10}$ mmHg. This indicates that the binding energy of oxygen on the $[1\bar{2}10]$ and $[11\bar{2}3]$ zones is extraordinarily large. Thus, the behavior of oxygen on rhenium at high temperatures is interpreted as arising from the formation of oxide layer.

Nitrogen*

The adsorption of nitrogen was studied on a $(11\bar{2}0)$ oriented emitter. Fig. 4 shows a sequence of pattern changes due to nitrogen adsorption at 77°K and subsequent desorption by heating successively to higher temperatures. Adsorption of nitrogen at a pressure of about 5×10^{-8} mmHg yielded no observable change of the pattern except that the dark $(10\bar{1}1)$ planes diminised (Plate 3). The average work function reduced to 4.76 eV ($\Delta\phi = -0.41$ eV) at saturation. It is to be noted that the emission patterns at 77°K (Plates 2 and 3) were insensitive to the surface topography and nitrogen adsorption causes decrease in the average work function.

On warming to room temperature the average work function increased to 4.80 eV ($\Delta\phi = -0.1$ eV) accompanying a small pattern change, *i.e.*, the bright

*) After this manuscript had been completed, we received a paper on field emission work of nitrogen-rhenium system [R. KLEIN and J. W. LITTLE, Surface Science, **6**, 193 (1967)], in which a pseudo-clean pattern accompanied by the average work function decrease of 0.4 eV has been reported.

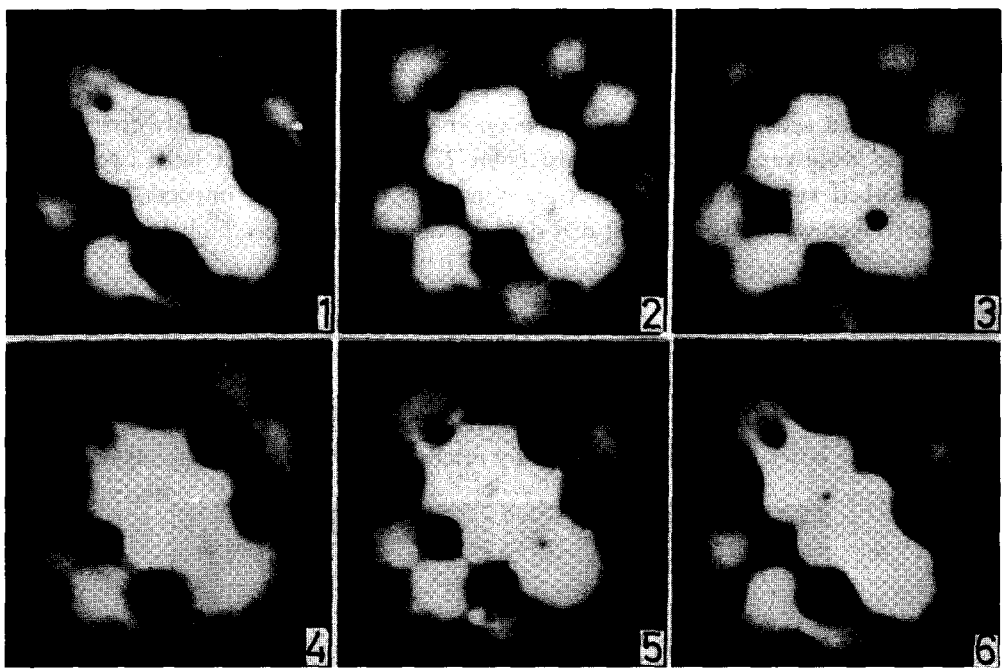

Fig. 4. Field emission patterns for nitrogen on rhenium: $I=5\times10^{-7}$ amp.
1: clean rhenium; $V=14.2$ kV.
2: adsorption of 5×10^{-8} mmHg nitrogen for 20 min at 77°K; $V=14.9$ kV, $\Delta\phi=-0.3$ eV.
3: after 40 min; $V=15.4$ kV, $\Delta\phi=-0.41$ eV, $\Delta\log A=.1.43$:
4: nitrogen desorbed by heating for 10 min at 300°K; V=14.7 kV, $\Delta\phi=-0.1$ eV, $\Delta\log A=0.49$.
5: heating for 2 min at 700°K; $V=14.65$ kV, $\Delta\phi=0.05$ eV.
6: heating for 2 min at 1000°K; $V=14.3$ kV, $\Delta\phi=0.00$ eV.

regions of the $(11\bar{2}3)$ planes spread out as seen in Plate 4. These behavior can be interpreted as due to partial desorption of nitrogen. By heating up to 700°K, a little change occurred, *i.e.*, relatively bright $[11\bar{2}3]$ zone lines appeared (Plate 5). At 1000°K the bright $[11\bar{2}3]$ zone lines disappeared and the original clean pattern was restored (Plate 6), while the average work function reduced to the clean value. These bright lines might be attributed to the field enhancement by the rearrangement of rhenium atoms in the $[11\bar{2}3]$ zones rather than the change in the work function because physisorption is not conceivable at these high temperatures.

The behavior of nitrogen on rhenium at 77°K was very similar to that on tungsten,[15] *i.e.*, both gave uniformly emitting patterns accompanied by average work function decrease. Above 300°K there is no resemblance between the pattern of nitrogen adsorbed on tungsten and that of nitrogen on rhenium;

i.e., the former is characterized by prominently emitting (100) region while the latter is very similar to that at 77°K. However the average work function changes in the both cases are nearly equal.

Thus, it seem likely that nitrogen on rhenium is homogeneously distributed over the wide range of temperature from 77° to 600°K and at least two kinds of adsorbed states are present, *i.e.*, a portion of adsorbed nitrogen is easily removed below 300°K and the rest desorbs only at relatively high temperatures above 700°K.

Hydrogen

The study of hydrogen adsorption was done with the same tip as used in the nitrogen case. Immediately after admitting hydrogen to the cell at a pressure of 2×10^{-8} mmHg the pattern changed from Plate 1 of Fig. 5 to Plate 2, the latter being characterized by relatively bright arcs and ovals bounded

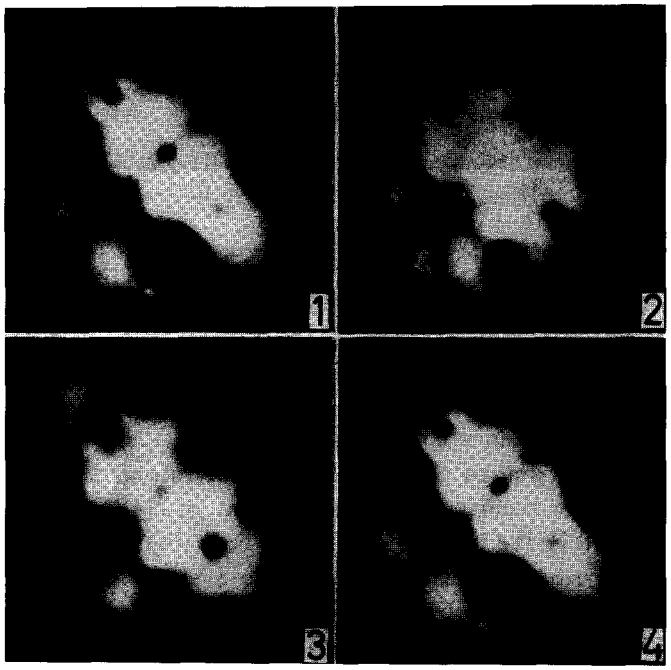

Fig. 5. Field emissiom patterns for hydrogen on rhenium : $I=5\times10^{-7}$ amp
1 : clean rhenium ; $V=9.8$ kV.
2 : adsorption of 2×10^{-8} mmHg hydrogen for 15 min at 77°K ; $V=11.7$ kV, $\Delta\phi=0.55$ eV.
3 : hydrogen desorbed by heating for 10 min at 300°K ; $V=11.5$ kV, $\Delta\phi=0.64$ eV.
4 : heating for 2 min at 900°K ; $V=9.8$ kV, $\Delta\phi=0.00$ eV.

by the dark [$1\bar{2}10$], [$1\bar{1}00$] and [$11\bar{2}3$] zone lines. The emission characteristics remained unchanged during subsequent exposure to hydrogen. The average work function first increased rapidly with time for a few minutes and then slowly reached 5.45 eV, *i.e.*, $\Delta\phi = 0.55$ eV, which is nearly the same as that for hydrogen on tungsten.[16] It is easily seem from the pattern and the average work function changes that adsorption occurs more prominently on rough planes of the ($11\bar{2}3$) regions and planes along the [$1\bar{1}00$] and [$11\bar{2}3$] zones. It is interesting that these dark zone lines appeared after adsorption, but not in the clean pattern.

On warming to room temperature the bright arcs and ovals faded away; dark region on and around the ($11\bar{2}3$) planes became relatively bright but the ($10\bar{1}3$) regtons remained dark. The average work function increased by 0.09 eV compared to the value at 77°K ($\Delta\phi = 0.64$ eV). It is therefore likely that some positively polarized hydrogen coexisted with negatively polarized one on the surface at 77°K. On heating up to 800°K the average work function gradually decreased to 5.0 eV, which is close to that of the clean surface, and the dark ($10\bar{1}3$) regions brightend. On heating above 900°K the initial clean pattern reappeared and the average work function was restored to the clean value.

The ($10\bar{1}3$) plane, where the most strongly adsorbed hydrogen was found, is in its atomic arrangement very similar to the (112) plane of b.c.c. crystal and the (110) plane of f.c.c. crystal, which are characterized by troughs formed by the surface atoms. It is of particular interest that all of these planes are similar as regards chemisorption of hydrogen, *i.e.*, the patterns of hydrogen on rhenium, tungsten[2] and nickel[1] are characterized by the enlargement of the dark regions around the ($10\bar{1}3$), (112) and (110) planes, respectively. It has been also reported[2] that hydrogen on the (112) plane of tungsten has the largest heat of adsorption, 46 kcal/mole, which is removed only by heating for 100 seconds at 760°K. In the case of rhenium, hydrogen on the ($10\bar{1}3$) plane is removed by heating to 800°K for 120 seconds, which is very similar to the behavior of hydrogen on tungsten just mentioned above.

Thus, it can be assumed that the planes constructed of troughs of the surface atoms play an important role in chemisorption of hydrogen.

Carbon Monoxide

A sequence of emission patterns for carbon monoxide adsorption and desorption are shown in Fig. 6. By admitting carbon monoxide to the cell at a pressure of 7×10^{-9} mmHg the pattern changed gradually from Plate 1 to Plate 6. After 20 minutes the emission characteristic became steady and the average work function attained a constant value, 5.62 eV, *i.e.*, $\Delta\phi = 0.72$ eV. This $\Delta\phi$ value is nearly close to that on tungsten,[17] tantalum[4] and niobium[5]

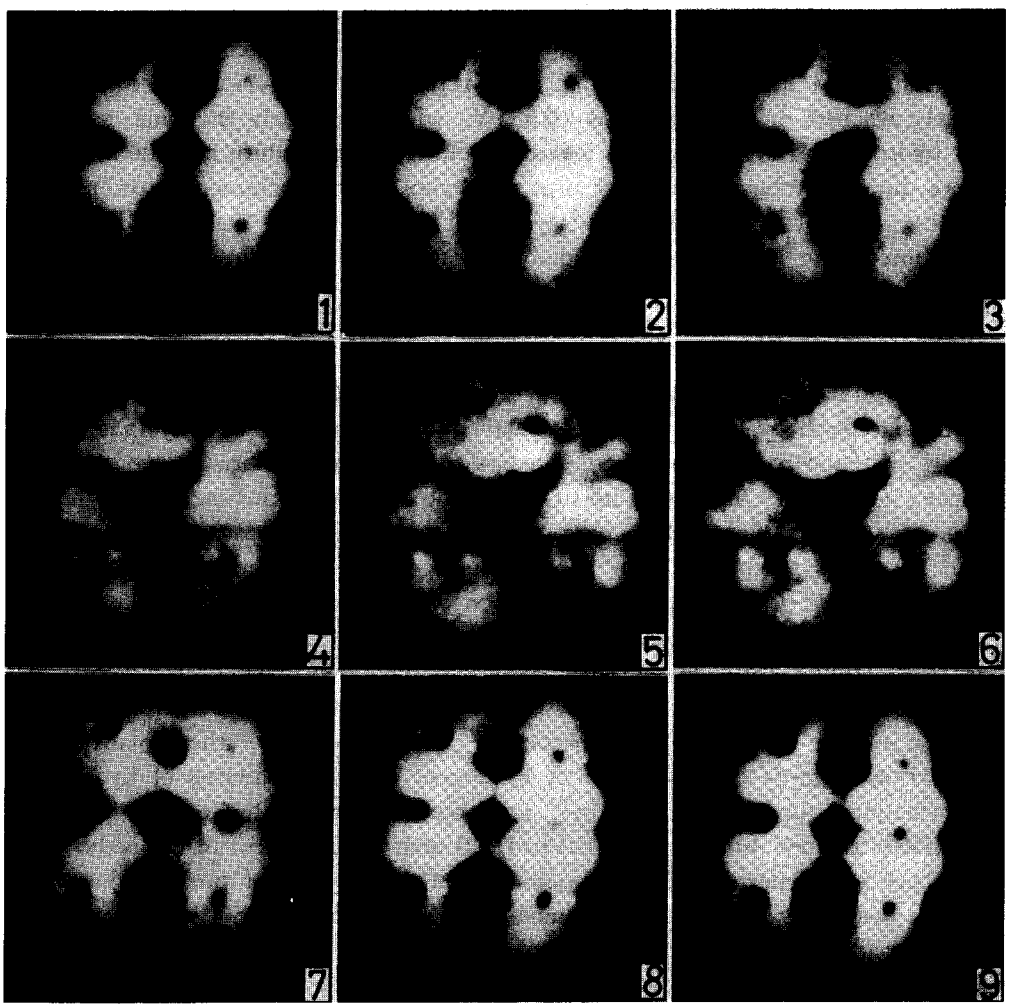

Fig. 6. Field emission patterns for carbon monoxide on rhenium: $I=5\times10^{-7}$ amp.
1: clean rhenium; $V=12.0$ kV.
2: adsorption of 7×10^{-9} mmHg carbon monoxide for 30 sec at 77°K; $V=13.0$ kV.
3: after 1 min; $V=13.7$ kV.
4: after 3 min; $V=14.8$ kV.
5: after 7 min; $V=15.7$ kV.
6: after 30 min; $V=16.8$ kV, $\Delta\phi=0.72$ eV.
7: carbon monxide desorbed by heating at 300°K for 10 min; $V=18.6$ kV ($I=2\times10^{-7}$ amp), $\Delta\phi=1.1$ eV.
8: heating for 2 min at 800°K; $V=12.6$ kV, $\Delta\phi=0.2$ eV.
9: heating for 2 min at 1000°K; $V=12.0$ kV, $\Delta\phi=0.00$ eV.

($\Delta\phi = 0.7 \sim 0.8$ eV). Carbon monoxide adsorption gave a pattern of mottled appearance with several dark stripes having no connection with the crystallographic zone lines.

On warming to room temperature, a uniformly emitting pattern was obtained as seen in Plate 7, and an average work function increased by 1.1 eV. This pattern was similar to that of clean surface except the dark regions around the (0001) planes. This fact can be ascribed to the desorption of weakly adsorbed carbon monoxide (physisorption) and/or interconversion from physisorption to chemisorption. On heating to 800°K most of carbon monoxide was removed from the surface and $\Delta\phi$ was 0.2 eV. By further heating to 1100°K the remaining carbon monoxide was completely removed from the surface, and the pattern and average work function of the clean surface were restored. There was no indication of decomposition of carbon monoxide on the surface; neither carbon residue nor trace of oxygen were observed on the surface. Therefore it is suggested that adsorption of carbon monoxide on rhenium is nondissociative as it is on tungsten.[17]

Xenon

Adsorption of xenon was studied with the $(11\bar{2}0)$-oriented tip used for the studies of nitrogen and hydrogen. Fig. 7 shows a sequence of the emission patterns for xenon adsorption and desorption at 77°K. As soon as xenon was allowed to flow over the tip at a pressure of 5×10^{-8} mmHg the $(11\bar{2}1)$ regions were much brightened, which implies increasing emission current; the applied voltage therefore had to be diminished steadily to maintain a constant current. After 5 minutes a stable pattern was obtained as shown in Plate 5; the pattern remained the same throughout the successive adsorption of xenon for about 30 minutes. When the tip was saturated with xenon at 77°K there appeared bright regions on and around the $(11\bar{2}1)$ and $(11\bar{2}3)$ planes along the $[1\bar{1}00]$ zone lines in contrast with the dark $(10\bar{1}1)$ planes enlarged and elongatad along the $[1\bar{2}10]$ zone lines. The average work function decreased gradually with time and attained the minimum value of 3.82 eV at saturation *i.e.*, $\Delta\phi = -1.08$ eV, which is slightly larger than $\Delta\phi = -1.4$ eV in the case of tungsten.[18]

On evacuating the cell to 2×10^{-9} mmHg at 77°K, some desorption was observed and the emitting region around the $(11\bar{2}1)$ and $(11\bar{2}3)$ planes gradually enlarged and therefore the dark $(10\bar{1}1)$ planes diminished as shown in Plates 7 to 9. The average work function increased by 0.48 eV. After about 90 minutes of desorption a stable pattern was obtained (Plate 9) and the average work function attained the maximum value of 4.53 eV, which is lower than that of clean surface by 0.37 eV but higher than that of minimum one by 0.71 eV. This pattern did not change appreciably by prolonged evacuation

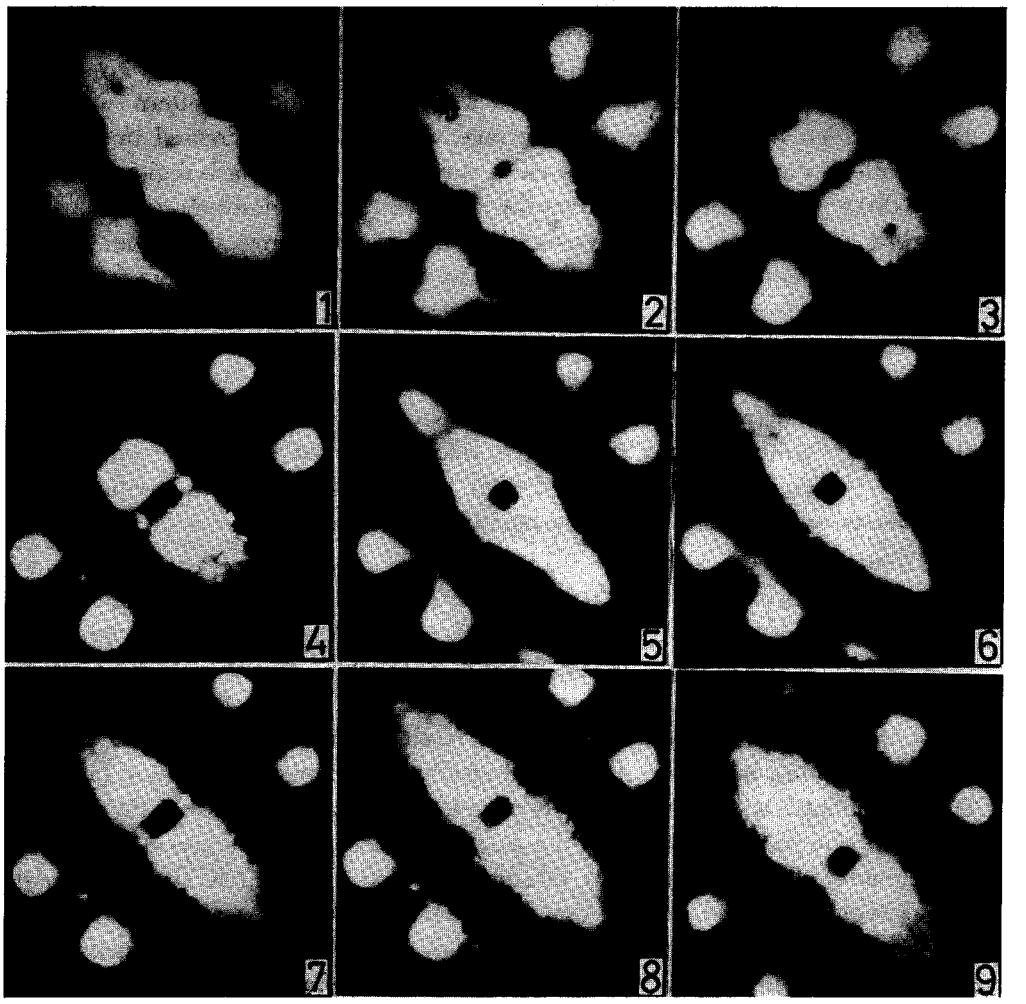

Fig. 7. Field emission patterns for xenon on rhenium: $I=5\times10^{-7}$ amp.
1: clean rhenium; $V=9.52$ kV.
2: adsorption of 5×10^{-8} mmHg xenon for 30 sec; $V=9.0$ kV.
3: after 1 min; $V=8.0$ kV.
4: after 3 min; $V=7.1$ kV.
5: after 5 min; $V=7.0$ kV, $\Delta\phi=-1.08$ eV.
6: ater evacuation to 2×10^{-9} mmHg for 5 min: $V=7.4$ kV, $\Delta\phi=-1.01$. eV.
7: after evac. for 10 min; $V=8.1$ kV,
8: after evac. for 15 min, $V=8.05$ kV, $\Delta\phi=-0.60$ eV.
9: after evac. for 50 min; $V=9.1$ kV, $\Delta\phi=-0.37$ eV.

for about 120 minutes. On warming up to room temperature, xenon was completely removed from the surface, and the initial clean surface and the average work function of clean surface were restored.

The fact that the emission was observed only from the rough planes along the [1$\bar{1}$00] zones suggests that the above interesting features of xenon adsorption are closely related to the surface topography. Similar structure-sensitive behavior has been observed for physisorption on tungsten by EHRLICH and HUDDA,[18] and by ROOTSAERT *et al.*,[2] who observed prominently bright rings around the dark (100) planes segmented by the dark [100] zones in patterns for xenon on tungsten. ROOTSAERT *et al.* have shown, by analysis of the topographical geometry of tungsten surface, that xenon atoms prefer bowl-shaped sites which fit the size of xenon. In the case of rhenium such a bawl-shaped sites are found just on the planes along the [1$\bar{1}$00] zones except densely packed (11$\bar{2}$0) planes. Thus, the physisorption of xenon at a low pressure takes place mainly on the rough planes composed of widely spaced protruding atoms.

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Appendix

A hard-sphere model of h.c.p. crystal whose surface was composed of low index planes along $[1\bar{2}10]$ and $[1\bar{1}00]$ zones are shown in Fig. 8. As seen here, the basal plane has the most densely packed atoms of the (0001) plane, whose direction is perpendicular to the emitter axis. The $[1\bar{2}10]$ zone consists of teraces and steps formed by close-packed atoms of the (0001) and $(10\bar{1}1)$ planes, while the $[1\bar{1}00]$ zone has an open structure composed of the rows of protruding atoms and widely spaced atoms. In the clean pattern (Fig. 2), the former zone is seen as dark longitudinal bands linking the (0001), $(10\bar{1}3)$, $(10\bar{1}1)$ and $(10\bar{1}0)$ planes, but on the contrary the latter zone appears as brightly emitting regions and dark small circles of the $(11\bar{2}2)$ and $(11\bar{2}0)$ planes.

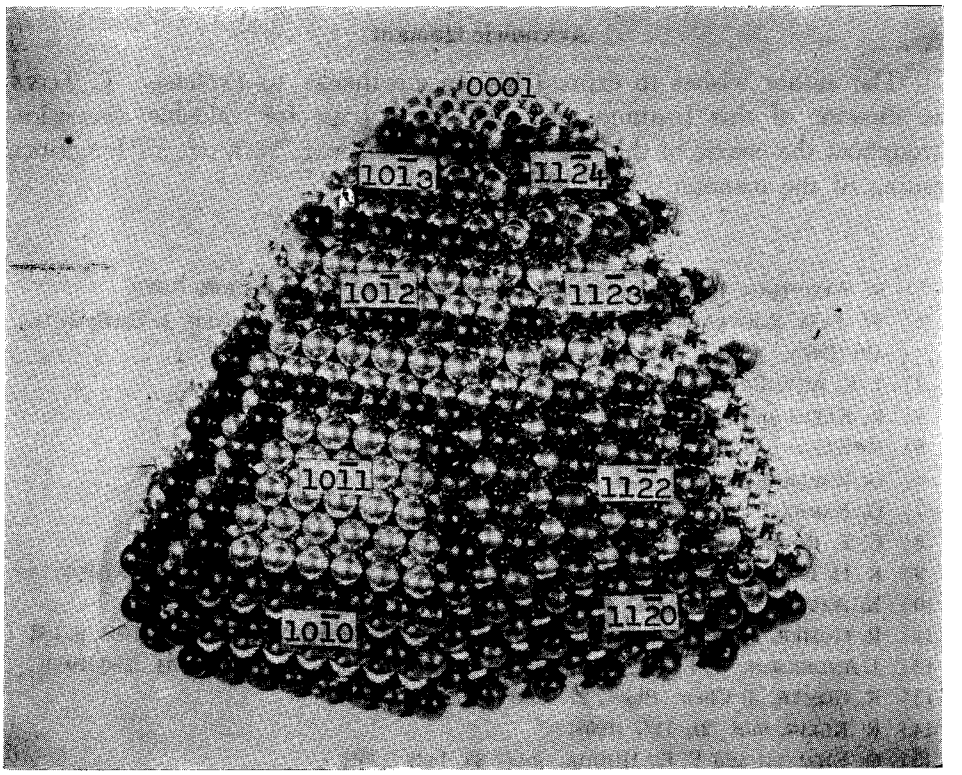

Fig. 8. Hard-sphere model of hexagonal closed packed crystal.