[94] Higher-order gradients might still be large.

[95] In fact, we conjecture that the situation is as follows: Unless the physical circumstances can be described by keeping only the first few terms in the expansion of the transport kernels in powers either of the thermodynamic forces (near local equilibrium) or of the fluctuations in the densities (near global equilibrium), this quasidifferential description will have limited utility.

[96] These properties were pointed out to me by B. Robertson.

PHYSICAL REVIEW VOLUME 175, NUMBER 1 5 NOVEMBER 1968

Metastable Atoms and Molecules. III. Metastable Impacts on Surfaces with Various Work Functions*

R. N. Varney
Lockheed Palo Alto Research Laboratory, Palo Alto, California

(Received 9 May 1968)

Surfaces of atomically clean tungsten, with work function 4.5 eV, tungsten oxidized with a monolayer of oxide and having a work function 6.6 eV, and tungsten coated with BaO with a work function probably under 2 eV were hit by metastable atoms or molecules of Ar, Xe, N_2, and H_2. The emission of secondary electrons by metastable atoms and the surface ionization of the atomic metastables were shown to follow the expected dependency on the work function. The N_2 molecular metastables were weakly surface ionized as N_2^+ on the oxidized tungsten but not on the surfaces of lower work function. Secondary electron emission either did not occur at all or was obscured by the large emission of CN^- negative ions. No CN^- emission nor electron emission was observed on the W-O surface. Metastables of H_2 dissociated on the clean and the oxidized surfaces. On the clean surface, one atom became H(2*p*) and gave out Lyman alpha radiation. On the W-O surface, one of the H atoms became a proton and no Lyman alpha radiation was produced. No other ion emission than H^+ occurred.

I. INTRODUCTION

The procedure described in Paper I of this sequence[1] has been used to produce beams of excited neutral particles of Ar, Xe, H_2, and N_2 with kinetic energies in the range of 25 to 200 eV. Their interactions with surfaces have been examined as described in Paper II.[2] The primary change in apparatus structure relative to the earlier work has been to replace the molybdenum target with a tungsten ribbon approximately 0.000 75-in. thick and connected so that it could be heated to high temperature by an electric current. This target was used in various states including coated with BaO to provide a low work-function surface, flash cleaned to give a normal work function for heterogeneous tungsten, and oxidized with approximately a monomolecular layer of oxide to give an elevated work function. In addition, studies were made of the behavior of the target under "dirty" conditions, obtained simply by letting the target stand at room temperature for hours or days in either a controlled, low pressure of oxygen or in the residual gases of a high-vacuum system.

II. PREPARATION OF TARGET SURFACE

The tungsten ribbon could be flash heated by the conduction current for purposes of cleaning. Flash temperatures were not measured, but the heating current which was around 25 A, was closely observed, and ultimately every target was burned out by only a slight excess of current above the normal flash-current used. Hence, it is believed that flashing was surely at temperatures above 2000°C and probably above 2500°C. On flash heating of a new target, or of an old target after several days of idleness even in the vacuum of 10^{-9} Torr or better, a burst of emitted gas was observable on ionization gauges. After several successive flashes, the gas evolution was negligible. In ensuing work, it is assumed without further measurement that the work function of the surface was then 4.5 eV.

For lowered work-function studies, the target was coated with $BaCO_3$ which in turn was reduced by heating the target to approximately 950°C in high vacuum until gas evolution was negligible. It is assumed that the work function was then of the order of 1.6 eV, but no results are presented which depend on any assumption other than that the work function was lower than for the clean tungsten. This surface was essentially a dirty one by contrast with others of the present paper so that only minor observations about its behavior are offered.

To oxidize the surface, oxygen was admitted to the closed-off system at 0.5×10^{-3}-Torr pressure, and the freshly cleaned tungsten was then heated to 900°C until the pressure dropped to 0.4×10^{-3}

Torr. The oxide layer was analyzed in the following way: the volume of the system was approximately 4 liters; the surface area of the tungsten target, including both sides, was approximately 2.8 cm^2. The drop in pressure thus corresponded to about 5×10^{15} molecules/cm^2 of oxygen on the surface. This value may be compared with the result of E.W. Mueller.[3] His Fig. 3 shows that the work function of tungsten rises to a saturation value of 6.6 eV with just this number of adsorbed oxygen molecules. It is accordingly believed that this work function was created on the tungsten surface and that the oxide layer was of the order of one oxygen-atom thick. It is remarked in substantiation that the phenomena to be described in this paper and correlated with the high work function decreased appreciably if only half as much oxygen was permitted to be adsorbed and did not increase significantly if 10 times as much oxygen was adsorbed.

III. CHARACTER OF POSSIBLE RESULTS

Based on the observation of Refs. 1 and 2 and on the extensive summary by Kaminsky,[4] the following possibilities for the results of impacts of metastable particles on surfaces are described:

(1) If the energy interval $I-M$ between the ionized state of the particle I and the metastable state M is less than the work function Φ of the surface, the particle may become surface or resonance ionized and an emitted positive ion may be observed.

(2) If the energy M of the metastable state is greater than the work function Φ, secondary electron emission from the surface may occur through Auger de-excitation. However, if $I-M<\Phi$, secondary emission may also occur by resonance ionization as in (1) followed by Auger neutralization of the ion, a process which Hagstrum[5] showed to be considerably more favored than the Auger de-excitation of the metastable itself. The energetic requirement for electron emission by the ionization-neutralization sequence is then that $I-2\Phi>0$. This is not identical with $M-\Phi>0$, but the alternatives cannot be validly distinguished in the present measurements.

(3) Instead of (or in addition to) secondary electron emission, negative ions may be emitted from the surface.

(4) Some sort of radiative de-excitation of the incident particle may occur leading to tertiary, photoelectric emission from surrounding surfaces.

(5) Surface dissociation of incident molecules may be expected with consequent alteration of available energies for secondary processes. This occurrence is extensively treated for the case of H_2 in Sec. VI.

Broad energetic considerations may exclude one or another mechanism, but when resonance ionization occurs ($I-M<\Phi$) and at the same time Auger neutralization is allowed ($I>2\Phi$), a question arises as to whether the ion will be emitted or be neutralized. If the ion is bonded to the surface with energy appreciably in excess of the thermal energy at laboratory temperature used in this work, the Auger neutralization process is surely favored. However, there are possible circumstances where this limitation does not arise. The choice between ion emission or ion neutralization then seems to be regulated by the probability of the Auger neutralization. Note that while the efficiency of secondary electron liberation decreases as $I-2\Phi$ approaches 0, this reflects only the probability of the escape of the Auger electron from the surface and not the separate probability of occurrence of the Auger neutralization process. Enhanced Auger neutralization might then reduce ion emission without at the same time showing increased electron emission.

In the present work, when the tungsten surface is oxidized, the band structure characteristic of the conductor must be critically altered to that of an insulator. The complete filling of a band with its resultant destruction of conductivity and motion of electrons would seem to reduce the chance of Auger transitions. If this picture is correct, the electron emission would be much diminished and the ion emission increased, a situation which is in fact observed for the case of argon metastables on the oxidized tungsten compared with clean tungsten, to be described in the next section. An alternative explanation of the data may be simply that the Ar$^+$ is much less strongly bound to the W-O surface than to the clean W surface. The choice is somewhat less attractive because the Ar$^+$ is not believed to be strongly bonded to the clean W in the first place. Resolution of this matter has not been found in the present paper.

IV. OBSERVATIONS WITH Ar AND Xe

The results with metastable atoms of these rare gases are described primarily to establish the intrinsic validity of the experimental procedures as they fall distinctly into the patterns of (1) and (2) of Sec. III. While the results are reasonable, it is believed that the only comparable direct tests of this sort with metastable atoms have been confined to mercury.[6] The values of the parameters involved are believed to be the following:

For argon, $I=15.8$ eV, $M=11.6$ eV, $I-M=4.2$ eV.

For xenon, $I=12.1$ eV, $M=8.5$ eV, $I-M=3.6$ eV.

Results are shown in Tables I and II. The strong secondary emission from surfaces of low Φ and the

TABLE I. Emission by Argon metastable impacts. (Strong corresponds to 1×10^{-11} A observed current. Weak corresponds to $\sim3\times10^{-13}$ A, Zero indicates $<10^{-13}$ A.)

Surface		Secondary Electrons	Positive Ions
BaO on W	($\Phi\sim1.6$ eV)	Strong	Zero
Clean W	($\Phi\sim4.5$ eV)	Weak but observable	Approximately same as secondary electrons
W-O	($\Phi\sim6.6$ eV)	Zero	Very strong (× 20 for clean W)

TABLE II. Emission by xenon metastable impacts. (See Table I for actual range of current magnitudes.)

Surface	Secondary electrons	Positive ions
BaO on W ($\Phi \sim 1.6$ eV)	Medium	Zero
Clean W ($\Phi \sim 4.5$ eV)	Weak	Zero
W – O ($\Phi \sim 6.6$ eV)	Weak	Medium

strong ion emission when the work function is high are compatible with expectation. The absence of secondary electron emission when the value of $I - 2\Phi$ is still slightly greater than zero is compatible with observations by Hagstrum[5] and has been ascribed to distortion of atomic energy levels of atoms or ions as they approach a metallic surface, lowering the effective value of I. The results for argon are shown schematically in Fig. 1. The results for xenon are not plotted in the same figure because the entire scale of effects was smaller than in argon and subject to greater uncertainties. It is likely that a weaker beam of metastable Xe was produced than for other gases, and this in turn may be attributed to the problems of differential pumping of Xe with an ion pump. Xe pumped less well than Ar and much worse than N_2 or H_2. Hence, only lower pressures of Xe could be used in the source.

V. OBSERVATIONS WITH NITROGEN

Reference is made to paper II[2] for most results on nitrogen. Specifically, the absence of secondary electrons but the presence of CN^- from a clean tungsten surface is parallel to the same observation of molybdenum. Nitrogen deviates to some degree from the simpler pattern for atomic metastables. The chief new result is that $N_2{}^+$ from the oxidized tungsten was observed. This observation indicates some boundaries on the metastable energy M of the incident N_2, namely $I - \Phi(\text{W-O}) < M < I - \Phi(\text{W})$. Numerical substitutions of 15.6 for I and the previously cited values for the two work functions gives $9.0 < M < 11.1$ eV. It is noted that the $a^1\Pi_g$ state of N_2 at 8.6 eV is a known metastable state. Since it can imaginably be vibrationally excited, the particle may still be in this state but have 9-eV energy. The observed $N_2{}^+$ emission is weak, indicating that M may be near to the 9-eV lower bound. Some NO^+ emission from the oxidized surface was also identified mass spectrometrically. The ion emission by N_2 metastables is also indicated in Fig. 1.

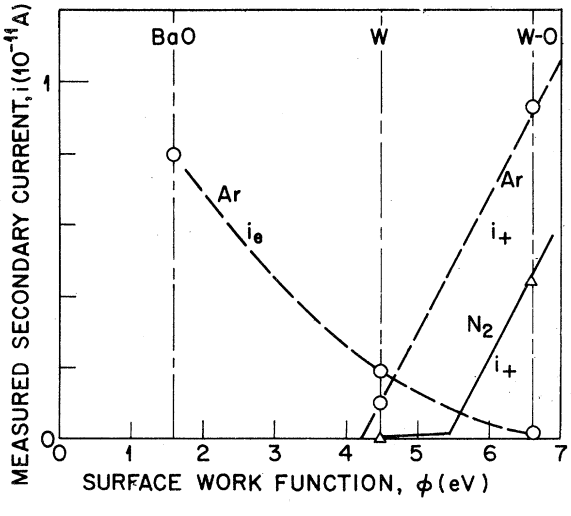

FIG. 1. Emission of secondary electrons and of positive ions for Ar metastables and of positive ions for N_2 metastables on impact with surfaces of various work function. Because of the limited number of points, specifically only two for N_2 one of which is at zero, the curves must be regarded as schematic. In addition, the flux of metastable particles was not measurable. It was, however, controlled by careful reproduction of conditions in the source.

VI. OBSERVATIONS WITH HYDROGEN

The results on hydrogen seems to offer the most significant new information; as for N_2 the behavior deviates from that of the atomic metastables. The observations are summarized in Table III.

As in Ref. 2, photon emission, identified as consisting at least in part of Lyman alpha radiation, was predominant with the clean target. Both the photons and the secondary electrons diminished to zero (i.e., by a factor of at least 20) when the target was oxidized. The surface ionization by contrast was unobservable with the clean or coated targets but was strong with the oxidized target. Use of a quadrupole mass spectrometer (Varian, Model No. 974-0002), attached so that it could collect the ions (if any) leaving the target and identify them, disclosed that with the oxidized target, the surface ionization consisted exclusively of protons. The hydrogen results are thus so different in character from those for Ar and even N_2 that they cannot be represented in Fig. 1.

Figures 2(a) and 2(b) depict schematically what appears to have been occurring at the clean and the oxidized targets, respectively. Referring to Fig. 2(a), it now seems to be confirmed that incident metastable H_2 dissociated on the clean tungsten surface and yielded one ground-state atom and one atom of hydrogen in the $2p$ state. It is possible but not verified in this study that a large percentage of the atoms remained bound to the surface. The $2p$ state was identified from the Lyman alpha radiation which in turn was identified at least roughly by window transmission measurements and by the max-

TABLE III. Emission by Hydrogen metastable impacts. (See Table I for magnitudes of observed currents.)

Surface	Secondary electrons	Photons (Lyman α)	Positive ions
BaO on W ($\Phi \sim 1.6$ eV)	Strong	Weak	Zero
Clean W ($\Phi \sim 4.5$ eV)	Weak	Strong	Zero
W-O ($\Phi \sim 6.6$ eV)	Zero	Zero	Strong, H^+

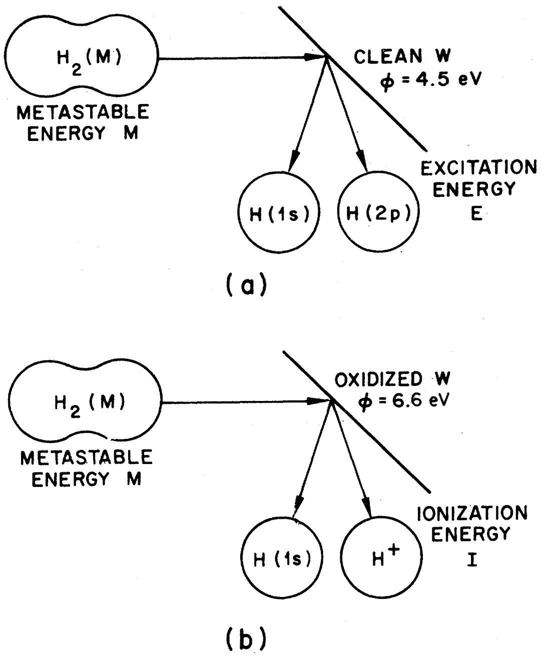

FIG. 2. Schematic illustration of the impact of incident metastable H_2 molecules: (a) on clean tungsten, and (b) on oxidized tungsten. It may be that, under the experimental conditions, both the H(1*s*) and H(2*p*) remained bound to the surfaces.

imum kinetic energy of ejected electrons. In Fig. 2(b), when impact occurred on the oxidized tungsten surface with a work function of 6.6 eV, dissociation and surface ionization seemed to occur without the appearance of any Lyman alpha radiation. The product of the surface ionization was exclusively H^+. The protons did not remain bound to the surface to a great degree as the emitted current was appreciable by comparison with the various other observed secondary currents.

The extensive studies of interactions of hydrogen on tungsten surfaces[7] do not appear to include certain of the present features, namely: (a) that the incident H_2 has kinetic energy of 25 to 200 eV, and (b) the incident H_2 is in an excited state. The results may, however, be analyzed in terms of the older studies and certainly furnish an interesting supplement to them. The older results are summarized in Ref. 7 and show that an H_2 molecule incident on tungsten with even a small "activation energy" becomes dissociated into two H atoms which are bonded by weak chemisorption to the metal with an energy given both theoretically and experimentally as ~3.2 eV. The metastable state of H_2 $(1s\sigma 2p\pi\,{}^3\Pi_u)$ (11.86 eV) has a dissociation energy of 2.77 eV, hence less than the 4.48 eV of ground state H_2. Hence no energetic obstacle appears to the dissociation of the metastable H_2 at the surface.

The presence of the excited H atom having excitation energy E and ionization potential I on the metal or oxidized surface is comparable with the case of Cs atoms on a tungsten surface. The energy $I - E$ needed to ionize the H(2*p*) is less than the work function Φ for both the clean and the oxidized tungsten, paralleling the situation for Cs, where the energy between ground state and ionized Cs is also less than Φ. In the present experiments, the tungsten is kept at room temperature during the collision studies. The vacuum was in the range of 10^{-8} Torr during runs, and the beam flux was probably near to 10^{10} particles/cm^2 sec. Experimental runs rarely lasted as long as 10 min., usually less than 5 min., so no significant amount of H_2 adsorption should have occurred.[8] In the respects of temperature and of surface contamination, the present work is different from the classical work of Langmuir[9] with Cs on W, where a steady state of the surface was produced with equal incoming and outgoing fluxes. Here, the surface can adsorb and retain much of the incident hydrogen. Kaminsky[10] suggests that the number of particles, n, adsorbed on the surface per unit area and time compared with the corresponding number incident, N, should be given by

$$n = N[K_i \exp(E_i/kT) + K_a \exp(E_a/kT)] \ . \tag{1}$$

[The equation is slightly altered from that of Kaminsky in the respect that in Eq. (1), E_i and E_a are to be inserted with positive signs, eliminating double negative signs from his form.] The subscripts i and a refer in this case to the ions or the excited atoms of H. K_i and K_a are coefficients which depend only slightly on the temperature. The meaning of E_i and E_a is shown schematically in Fig. 3. E_i is the energy needed to remove an H^+ ion from the surface and is therefore given by

$$E_i = B_i - [\Phi - (I - E)] \ , \tag{2}$$

where B_i is the bonding energy of the ion to the surface. E_a is the energy needed to remove the H(2*p*) atom from the surface in an unchanged state. It is presumably simply the atomic bonding energy although this may not have the same value of 3.2 eV as for a ground-state atom. It is drawn as being 3.2 eV in Fig. 3 for lack of any definitive alternative evidence. At room temperature, if the value of E_a is of the order of magnitude of 3 eV, the atomic adsorption term in Eq. (1) involves exp(3/0.04), a number in excess of 10^{30} and indicating essentially complete adsorption and no evaporation of the H atoms. The experimental absence of H^+ emerging from the clean W surface suggests that E_i for this surface is also of this magnitude so that $\exp(E_i/kT)$ should also be very large. The ejection of H^+ from the W – O surface by contrast suggests that E_i for it must be either in the range of thermal energy or actually negative.

These observations, which may be seen in graphical form in Fig. 3, are analyzed with the following numerical test: the value of $I - E$ is 13.65 – 10.15 or 3.5 eV. The two values of Φ are 4.5 and 6.6 eV, respectively, giving the bracket term of Eq. (2) the values 1.0 and 3.1 eV. The value of B_i to make E_i fit the observations of the paragraph just above must then satisfy $1.0 < B_i \lesssim 3.1$ eV. In fact, the observations further suggest that B_i is at least several multiples of the thermal energy of 0.04 eV above the lower limit.

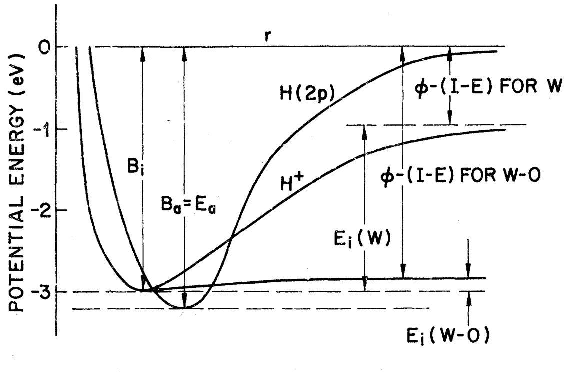

FIG. 3. Schematic plot of the various energies of H(2p) and H^+ at distances r from a W and a W-O surface. The value of E_i(W-O) may actually have an opposite sign to that shown, according to data of this paper. This work only establishes that the minimum of the H^+ curve lies appreciably below the −1-V ordinate and near or above the −3.1-V ordinate. The curve for H(2p) is drawn in accordance with known behavior of H(1s). It is not established that E_a should have the same value.

An alternative argument can be made that the layer of oxide on the tungsten simply reduces the effective bonding energy of the hydrogen atoms to the tungsten. This alternative seems less attractive than the first because the dissociation of the incident molecules might also be diminished by the weakened bonding. No data are known to exist on changes of bonding energy of hydrogen to a tungsten surface with degree of coverage with oxygen.

Some miscellaneous comments about the findings are added:

(1) Pure oxygen at about 10^{-3}-Torr pressure was allowed to stand in the tube for 4 h, and on another test for 48 h, but with the tungsten which had just previously been flash-cleaned standing at room temperature. The resulting behavior fits into a general pattern of "dirty"-target conditions and specifically *not* oxidized target characteristics. Dirty-target phenomena are that secondary electron emission is dependent on the kinetic energy of the incident particles. For the present experimental conditions, this proves to be greater than for the clean target. No proton emission was observed. A distinction between an oxygen-gas coated W surface and an oxidized W surface is indicated.

(2) Since in Ref. (2) it was noted that metastable beams of N_2 on a surface of Mo led to ejection of CN^- ions, a search was made for various positive and negative ions such as $OH^{\pm}$. It is reiterated that no ions other than H^+ were seen.

(3) If *ions* from the source of metastables were permitted to reach the target by the expedient of applying no stopping or deflecting voltage (see Ref. 1) the current of positive ions was in the range of 5×10^{-9} A. The secondary current measurements from the metastables, arising largely from the Lyman alpha radiation, showed values near 10^{-11} A, and the positive current from the oxidized target was of the same order. These numbers are furnished to indicate the range of currents that were measured.

VII. CONCLUSIONS

Secondary electron emission and surface ionization by metastables of argon and xenon have been examined on impact with surfaces having three different work functions. The surface ionization increased with increasing work function and the secondary electron emission decreased. The results are both anticipated and compatible with observations with mercury metastables and with metastable ions of the rare gases but are essentially new and cover a more extended range of values of the surface work function.

Molecular metastables of nitrogen and hydrogen on impact with surfaces of various work function behave differently from atomic metastables. The dissociation of the molecules at the surface is the primary cause for the differences. For N_2, surface ionization with ejection of the undissociated molecular ion N_2^+ was observed on the W-O surface with high work function. By contrast, the H_2 metastables appeared to dissociate on all surface. With the W-O surface giving a high work function, surface ionization occurred giving only H^+. Impact on the clean tungsten surface led to Lyman alpha radiation as previously observed with molybdenum targets. The bonding energy of the H^+ on the surface was assessed within somewhat wide limits to be distinctly greater than 1 eV but less than or equal to 3.1 eV.

---

*Work supported by Lockheed Independent Research Funds.

[1] R. N. Varney, Phys. Rev. 157, 113 (1967).

[2] R. N. Varney, Phys. Rev. 157, 116 (1967).

[3] E. W. Mueller, Z. Elektrochem. 59, 374 (1955).

[4] M. Kaminsky, Atomic and Ionic Impact Phenomena on Metal Surfaces (Academic Press Inc., New York, 1965), Chap. 12 and 13.

[5] H. D. Hagstrum, Phys. Rev. 104, 317 (1956).

[6] A. Buehl, Helv. Phys. Acta 6, 231 (1933).

[7] Kaminsky, Ref. 4, pp. 36–39 and 48–50.

[8] According to Kaminsky (see Ref. 4, p. 103), if the surface of the tungsten should indeed be contaminated with hydrogen, the work function of the surface would be raised ~0.45 eV. This is not believed to have been the case and would introduce only a small change in the numerical test shown below.

[9] J. B. Taylor and I. Langmuir, Phys. Rev. 44, 423 (1933).

[10] M. Kaminsky, Ref. 4, p. 104.