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SURFACE CLEANLINESS RESEARCH
USING THE WORK FUNCTION TECHNIQUE

By F. J. Brock

FINAL REPORT

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ABSTRACT

The surface cleanliness of a polycrystalline tungsten sample was studied by measuring its work function. Argon ion bombardment, electron bombardment, radiation heating, and controlled oxidation (vacuum) were evaluated with respect to their effectiveness in initial cleaning as determined by surface potential measurements. Work function measurement techniques were evaluated with respect to determining their usefulness in detecting surface contamination, by controlled oxygen adsorption on the sample surface. It was found that a surface oxygen relative coverage $\theta < \frac{1}{2}\%$ could be observed. For surface oxygen relative coverages $\theta \leq 2$ it was found that the surface could be cleaned by argon ion bombardment doses $D_{Ar^+} \leq 50 \times 10^{14} \text{ Ar}^+/\text{cm}^2$ (the approximate equivalent of 10 monolayers of argon) for ion energies within the range $(250 \leq \bar{E} \leq 500) \text{ eV}$. It was also found for low coverage, that surface oxygen could be completely removed by electron bombardment for 30 seconds at an electron current density of $J = 10^{-2} \text{ A/cm}^2$ at surface temperatures $T_s \approx 1200^\circ\text{K}$ but that radiation and resistance heating alone at the same temperature did not completely remove the adsorbed oxygen.

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INTRODUCTION

This report presents the results obtained during the experimental evaluation of the usefulness of work-function measurement techniques in determining surface cleanliness and the effectiveness of ion and electron bombardment in cleaning surfaces and the dependance of cleaning rate on various operating parameters.

APPARATUS

The system is shown schematically in Fig. 1. The main vacuum enclosure contained the sample, the sample holder and positioning mechanism, sample heater, oxygen source, electron gun, ion gun, ion energy analyzer, ion gage, and mass spectrometer ion source. The latter two instruments were attached to the front flange of the enclosure along with main pump (orbion) and the roughing pump (G.E. ion pump). The roughing pump plumbing contained a system isolation valve. All other apparatus, above, was attached to the rear

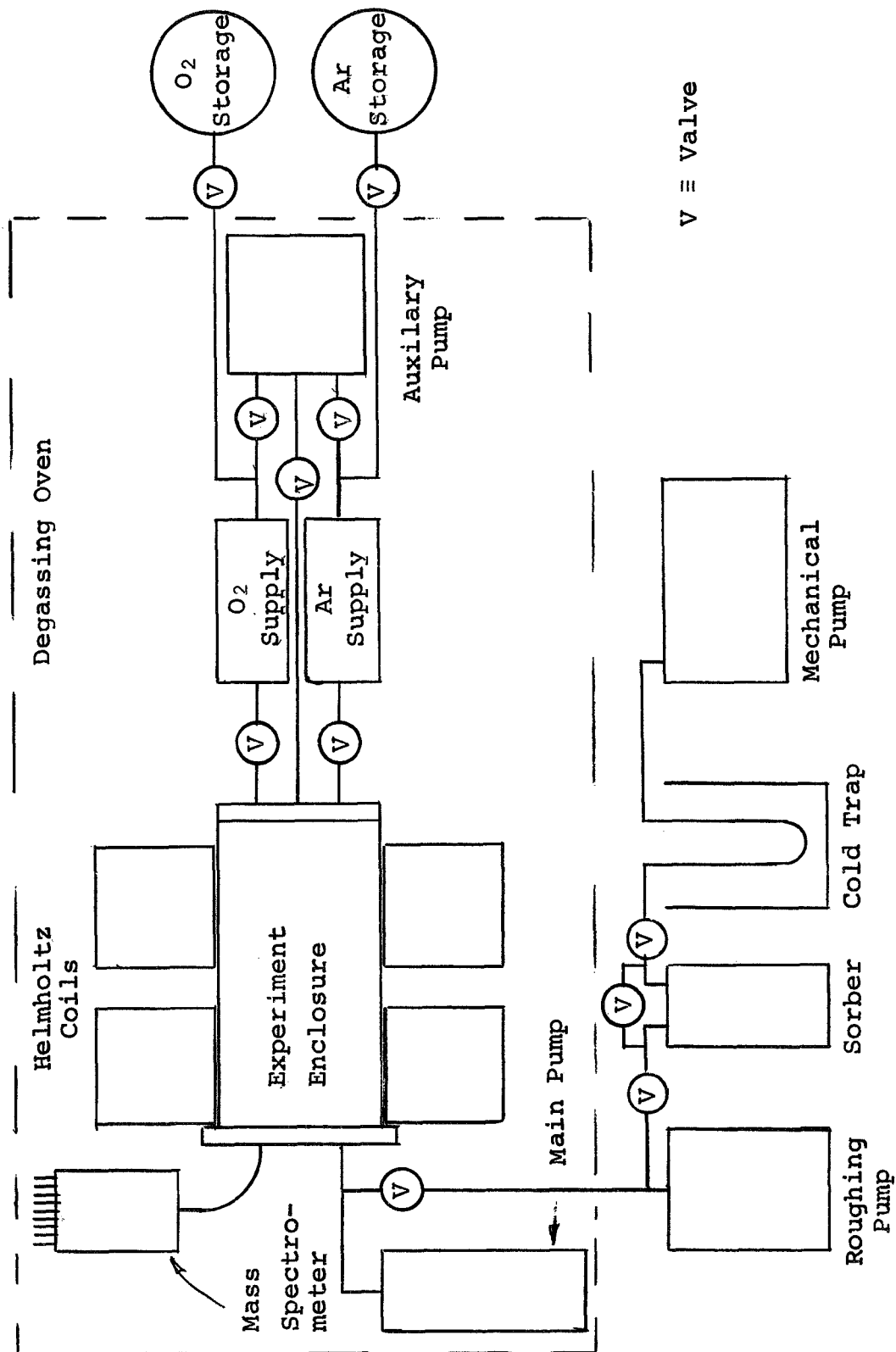


Fig. 1. System schematic.

flange of the enclosure. Also attached to this flange were the argon supply for the ion gun, the oxygen supply, (each of which contains an ion gage) and an auxiliary pump (G.E. ion pump) for evacuating both gas supply systems independent of main system operation and for assisting in evacuating the main system during oxygen input. Attached to the roughing pump plumbing was a sorber pump and a cold trapped, 2-stage mechanical pump for removing atmospheric gases. Gas storage bottles with isolation valves were attached to the gas supply volumes for recharging them with ultra pure O_2 or Ar as required. In operation the main vacuum enclosure was inside a pair of Helmholtz coils which were mounted on a dolly such that they could be removed during degassing. A $450^\circ C$, removable degassing oven enclosed the main vacuum system and all components, except the roughing system and the gas storage bottles.

Sample

The sample was made from high purity tungsten wire rolled into a ribbon 1 mil thick. The sample, cut from a short length of this ribbon selected by microscopic inspection for minimum mechanical imperfections, was 2 mm wide and 5 mm long. It was attached to 2 support posts by 2 U-shaped 5 mil wires, each welded to the back of the sample 1 mm on either side of the sample center. The U-shaped wires were attached with 2 welds each to support posts, each of which coiled around the end of a ceramic (high purity Al_2O_3) support rod. One side of this sample mount was tungsten and the other was rhenium thus providing a thermocouple for measuring the sample temperature. See Fig. 2.

Heater, eb Cathode,
and Reference Cathode

Sample Holder

Sample

Electron Gun
Energy Analyzer

O₂ Source

Fig. 2.- Experimental apparatus subassembly.

Sample Holder

The sample support was attached to a sample holder which provided two rotational degrees of freedom for moving the sample about inside the vacuum system and positioning it in front of the diode cathode or heater, oxygen source, electron gun, ion gun, and mass spectrometer. The sample holder (gear box) was actuated by 2 push-pull rods passing through bellows seals at the rear flange. The rods were threaded on the end and driven by rotating a nut-like device secured in a bearing. See Fig. 2. The apparatus shown was secured to two parallel stainless steel beams, cantilevered from the rear flange (a portion of one beam may be seen in the bottom photo in Fig. 2).

Sample Heater

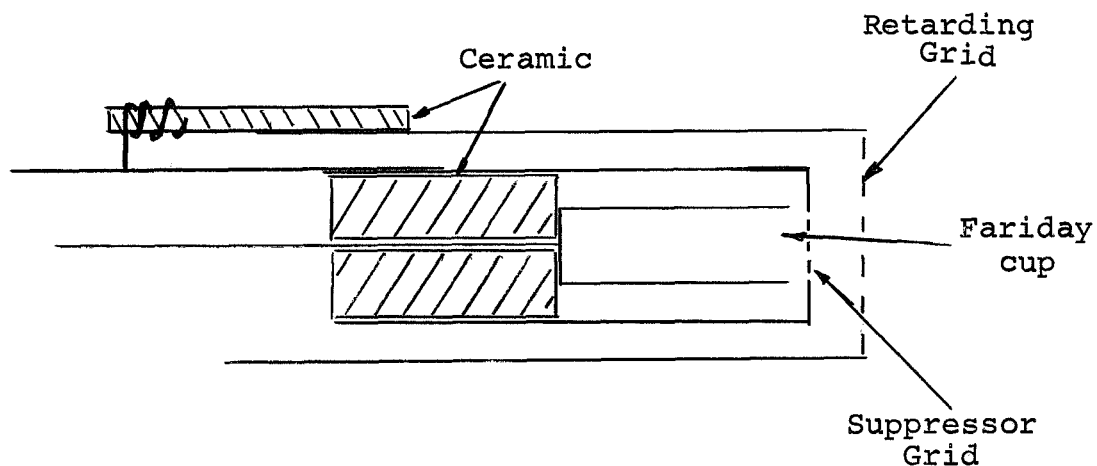
The sample heater was a 20 turn coil made of 5 mill tungsten wire, 1.5 mm O.D. and 1 cm long. The coil was thoriated. The sample could be radiation heated to about 1000°C if positioned immediately adjacent to the heater operating at maximum safe temperature. This coil was also used as a cathode to electron bombard the sample, providing any temperature desired. This was a particularly efficient method of heating the sample in the 2.2 KG axial field provided by the Helmholtz coils. A sample temperature of the order of 2000°C could be attained with the cathode temperature less than 1200°C. This cathode was also used as an electron source in relative surface potential (relative work-function) measurements. See Fig. 2.

Electron Gun

The electron gun was a 2 element structure mounted on 1 mm diameter, 5 cm long ceramic rods. The cathode was made of the same material as the sample 1.5 mm wide and 3 mm long. Each end was attached to a 20 mil O.D. tantalium tube over a 15 mil tungsten support post. The support posts were attached to 3 coils on the ends of ceramic rods. Current leads attached to the free ends of the support posts. The anode was a 7 mil nicrome V ribbon 3 mm wide and 10 mm long with a 0.5 mm diameter aperture located such that its projection onto the cathode was in the center of the cathode. The anode was mounted on the end of a 5 cm long ceramic rod. The electron gun in a 2.2 KG field supplied by a pair of Helmholtz coils was used to measure the sample work function by measuring sample current as a function of potential difference between sample and gun cathode. (In Fig. 2 the electron gun is shown with an indirectly heated cathode which was later replaced with the directly heated cathode described above.)

Ion Gun

The ion gun is illustrated schematically on the following page.



The energy analyzer was attached to the sample holder such that it could be placed in front of the ion gun on the axis of symmetry and rotated through the ion beam. See Fig. 2.

Ion Gage

The ion gage was an Extractor Gage fully described elsewhere (ref. 2). This gage was selected for its ability to measure oxygen pressure correctly which follows from the experimental verification that it is insensitive to ions desorbed from the grid by electron impact. It also has a low x-ray induced collector current.

Mass Spectrometer

The mass spectrometer (G.E. Model 22PT 12, modified) was mounted on the front flange such that the gas desorbed from

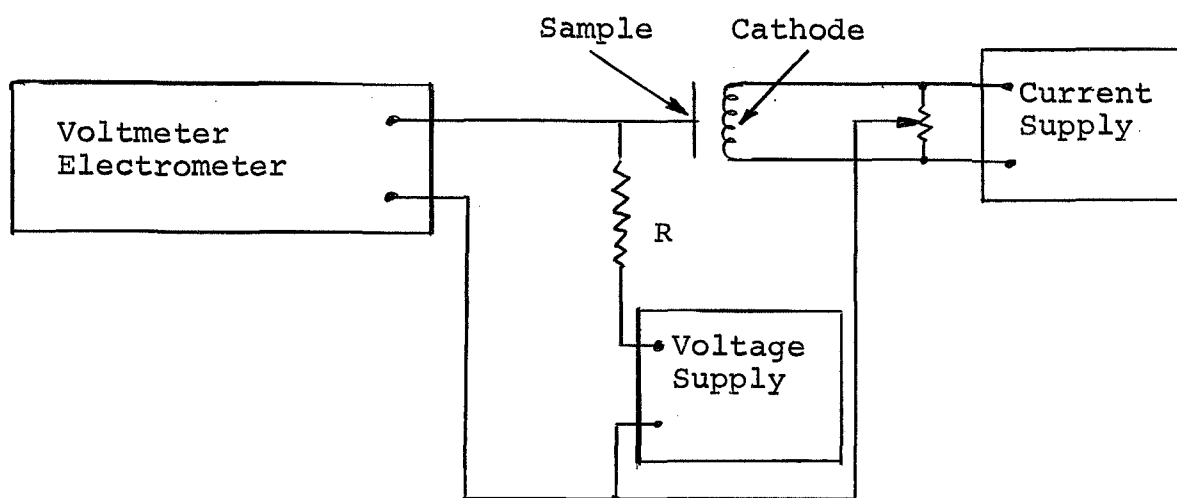
the sample during eb heating could enter the mass spectrometer ion source directly. A precision mounting was provided for the variable field magnet to permit rapid removal and replacement such that returning and realignment were unnecessary.

Oxygen Source

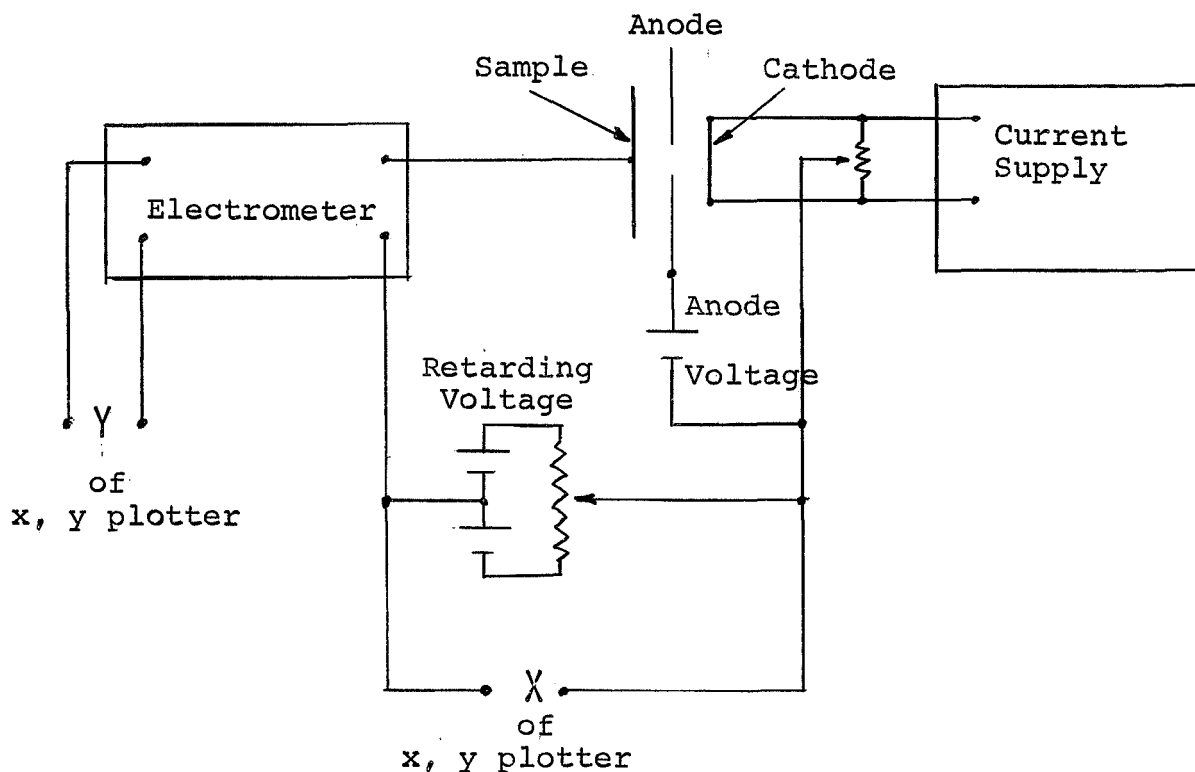
The oxygen source was a molecular beam type. The beam was formed by a close packed array of 22 gold tubes (15 mil ID, 3 mil wall, 2 cm long) in the end of a balast volume which was connected to the oxygen supply valve by a nickel tube. The end of the tube array was located 1 cm away from the sample plane. The array axis passed directly through the mass spectrometer ion source to permit direct calibration of the oxygen beam. The oxygen source was attached to the apparatus support beams such that its axis was orthogonal to the sample plane and the same distance from the axis of rotation as the sample center.

SETUPS AND CALIBRATIONS

A typical setup used for surface potential measurements is illustrated schematically below.



A typical setup used for measuring sample current vs retarding potential characteristics is schematically illustrated below.



The ion gun sensitivity was found to be linear with pressure over the argon pressure interval (10^{-9} , 5×10^{-6}) Torr (the range over which it was evaluated). The optimum electrode voltages were independent of pressure within the above pressure interval. The extracted (sample) ion current was approximately a linear function of electron grid current. Approximately 20% of the cathode emission current was collected by the repeller.

The current density of the extracted ion beam was uniform across the exit aperture as determined by passing the energy analyzer through the ion beam. The exit mask current was approximately 25% of the current collected by the sample. However the exit mask aperture was approximately 1 mm larger than the sample on each side. The total current passing through the mask aperture was not measured but only that fraction of the exit beam collected by the sample. Thus it is estimated that the total beam current was approximately 100% larger than the measured current. The ratio of sample ion current to pressure, evaluated at 5 ma grid current (a typical value), was 0.05 A/Torr over the pressure range 10^{-9} to 5×10^{-6} Torr.

Since the potential within the ionization volume (grid volume) is not only a function of grid potential but also electron density (emission current), the lens voltages for optimum focus should depend on emission current. This was experimentally confirmed.

Several ion energy analyses were made of the exit beam with the energy analyzer located on the ion gun axis of symmetry. Fig. 3 and 4 present the results of ion energy analyses for two sets of ion gun operating parameters (normalized and corrected for secondary electron emission from the suppressor grid and for ion focussing).

It may be seen that the total ion energy spread is less than 20 eV for a grid potential of 300 volts and is about 20 eV for a grid potential of 500 volts. It may also be observed that the potential of the region from which ions were extracted

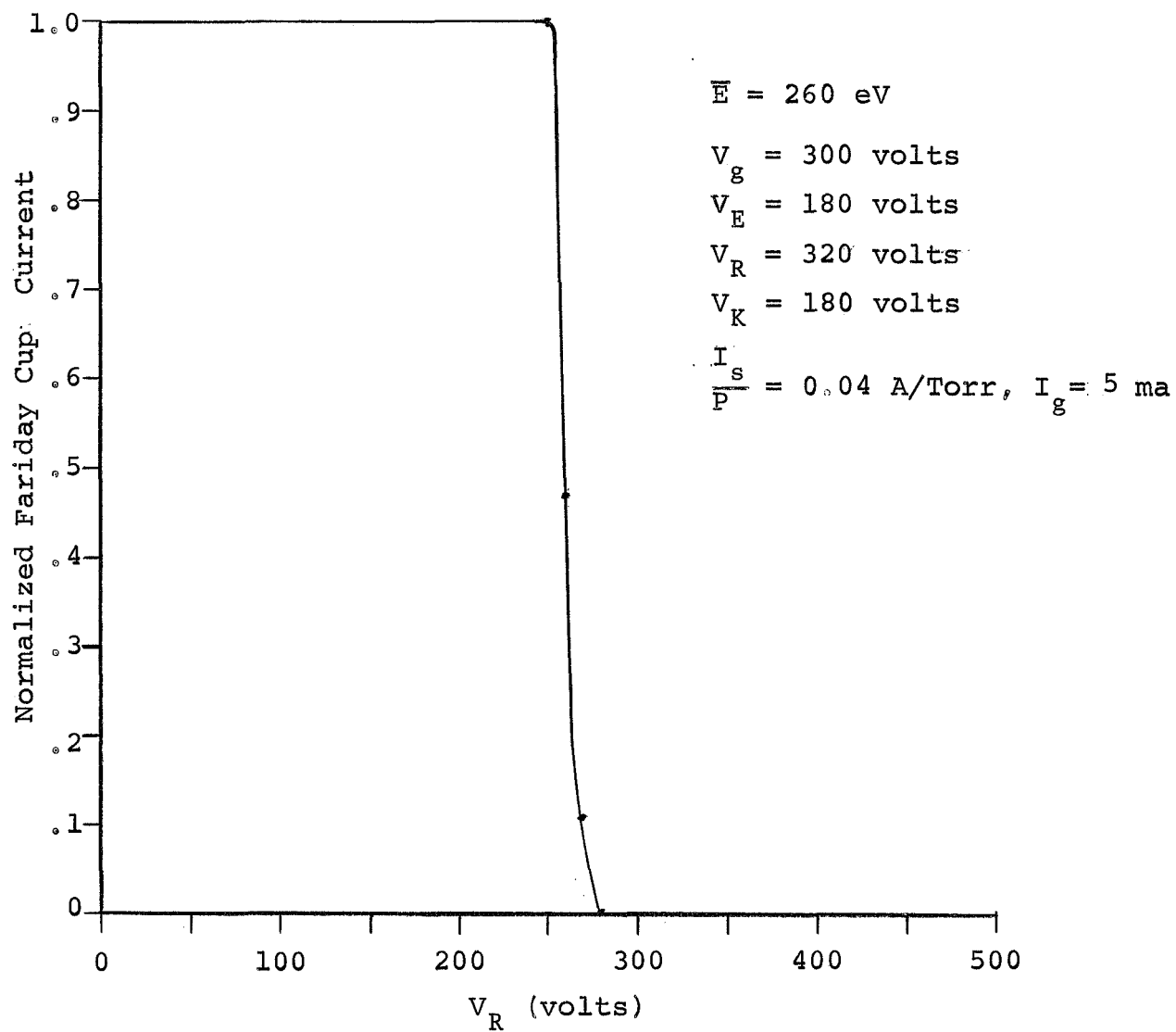


Fig. 3. Ion energy distribution.

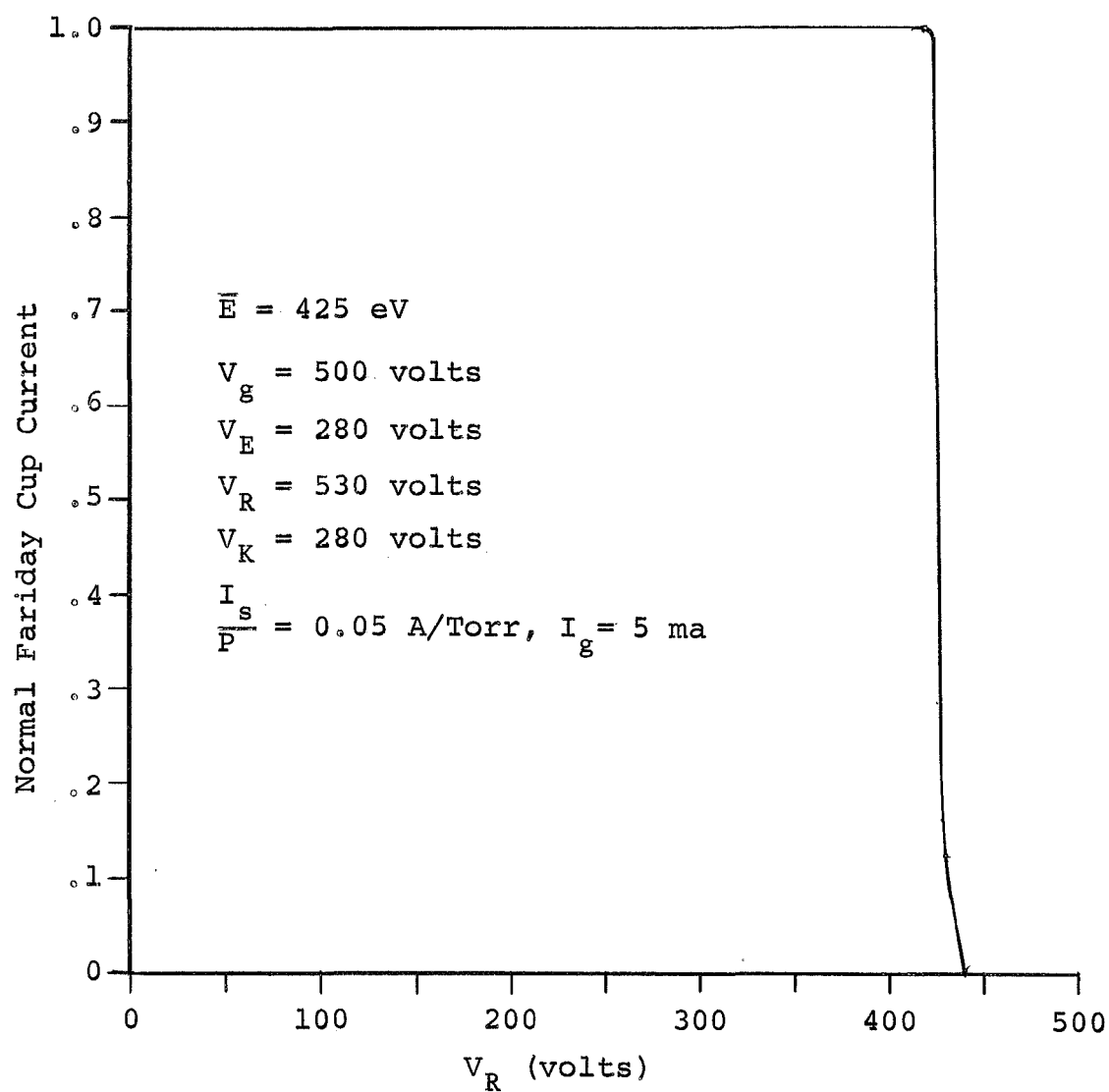


Fig. 4. Ion energy distribution.

is noticeably lower than the grid potential, indicating a non-negligible electronic space charge density in the ionization volume. This implies that the mean ion energy is a function of emission current as well as grid potential. It also requires that the optimum lens voltage ratio be searched out by tuning.

During initial operation, the system pressure varied from 2×10^{-10} Torr to 5×10^{-6} Torr (the highest argon pressure used during ion bombardment). The lowest pressure was obtained during initial operation with the roughing pump and auxiliary pump operating and the main pump turned off. The oxygen source was calibrated by measuring the equilibrium pressure resulting from an arbitrary oxygen flux with only the roughing pump in operation. The conductance between the system and the roughing pump was calculated and then checked experimentally using argon, while simultaneously measuring the pump pressure and system pressure. From the known conductance and pressure the O_2 beam flux was calculated.

Figure 5 gives two views of the apparatus during operation.

PROCEDURE AND RESULTS

The first operation on the sample was to remove the surface of both sides of the sample by argon ion bombardment. Since it was expected that a relatively large amount of adsorbed material remained on the sample surface after system degassing, large ion doses were applied and the relative sur-

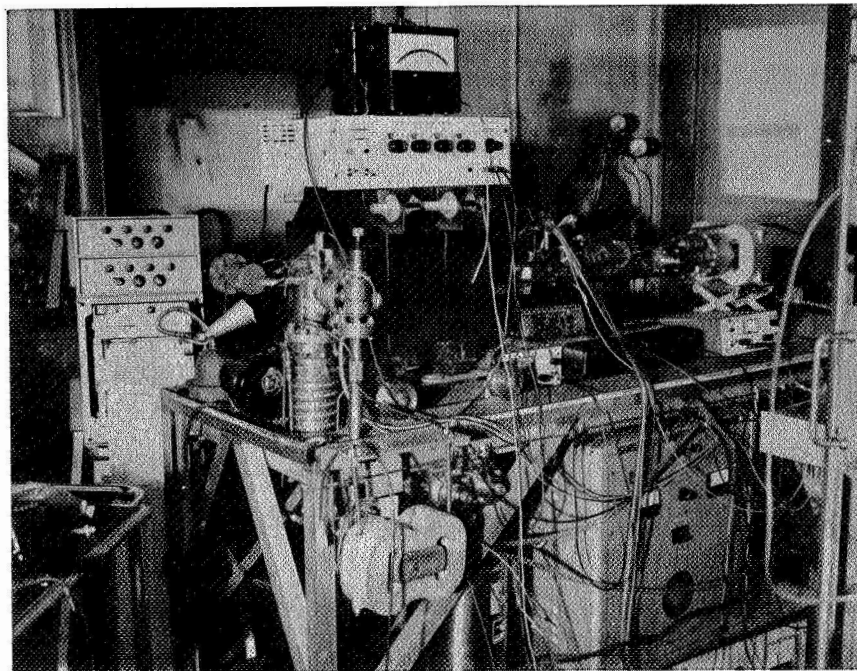
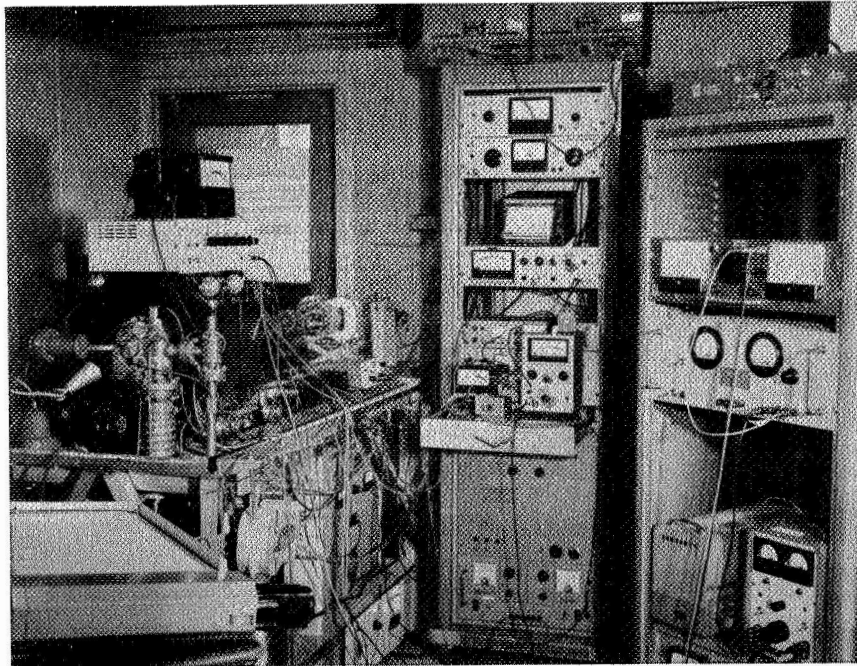


Fig. 5.- System in operation.

face potential was measured after each dose. The ion energy was 425 eV and the angle of incidence (measured from the surface normal) was 30° for the sample front surface and 0° for the sample back surface. The ion dose was determined by measuring the ion beam current collected by the sample (which was maintained at $V = 0$) and the bombardment time. It had been previously determined that the current density across the ion beam was uniform. The results of the first series of ion bombardments are presented in Fig. 6 for the front surface of the sample.

During initial ion bombardment of the sample the slope of the change in surface potential as a function of ion dose approached zero for an ion dose of approximately $60 \times 10^{14} \text{ Ar}^+/\text{cm}^2$ (see Fig. 6). This ion bombardment dose is principally a function of the quantity and type of contamination on the sample surface. Samples of different materials and different histories very probably would require different ion bombardment doses to achieve a constant surface potential. For example, Bradford (Ref. 3) found for a nickle sample, that after an ion dose of about $275 \times 10^{14} \text{ Ar}^+/\text{cm}^2$ no further change occurred in surface potential. His sample had been degassed for 2 hrs at 550°C. The sample used in this work had been degassed many times, each in excess of 10 hrs at temperatures between 400 and 450°C. Another example, which required no ion bombardment to achieve a constant surface potential, is the electron gun cathode which had a history very similar to the sample. It was however given a very sever degassing and cleaning treatment, as described later, before achieving a constant work function.

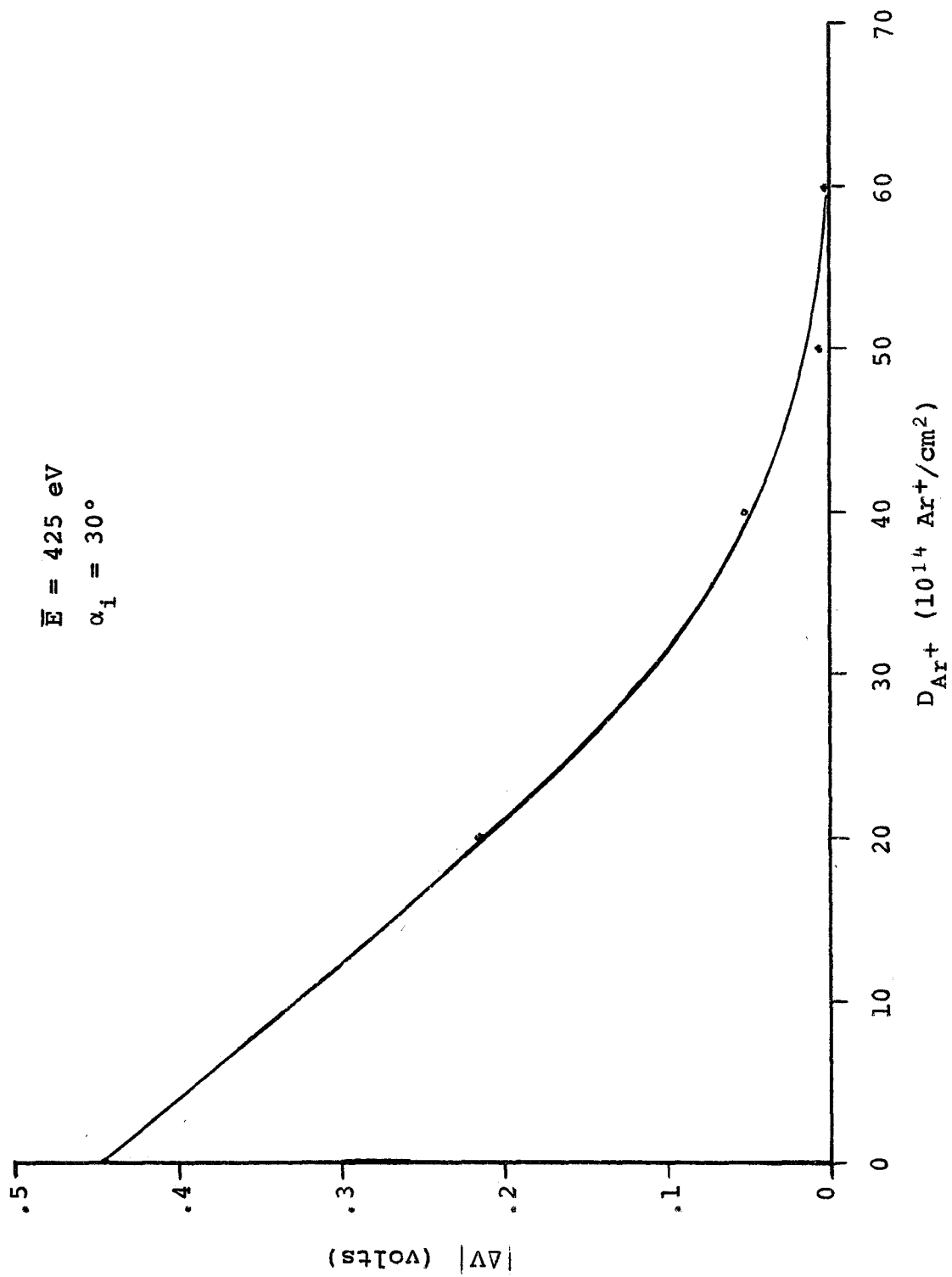


Fig. 6. Initial ion bombardment.

The sample was heated by electron bombardment to 600°C. As the gas desorption rate from the sample decreased the sample temperature was gradually increased until the temperature reached 1000°C. The relative work function was measured frequently during the electron bombardment process. The bombardment was, of course, suspended during work function measurement. Since the accelerating voltage applied to the sample during electron bombardment was of the order of 1000 volts, the constant current source and electrometer used to measure the surface potential were disconnected during electron bombardment to eliminate insulation polarization and thus permit measurement of the surface potential immediately after reconnecting the current source and electrometer.

It was observed during several thermal pulses between 1200°C and 1350°C that the resistance between the sample and ground decreased rapidly at these temperatures. It is suspected that the thin (probably discontinuous) conductive film known to have been deposited on the sample ceramic support rods during the system bake, decreased the effective resistivity of the rods as their temperature increased. This was partially verified by applying a high voltage to the sample (cold) for short time intervals and subsequently measuring the resistance between the sample and ground. The sample-to-ground resistance was increased by several orders of magnitude (to a useable value) using this technique. In all subsequent operations the maximum sample temperature was restricted to 1000°C with only very brief flashes to temperatures above this value.

This restriction substantially reduced the rate at which the bulk material of the sample could be cleaned (which was necessary to assure that during later measurements the surface did not become contaminated by bulk impurities arriving at the surface by diffusion). After a number of ion bombardment-electron bombardment ($T_{\text{max}} = 1000^{\circ}\text{C}$) cycles it became obvious that the cleaning process was indeed slow. During these cleaning cycles the sample work function would sometimes increase as a result of either ion or electron bombardment and at other times the same operation would decrease the relative work function. Electron bombardment occasionally produced no measurable change in surface potential, however ion bombardment always yielded a change in surface potential. The erratic behavior of the relative work function at the end of a cleaning cycle depended not only on the previous temperature-time history of the sample but also on system pressure and which pumps were operating.

To accelerate the cleaning process the sample was maintained at a temperature between 750 and 1000°C for many hours during which time a continuous oxygen flow was admitted to the system and the pumping speed adjusted to maintain a moderately high O_2 pressure within the system. Progress was evaluated by terminating the oxygen flow and pumping the system down, then cooling the sample, and admitting a prescribed oxygen dose to the sample surface. The change in relative work function was observed during the O_2 dose. The sample surface was then ion bombarded. Each ion bombardment was interrupted several times and the sample relative work function measured.

Data from 3 of the above cleaning progress evaluations are presented in Fig. 7. The curves give the decrease in relative work function as a function of accumulated ion dose ($\bar{E} = 425$ eV, $\alpha_i = 0$). The total oxygen dose admitted to the sample surface immediately prior to the ion bombardment results plotted in the bottom curve was that expected to produce a monolayer of adsorbed atomic oxygen. The O_2 dose admitted to the sample surface prior to the ion bombardment plotted in each of the other two curves was somewhat larger than that expected to produce a monolayer. The total change in relative work function decreases slightly as the quantity of adsorbed oxygen increases (variation in the opposite direction was anticipated). This may result from different surface conditions prior to O_2 adsorption or differences in the time intervals between O_2 adsorption and ion bombardment or from differences in sample temperature immediately prior to ion bombardment. The final surface potentials resulting from the 3 series of ion bombardments shown (taken at different times in the cleaning process) are approximately equal (the zero reference is arbitrary but consistent for these 3 curves). The above results imply that the relative work function of the sample surface had stabilized and considering the technique used to produce this stability, that the surface was probably bare tungsten at least immediately after either electron bombardment or ion bombardment. The data in Fig. 7 imply that the ion bombardment removal of an adsorbed layer of oxygen requires an accumulated ion dose which corresponds to something between 2 and 3 ions incident on each adsorption site (statistically). This result appears to be consistent with other data.

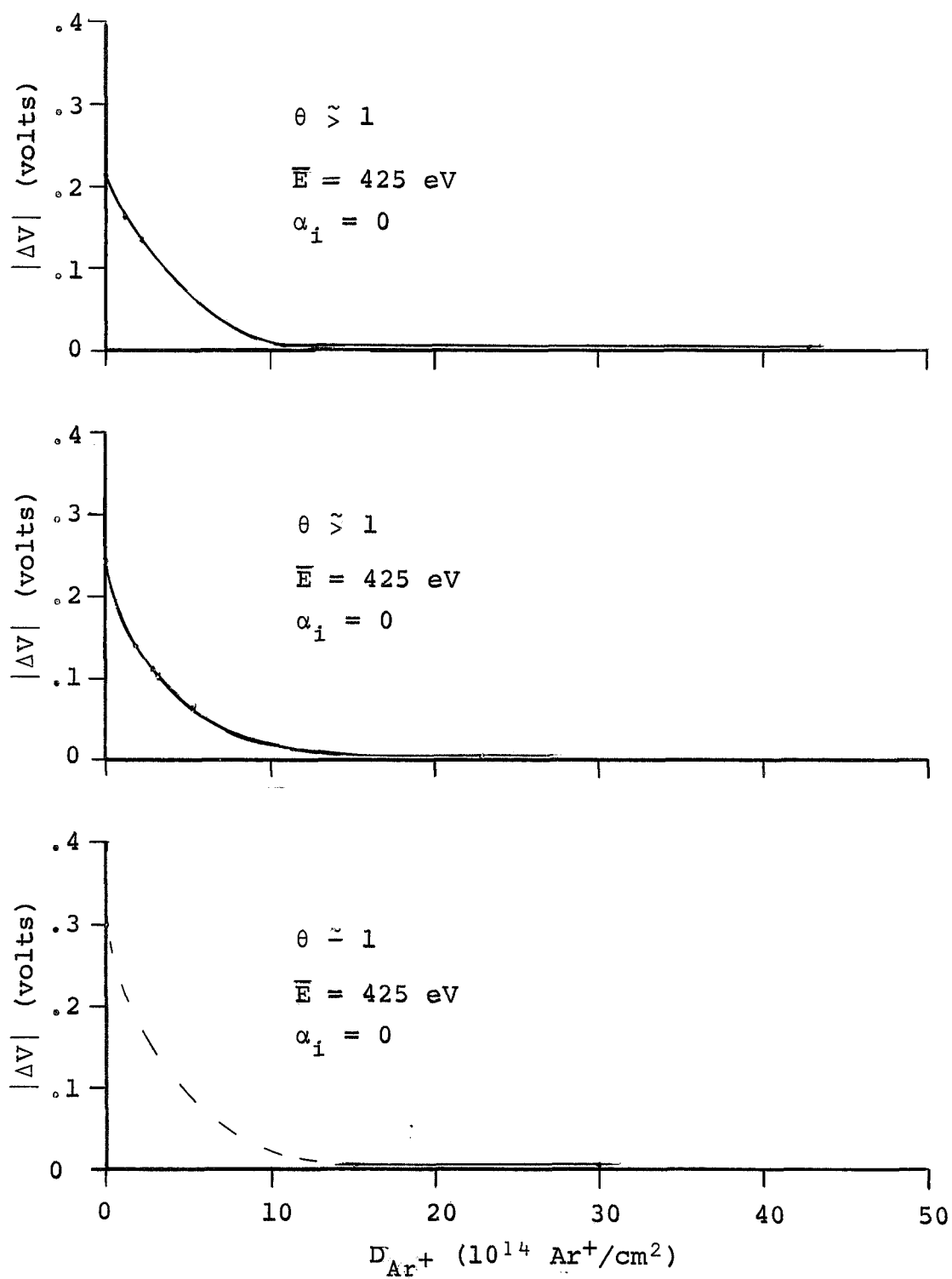


Fig. 7. Ion bombardment after O_2 adsorption.

While conducting other operations in the system which caused the system pressure to increase to about 5×10^{-8} Torr, the sample remained idle for about 9 hrs. During this time it adsorbed gas from the various species within the system. The sample surface was recleaned by heating the sample to about 850°C and relative work function measurements were made during the process. The results are presented in Fig. 8. The sample surface potential increased with heating time finally arriving at a constant value. Between heating pulses the relative work function was independent of time. The peak amplitude of the gas pulse observed in the system as a result of a sample heating pulse, decreased with the number of heating pulses. Just before the relative work function reached a constant, stable value the peak amplitude of the system gas pulse was a few times 10^{-11} Torr and lasted for only a few seconds. It disappeared completely after the surface potential became constant. From Fig. 8 it is clear that the last two heating pulses produced no further change in surface potential and a subsequent ion bombardment produced no further change in the surface potential.

The change in relative work function produced by oxygen adsorption and removal by radiation heating the sample was investigated. Representative results are presented in Fig. 9. A constant O_2 flux was admitted to the sample and the surface potential measured frequently. The bottom curve in Fig. 9 gives the accumulated O_2 dose as a function of time and the top curve gives the sample surface potential as a function of time. After 725 sec the O_2 flux was turned off and the sample temperature

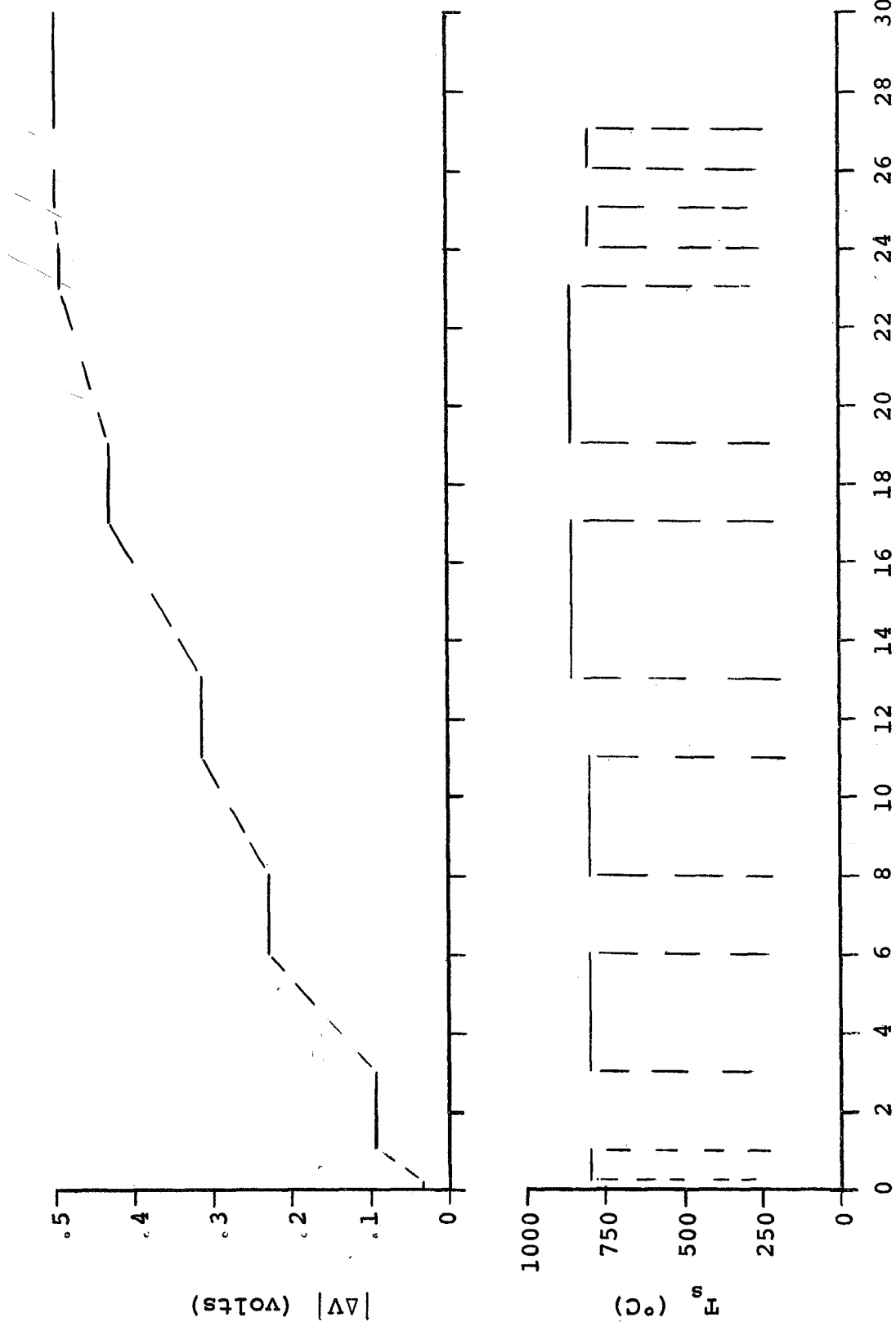


Fig. 8 Adsorbed gas removed by radiation heating.

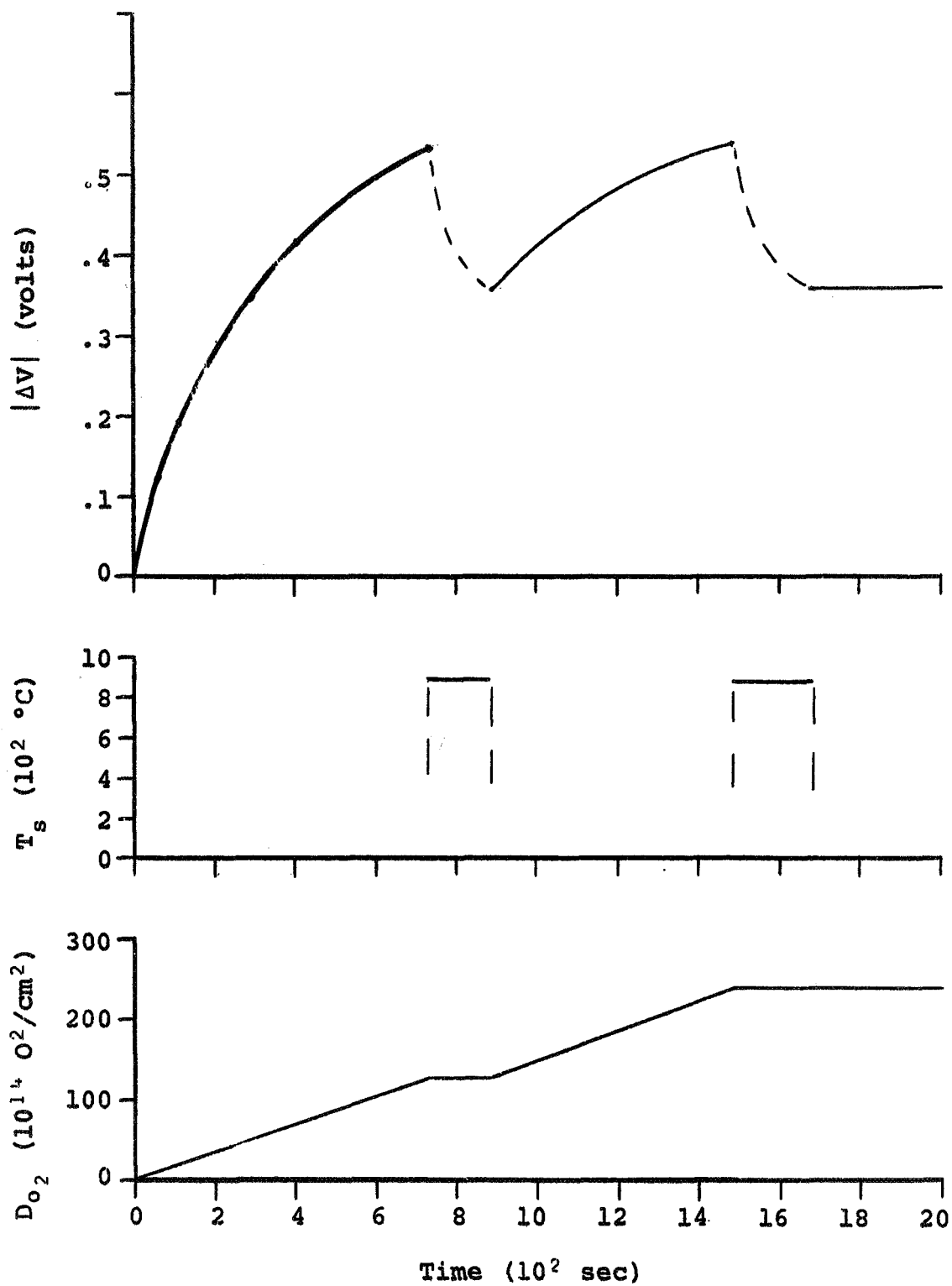


Fig. 9. Oxygen removal by heating

increased to approximately 900°C. Since the sample heat mass was very small, the warm-up time was negligible. While the sample was hot a fraction of the O₂ previously adsorbed was desorbed from the sample surface. The desorbed O₂ was observed as a sharp pressure pulse lasting only for a few seconds. This implies that substantially all the O₂ removed from the sample surface was removed in the first few seconds of the heating interval and that the relative O₂ coverage remained approximately constant for the remainder of the heating interval. The sample surface potential was measured immediately following cool down (a few seconds) and the O₂ flux was again turned on. The results for 2 cycles of this procedure are given in Fig. 9 to show the repeatability of each operation involved. It may be observed that the adsorbed O₂ was not completely removed after 150 sec. at about 900°C and that repetition of the heating cycle for 200 sec did not reduce the fraction of the adsorbed O₂ which remained on the surface after cool down. It was consistently found that adsorbed oxygen could not be completely removed from the sample surface by radiation heating alone (consistent with the maximum sample temperature limitation discussed previously).

Adsorbed oxygen removal by electron bombardment was investigated by admitting a small O₂ dose onto the sample surface, the relative work function was measured, the surface was electron bombarded for a short time interval, and the relative work function was again measured. Representative data are presented in Fig. 10. The current density used during electron

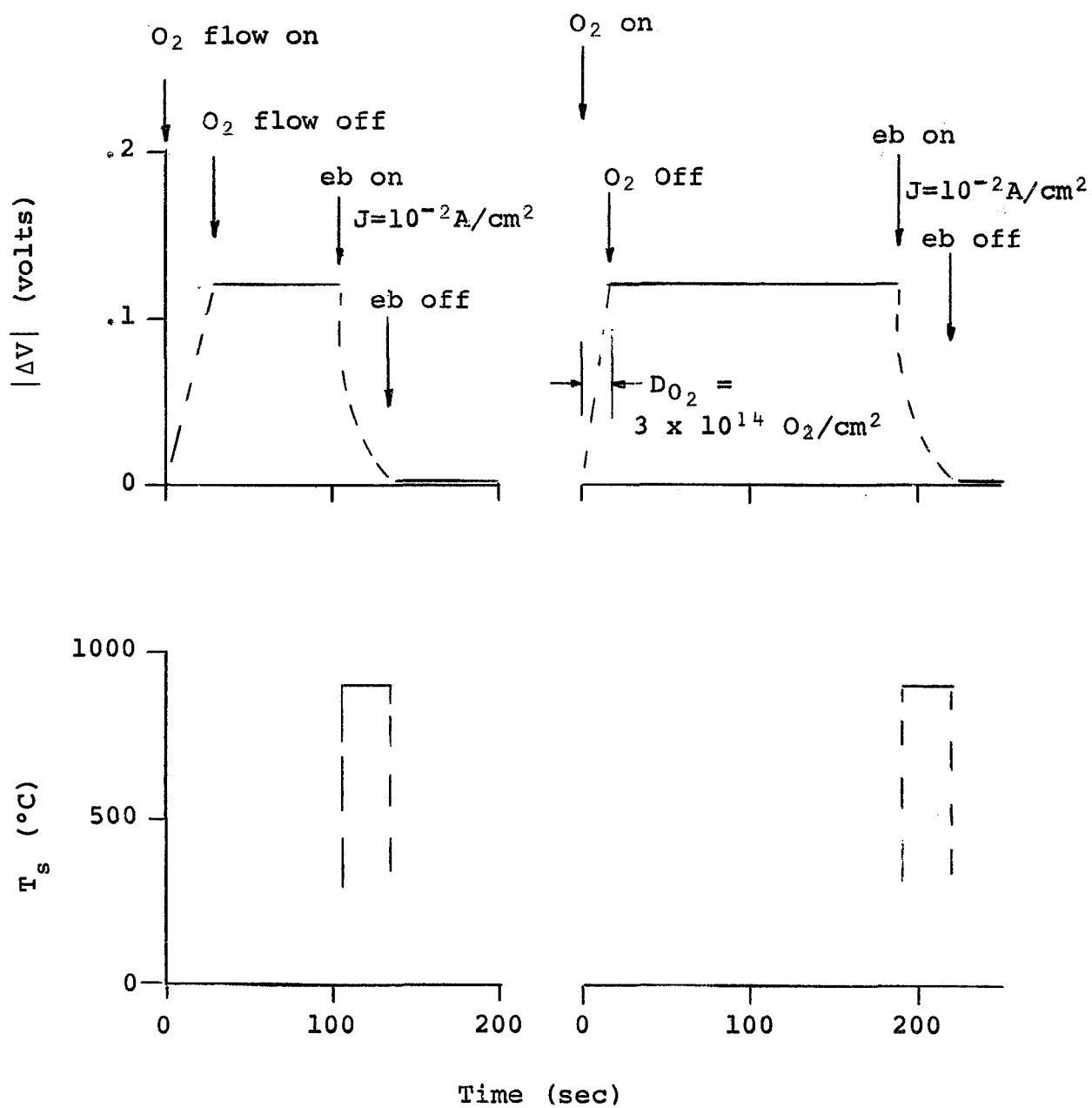


Fig. 10. Oxygen removal by electron bombardment.

bombardment was $J = 10^{-2}$ A/cm² and the accelerating voltage applied to the sample was adjusted such that the sample temperature was the same as that used during radiation heating only. The electron bombardment interval was 30 sec. The accumulated O₂ dose incident upon the sample surface was $D_{O_2} \approx 3 \times 10^{14}$ O₂/cm², which corresponds to $\theta \approx .15$ (for adsorbed oxygen atoms). The adsorbed oxygen was observed as a sharp pressure pulse lasting only for a few seconds.

The data presented in Fig. 10 indicates that an oxygen coverage $\theta \approx 0.15$ was removed by the combined effects of sample heating and electron impact desorption during electron bombardment with a current density of approximately 10^{-2} A/cm² in 30 sec. Supposing that all the oxygen was removed by electron impact desorption (a conservative assumption for a sample temperature of approximately 1175°K) as atomic oxygen, the rate of change of surface coverage may be written

$$-\frac{d\theta}{dt} = \frac{Jg\theta}{e} ,$$

where g is the number of oxygen atoms removed per electron and θ is the relative coverage. Integrating this equation gives

$$\theta(t_b)/\theta(0) = -\frac{t_b}{\tau} ,$$

where t_b is the electron bombardment time and $\tau = \frac{\sigma_o e}{J - g}$, where

σ_o is the number of surface sites per cm^2 . For $\theta(t_b)/\theta(o) = 0.1$ (a final coverage of 1.5% after 30 sec, for the present example), it follows that

$$g = 2.3 \frac{\sigma_o e}{J - t_b}$$

Using the data given in Fig. 10 and taking $\sigma_o = 5 \times 10^{14} \text{ cm}^{-2}$ gives $g = 6.1 \times 10^{-4}$ oxygen atoms removed per incident electron at $T_s \approx 1175^\circ\text{K}$. Values of $g = 6.5 \times 10^{-4}$ o/e have been measured for the O_2 , Mo system at about room temperature (ref. 4). Since the above calculation neglects the oxygen thermally desorbed during the bombardment interval, the actual value of g is probably smaller than the value calculated above.

Oxygen removal from the sample surface by ion bombardment was investigated under a number of conditions. The procedure used was as follows: A reference geometrical and electrical configuration was setup for which the stable (clean), relative work function of the sample surface had been established by measurements taken after many ion and electron bombardments. The sample surface potential was measured and compared to this expected value. If the measured value clearly differed from the expected value the sample surface was recleaned by ion bombardment or electron bombardment or both. Frequently, several short electron bombardments were sufficient to recover

the expected relative surface potential. This procedure was preferred since pumpdown following an argon bombardment was a slow process. A prescribed oxygen dose was applied to the sample. During application of some of the oxygen doses a different geometrical and electrical configuration was used which permitted continuous measurement of the relative surface potential, at other times, to satisfy other requirements, a configuration was used which did not allow continuous measurement of the surface potential. Since the numerical values of the relative work function differ with different configurations, quantitative comparison of different data sets is sometimes not possible, although qualitative comparison is always valid. After a prescribed O_2 dose had been applied the O_2 flow was abruptly terminated, the surface potential measured, and the sample immediately moved to a neutral location. The argon flow was turned on, the roughing pump valved off (to prevent saturation with argon), and the ion gun was turned on. The argon flow and the speed of the main pump were adjusted to obtain the desired beam current, which was determined by measuring the exit mask current. This procedure was preferred over adjustment of the beam current by adjusting the gun grid current, since the energy distribution of the ion beam was known to be a function of electron current to the grid (for a fixed set of electrode potentials). The sample was then moved in front of the ion gun and centered in the beam. After bombarding the sample with a prescribed ion dose, the ion gun was turned off (argon flow remained on) and the sample was moved in front of the reference cathode. After measurement of the

surface potential the sample was moved to a neutral position, the ion gun turned on again, and the sample centered in the ion beam. This procedure was continued until the surface potential returned to the expected value.

Figure 11 presents the variation of relative work function with argon ion bombardment dose for a sample surface initially at a low relative oxygen coverage. The total oxygen dose admitted to the surface was $D_{O_2} = 7.2 \times 10^{14} \text{ O}_2/\text{cm}^2$ which is estimated to yield a relative coverage of approximately $\theta \approx 0.36$. The relative coverage θ , is calculated from a measured oxygen dose based on published results for the surface total capture cross section (sticking probability) (ref. 1). It is assumed that dissociation accompanies adsorption. Data presented later on, tend to validate this procedure and confirm Beckers results. The ion beam was incident at an angle $\alpha_1 = 0$ (parallel to the surface normal) and the mean ion energy was $\bar{E} = 425 \text{ eV}$. The surface potential had returned to the value measured prior to the oxygen dose after an argon ion dose $D_{Ar^+} = 3.25 \times 10^{14} \text{ Ar}^+/\text{cm}^2$. The ion dose required to reduce the change in surface potential associated with oxygen adsorption, by a factor e^{-1} is $.62 \times 10^{14} \text{ Ar}^+/\text{cm}^2$. If the surface potential is taken as a linear function of surface coverage (at this low coverage), then θ is reduced by the same factor e^{-1} . The number of oxygen atoms/ cm^2 removed by the above ion dose is then $\theta(1-e^{-1}) \sigma_0$, where σ_0 is the number of surface sites available per cm^2 . The mean sputtering yield (averaged over the same interval) is $1.8 \text{ O}/\text{Ar}^+$.

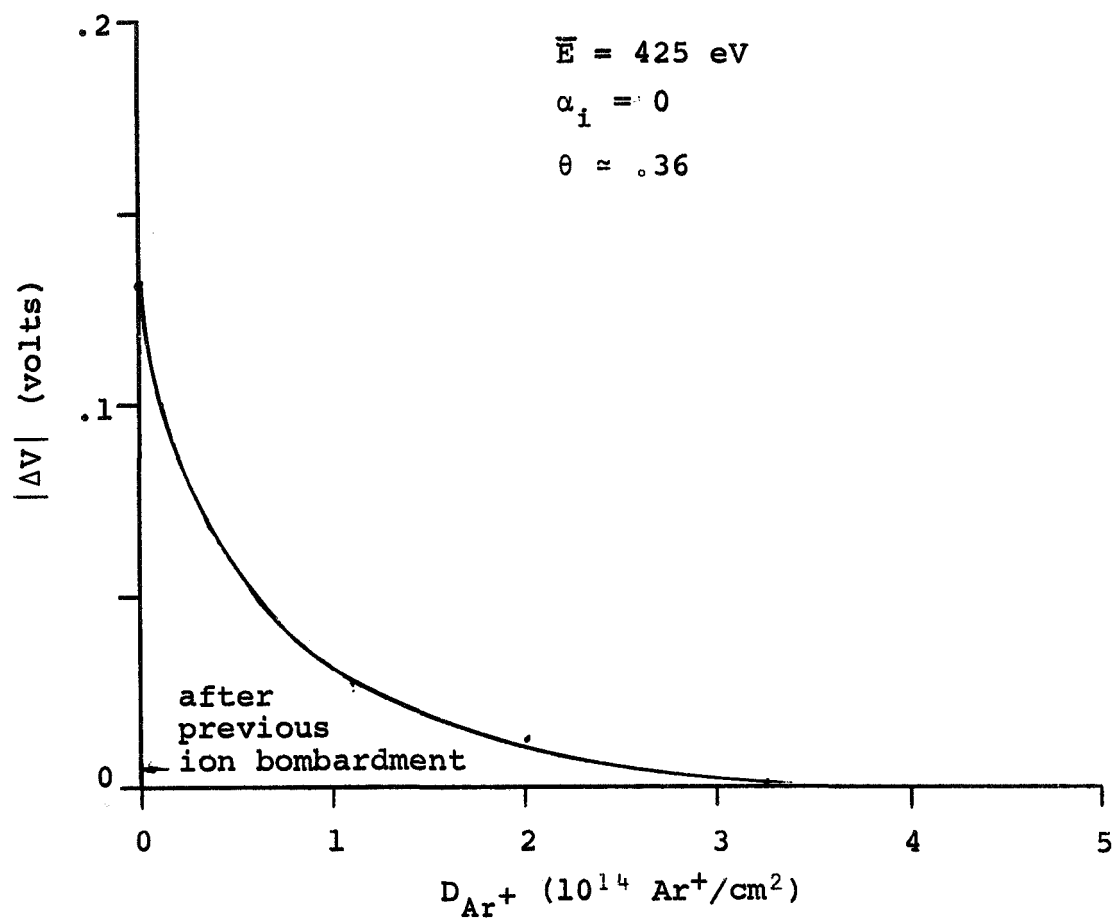


Fig. 11. Oxygen removal by ion bombardment.

Figure 12 presents the results of a similar series of measurements except that the oxygen dose was $D_{O_2} = 12.6 \times 10^{14} \text{ O}_2/\text{cm}^2$. It is estimated that the resulting relative coverage was $\theta = .62$. The ion dose required to reduce the oxygen associated potential change by a factor e^{-1} was $2.3 \times 10^{-14} \text{ Ar}^+/\text{cm}^2$ and the number of oxygen atoms/ cm^2 removed (assuming linearity between ΔV and θ) was $1.96 \times 10^{14} \text{ O}/\text{cm}^2$. This gives a mean yield of $.85 \text{ O}/\text{Ar}^+$.

Figure 13 presents the results of a similar series of measurements except that the surface coverage was approximately $\theta \approx 1.5$. It may be observed by comparing the results in Figs. 11 through 13 that the ion dose required to remove adsorbed oxygen is not a linear function of coverage but that the dose required to clean the surface increases faster than the coverage increases.

Figure 14 presents the relative work function variation with ion bombardment dose for an ion beam angle of incidence $\alpha_i = 45^\circ$ and a mean ion energy $\bar{E} = 425 \text{ eV}$. An oxygen dose corresponding to $\theta = 2$ had been previously applied in one continuous dose with the sample maintained at 20°C . The sample had been electron bombarded ($J = 10^{-2} \text{ A}/\text{cm}^2$ and $T_s = 1000^\circ\text{C}$) immediately prior to oxygen adsorption. Comparing Figs. 13 and 14 it may be observed that for $\alpha_i = 45^\circ$ the ion bombardment dose required to remove the adsorbed oxygen is smaller than that required to remove the adsorbed oxygen for $\alpha_i = 0$, even though in the latter case the initial coverage was lower. This implies that the adsorbed oxygen removal rate increases

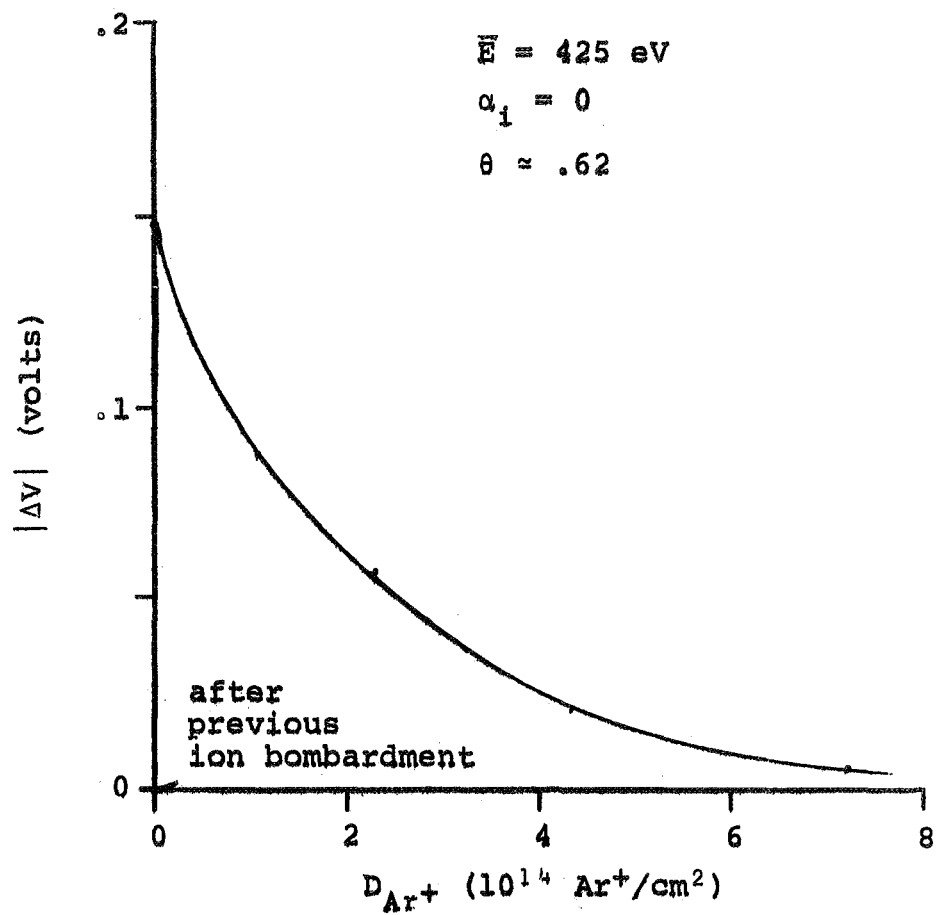


Fig. 12. Oxygen removal by ion bombardment.

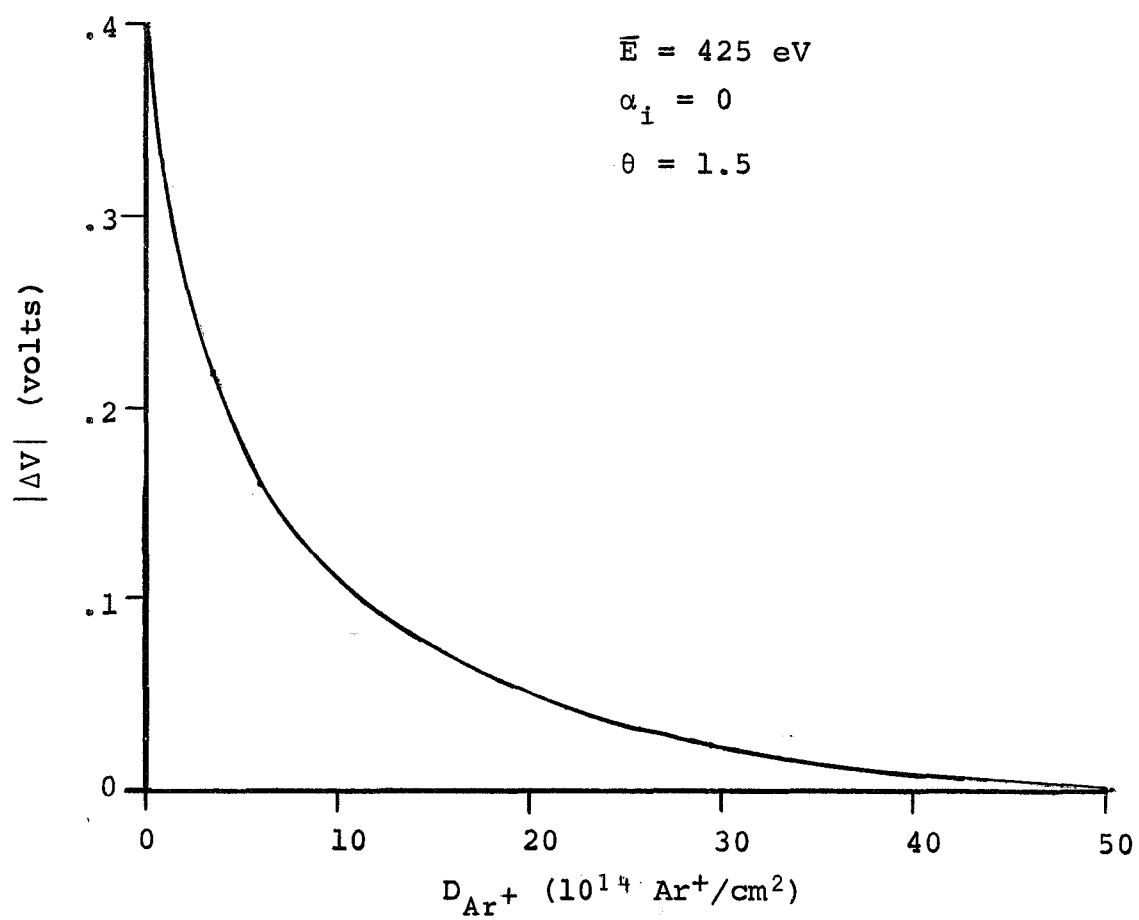


Fig. 13. Oxygen removal by ion bombardment.

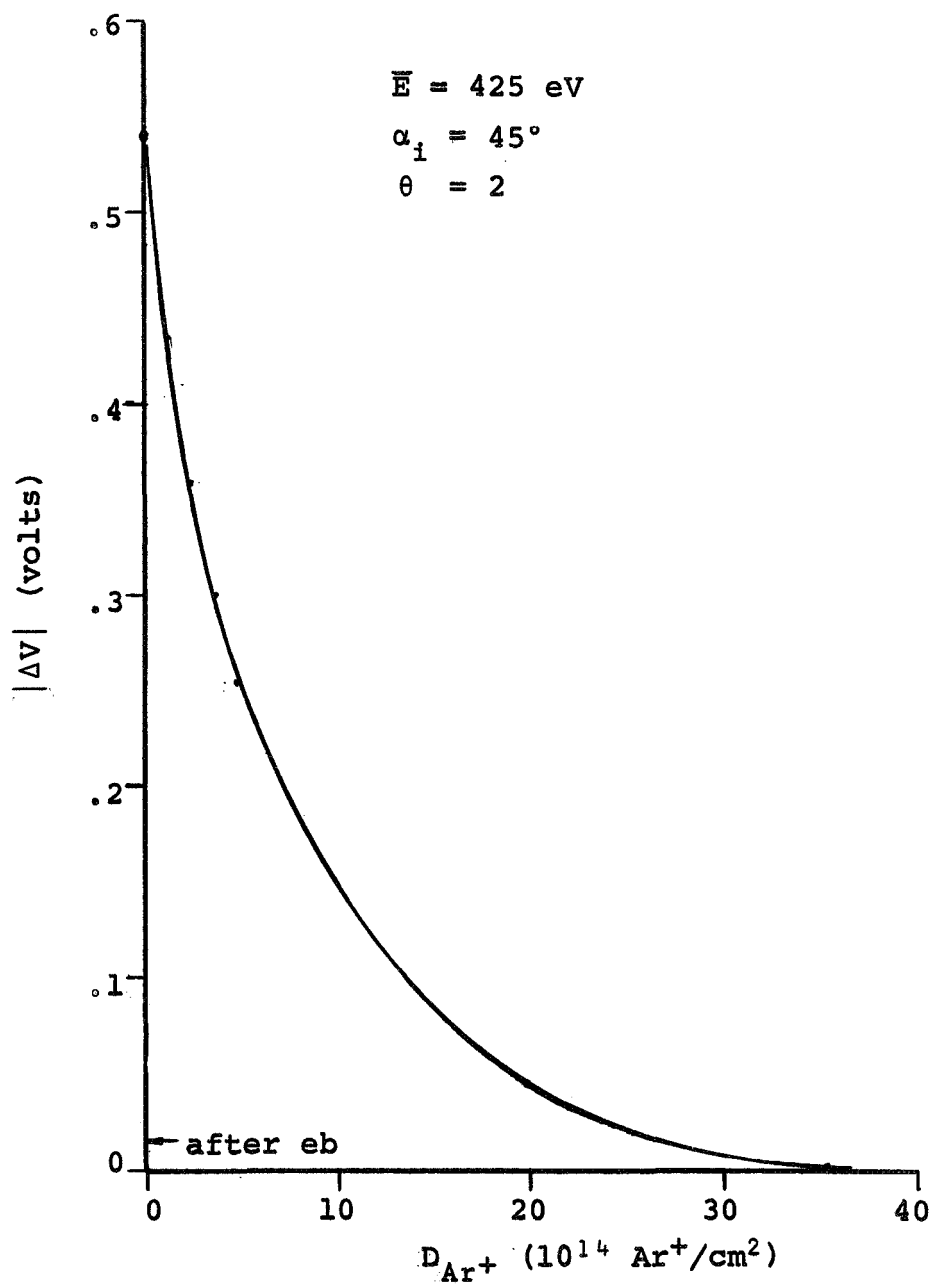


Fig. 14. Oxygen removal by ion bombardment.

with ion angle of incidence. (Sputtering tungsten atoms from a bare surface would not be expected to show this dependance an angle of incidence for ion energies in the neighborhood of 400 eV, see ref. 8.)

Figure 15 presents data on the variation of relative surface potential with oxygen dose admitted to the sample surface. The surface had been previously electron bombarded and then ion bombarded. The oxygen was admitted to the sample in increasing increments beginning with a dose which corresponded to $\theta < 0.05$. The surface potential was measured before each increment. Attention was given to maintaining all other variable parameters fixed during the entire dose. The curve drawn through the data points, although a good fit, is somewhat idealized. The changes in slope are probably not as abrupt as shown. The change in slope at point A is interpreted to imply that the sample surface has been covered with an atomic layer of oxygen, $\theta = 1$. The change in slope at point B is interpreted to imply that the surface coverage has arrived at $\theta = 2$. (If dissociation did not accompany adsorption this would correspond to one oxygen molecule per surface site.) Beyond point B no measurable change occurred in the relative surface potential until the surface was ion bombarded about 25 min. later. The oxygen flux incident upon the sample was maintained constant for about 1/3 of the above interval. The above data imply that the surface capture cross section for oxygen (sticking probability) is 0.139 below 1 atomic layer.

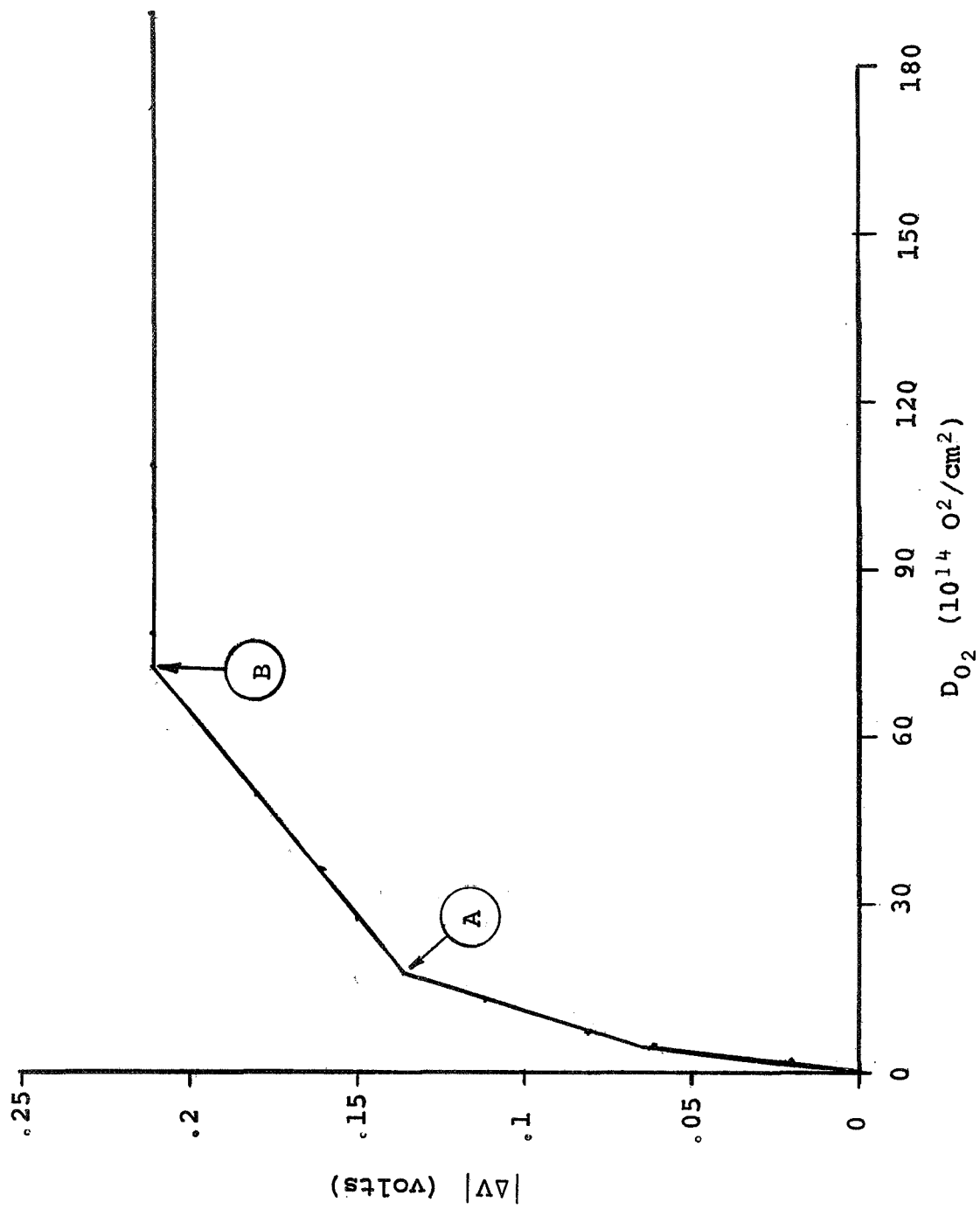


Fig. 15. Oxygen deposition.

and is 4.5×10^{-2} between 1 and 2 atomic layers (based on 5×10^{14} sites/cm²). Deviations between the above data and previously published results (ref. 1) are everywhere less than 10%.

Occasionally the change in relative work function was continuously observed during admission of oxygen to the sample. Although the setup was modified during such observations, certain semiquantitative conclusions may be drawn from the observations. As the oxygen flux was turned on, the relative surface potential was observed to begin changing at about the same time that the ion gauge began to indicate a pressure rise. From an estimate of the oxygen dose during these transient operations and the very short delay time involved, it was estimated that the relative surface potential had begun to change by the time the oxygen coverage had reached about 1/2%.

Figure 16 presents the variation in relative surface potential with ion bombardment dose during the removal of the oxygen dose discussed above. The mean ion energy during this bombardment was $\bar{E} = 260$ eV and the angle of incidence was $\alpha_1 = 0$. The argon ion dose required to remove the adsorbed oxygen is about the same as that required at $\bar{E} = 425$ eV and $\alpha_1 = 45^\circ$. It may be observed that a given oxygen coverage does not always yield the same change in surface potential. Part of this variation results from differences in sample temperature either during oxygen adsorption or during the relative surface potential measurements. However part of the variation probably results from operating too near the knee of the diode I, V characteristic. The operating point used was not always the same.

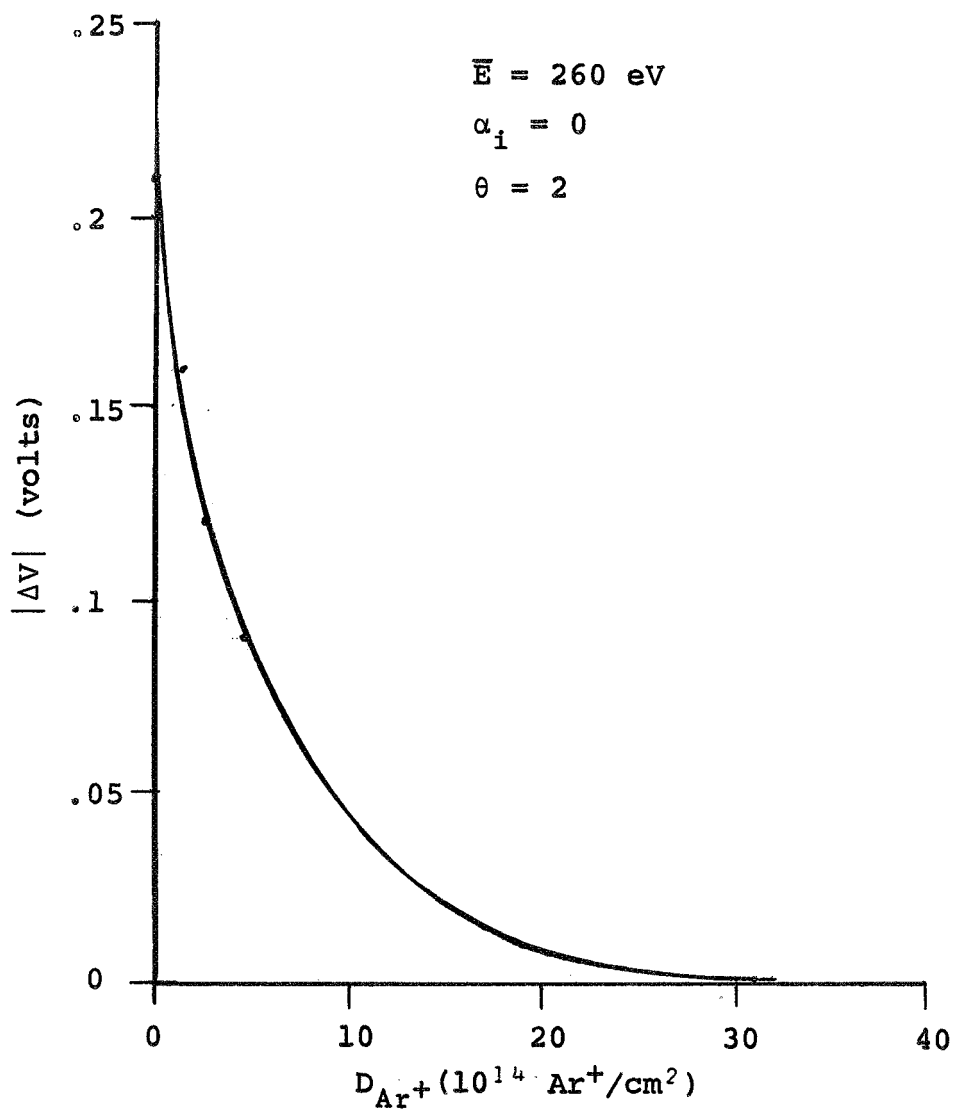


Fig. 16 Oxygen removal by ion bombardment.

The value chosen for the constant current source was generally not the value desired but rather a value which was sufficiently large that the sample leakage to ground did not introduce substantial errors in surface potential. It may be that in some cases the magnitude of the constant current source used was sufficiently large that the operating point was driven up near the knee of the I, V characteristic. If so this could introduce substantial errors in the relative surface potential measurements. Such errors would not however, invalidate the qualitative content of any of the results by only the numerical magnitude of the measurements.

Changes in work function of the sample surface were measured using the retarding field technique with an electron gun as the electron source and the sample as the target. These measurements were conducted with the apparatus in a 2.2 KG axial magnetic field. The cathode was cleaned by maintaining it at about 2000°C for long time intervals. During part of these clean-up operations, while the cathode was hot, a pure oxygen flux was admitted to the system. At the end of the cleaning process the cathode temperature could be raised from room temperature to operating temperature without producing a measurable gas pulse within the system. The gun anode was cleaned by electron bombardment. During work function measurements the anode current used was within the range (10^{-7} , 5×10^{-6}) amp. and the anode accelerating voltage was within the range (20, 100) volts. The sample was maintained at electrometer input potential and the measured voltage between cathode and ground was corrected for the electrometer input potential.

Figures 17 and 18 present typical results obtained using the above technique. Figure 17 gives the change in sample work function resulting from a few seconds of electron bombardment at about 1000°C (during sample cleaning). After the sample was clean the left curve in Fig. 18 was measured after admitting to the sample surface an oxygen dose corresponding to $\theta \approx 2$. During application of the oxygen dose it was discovered that the oxygen supply pressure was low. Thus the coverage is not known exactly. However neglecting this temporary reduction in flux the coverage could not have been greater than 2. The sample was then electron bombarded for a few seconds ($J = 10^{-2}$ A/cm² and $T_s \approx 1000^\circ\text{C}$) and the work function again measured. The results are given in the right curve of Fig. 18. It may be observed (from the change in target work function) that the one short electron bombardment has removed a substantial fraction of the adsorbed oxygen.

DISCUSSION OF RESULTS

It was generally found that sample conditions, sample processing and experimental measurements were quite repeatable. There is little doubt that the sample surface was frequently bare tungsten and independent of the level of contamination at any given time, could be returned to that condition in a relatively short interval using straight forward techniques. It is also clear that if the surface were contaminated this condition could be detected with reliability.

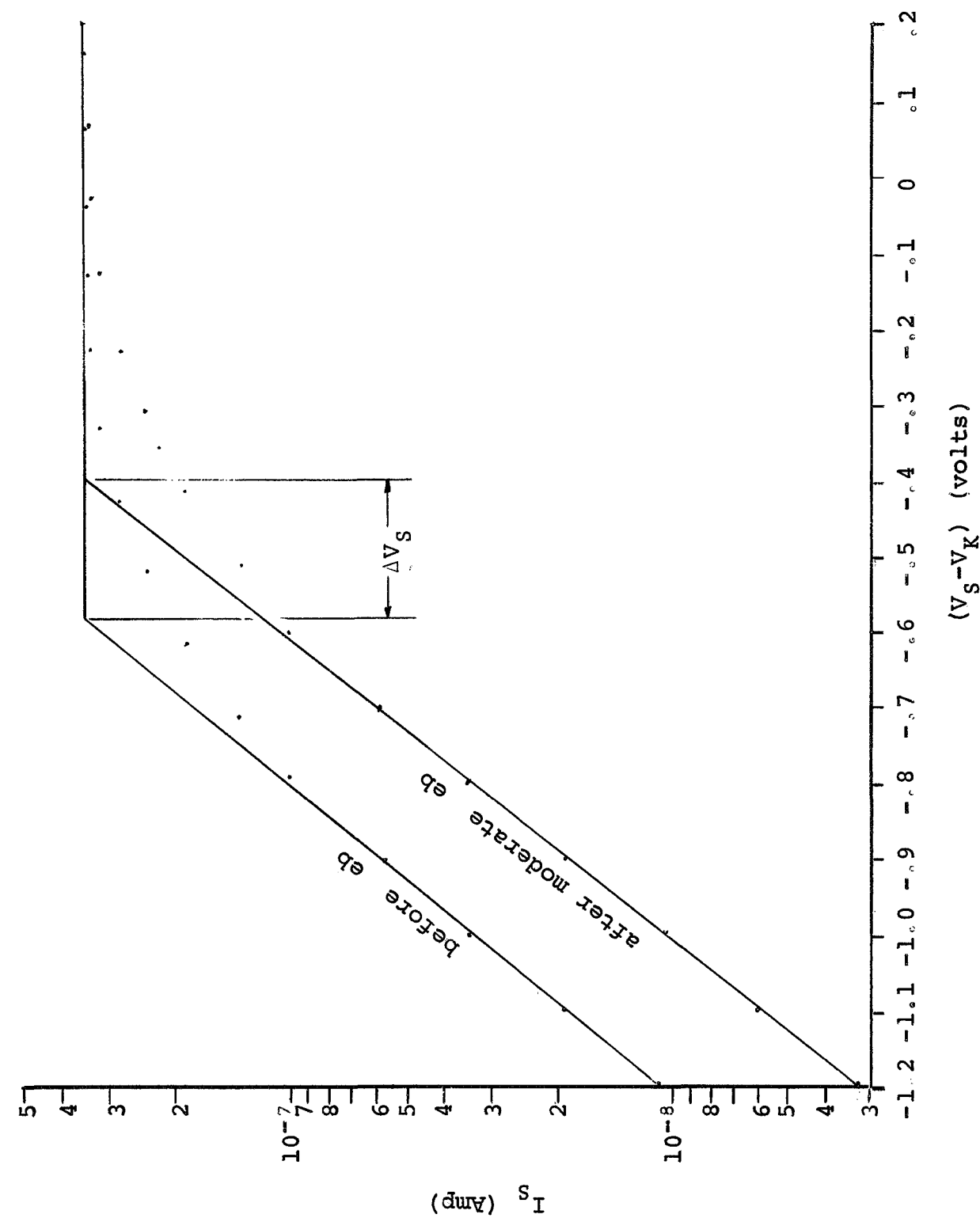


Fig. 17. Retarding potential characteristic.

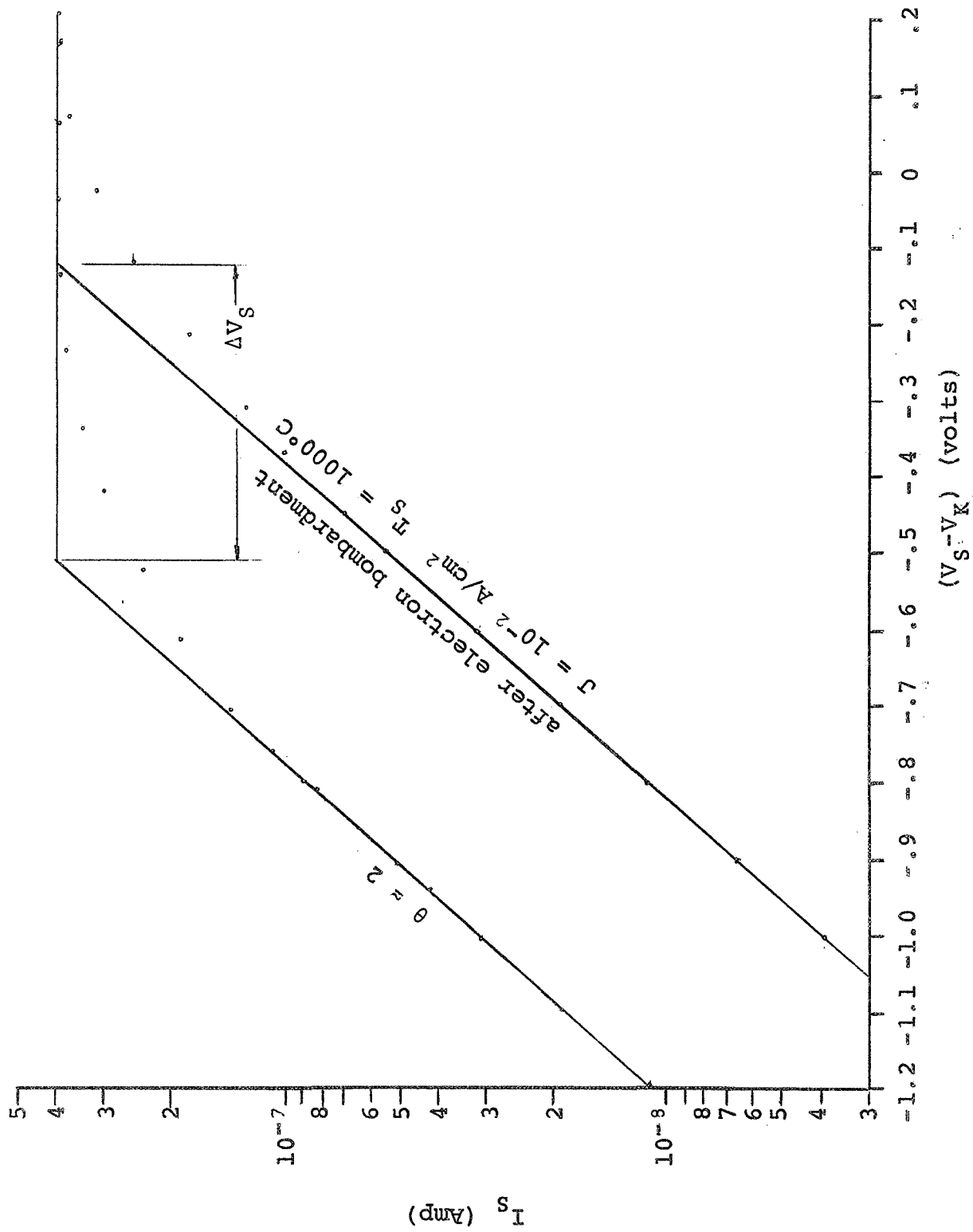


Fig. 18. Retarding potential characteristic.

Even without the service of the mass spectrometer, it was quite clear that a prescribed oxygen coverage could be applied to the sample surface and that the ion bombardment dose or the electron bombardment parameters required to remove it could be predicted.

By exercising careful control over internal operations, the pumps in operation, and the system pressure it was routinely found that the sample work function could be maintained independent of time for a clean surface or a partly covered surface for sample temperatures within the range 20° to 750°C . For example the surface potential was continuously monitored immediately after an ion bombardment cleaning for something in excess of 2 hrs., during which the drift in surface potential was less than 0.015 volts. This time is very large compared to the usual time interval between measurements. It is therefore concluded that the observed changes in relative surface potential are principally associated with the operations performed on the sample.

It was generally found that the total ion bombardment dose required to remove an oxygen relative coverage θ , increased faster than θ , however the initial relative removal rate for an oxygen coverage θ appears to be nearly independent of θ . There does not appear to be a strong dependance between removal rate and ion energy within the energy interval used (250, 500) eV. It does appear that the removal rate increases with angle of incidence. The removal rate was not observed to depend on the ion bombardment flux density over the interval used (10^{11} , 2×10^{13}) $\text{Ar}^+/\text{cm}^2\text{sec}$ but rather only on its time integral (dose).

The maximum ion energy used in this work did not exceed 500 eV. This was done to minimize the quantity of inert gas buried (ref. 5) in the sample and thus minimize the change in work function induced by lattice distortion. It is suspected that the minimum ion energy required to efficiently remove adsorbed oxygen from the surface is substantially lower than the lowest ion energy used in this work. Sputtering yields are found to be a very strong function of ion energy only below about 150 eV for a number of metals (ref 6) and thresholds as low as 8 eV have been measured for nickel (ref. 7). It is therefore expected that an adsorbed surface layer having a binding energy somewhat lower than the atoms of the substrate, could be efficiently removed by ions having energies of the order of 100 eV or perhaps less. Argon ion beams in this energy range have the advantage that less than 0.1% of the incident ions are trapped in the sample surface (ref. 5).

Electron bombardment was also found to be an effective cleaning method but of course, involves relatively high sample temperatures. Radiation and resistance heating alone were not found to be satisfactory cleaning methods.

Absolute and relative work function measurements were both found to be satisfactory methods of detecting and measuring surface contamination. A definite response in surface potential is observable for very low relative oxygen coverage, $\theta < \frac{1}{2}\%$.

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