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Thermal Desorption Mass Spectrometry of Oxygen Chemisorbed on Thermally Etched and Polycrystalline Silver Filaments

R. J. EKERN* AND A. W. CZANDERNA

Department of Physics, Clarkson College of Technology, Potsdam, New York 13676

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Thermal desorption spectra for oxygen chemisorbed on thermally etched and polycrystalline silver filaments have been obtained using a modified flash filament technique with mass analysis in an ultrahigh vacuum system. Cleaning and adsorption cycles were carried out at partial pressures $<2 \times 10^{-6}$ Torr while desorption measurements were obtained in a total pressure environment $<5 \times 10^{-9}$ Torr. The spectra from the two dissimilar surface structures differ primarily in the number of desorbing phases. For thermally etched silver, a single phase desorbs after exposures to 500–11,000 Langmuirs of oxygen at adsorption temperatures of 375–510°K. The adsorption is activated and the activation energy, E_d, for the second order desorption reaction is estimated to be 34 kcal/mole. For polycrystalline silver, two phases desorb after exposures to 500–6000 Langmuirs of oxygen at temperatures of 300–535°K. The doublet desorption spectra result from a nonactivated adsorbed phase with E_d of ca. 27 kcal/mole and an activated adsorbed phase, with E_d of ca. 37 kcal/mole. The desorption for both phases from polycrystalline silver is second order in concentration.

I. INTRODUCTION

Thermal desorption mass spectrometry has been used to study the oxygen–silver chemisorptive system. The object of these experiments was to obtain, in an ultrahigh vacuum system, the thermal desorption spectra of oxygen adsorbed in low concentrations on silver filaments of high purity, with either thermally etched or polycrystalline surfaces. The thermal desorption of oxygen from silver filaments has not been reported although such measurements have been made on powders (*1–4*), monocrystals (*5, 6*) and field emitters (*7, 8*). The desorption spectra in most of these studies consist of singlet desorbing phases although at least two different phases of oxygen adsorption on silver are possible (*1, 3, 5, 8*). The two adsorbed phases have different activation energies for adsorption (*1, 9*) and desorption (*1, 3, 5, 8*) but have only been observed to exist simultaneously on the surface after exposure to oxygen at 10 Torr (*1, 3*). Spectra obtained in this work from polycrystalline silver reveal that the two phases can also coexist at very low surface coverages.

The previous volumetric, gravimetric and thermal desorption studies [exclusive, in part, of the FEM studies on silver whiskers (*8*)] involved adsorption of oxygen at pressures $>10^{-3}$ Torr ($>1.33 \times 10^{-1}$ Pa) with exposures in excess of 10^6 L (10^6 L = 1 Torr sec). In this work, low initial surface coverages were obtained prior to thermal desorption by adsorbing oxygen at partial pressures less than 2×10^{-6} Torr to various exposures between 500 and 11,000 L. Low partial pressures of oxygen were used during the cleaning and adsorption cycles

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* Present address: Gould Laboratories, 40 Gould Center, Rolling Meadows, Ill. 60008.

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to prevent any gross changes in the established surface structures. Extensive pretreatment procedures, based on chemical reactions occurring in an oxygen-enriched environment, were found necessary before adsorption would occur at these low oxygen partial pressures.

Mass analysis was used to ensure positive identification of the desorbing species and as an aid in the control of the purity of the adsorbing gas. The classical flash filament technique was used in these experiments with slower heating rates in order to satisfy the kinetic relationship between the heating rate, the activation energy for desorption, and the temperature where the desorption rate is a maximum (*10*). Thus, this work combines the first reported investigations of the thermal desorption of oxygen from silver filaments with characterized surfaces with the results for oxygen adsorption at lower exposures and lower initial surface coverages than in most of the previous studies. The spectra from thermally etched silver are similar to results previously published for surface structures not characterized *a priori* as thermally etched. The spectra from polycrystalline silver consist of two phases desorbing successively during a single thermal desorption cycle. The occurrence of these two-component desorption spectra is independent of adsorption temperature for the low coverages used in this work.

II. EXPERIMENTAL METHODS

1. *Apparatus*

A conventional ultrahigh vacuum (UHV) system was utilized for processing the filaments and obtaining the desorption spectra. Pumping was accomplished with a cryosorption forepump, a titanium sublimation pump (water and liquid nitrogen cooled) and a sputter ion pump. The base pressure after bakeout at 473°K was typically 2–3 $\times 10^{-10}$ Torr as measured by a nude ionization gauge. The residual gases after bakeout were predominantly hydrogen and carbon monoxide. The dominant residual gases after a few cycles of oxygen adsorption were water vapor, carbon monoxide and hydrogen, in decreasing order of intensity. The residual gas composition was fairly constant between bakeouts.

The oxygen partial pressure (amu 32), corrected for the various pumping sources, was monitored using a partial pressure gauge (PPG) with a thoria-coated iridium filament. The usual precautions were followed for analyzing for oxygen with a hot filament. In order to enhance the detection of oxygen at low partial pressures (*11*), the PPG was operated at an electron emission of 0.5 mA, reduced from the usual value of 6 mA. The reduced emission permitted operation of the filament at a lower temperature, thus reducing the rates of thermal decomposition (pumping) and catalysis at the filament. A magnetic sector residual gas analyzer (RGA), with a standard tungsten filament, was also incorporated on the UHV system to monitor occasionally gases other than oxygen during desorption. The RGA was operated at a reduced electron emission of 0.8 mA.

A silver permeation leak (*12*) was used as the source of high purity oxygen for these experiments except for the last eight desorption runs where reagent grade oxygen was obtained from a break-seal flask. No differences were observed between desorption spectra taken in comparison runs.

2. *Filament Material and Preparation*

The silver wire (0.254 mm diam) was purchased from the Materials Research Corp. with a prefabrication purity of 99.9995% (MARZ grade). Separate samples of the as-received wire were ultrasonically degreased and examined for surface impurities using ion scattering spectrometry (ISS). Oxygen was the only other element detected on the surface or in the near-surface region (depth profile) of the silver wire. The presence of other impurities such as carbon, sulfur and chlorine can not be ruled out completely since the detection sensitivity of ion scattering is reduced for low-Z, nonmetallic elements (*13*). These and other impurities may have been present in concentrations less than that required for detection by ion scattering. Since an alternative *in situ* surface analytical technique was not available for further assessment of surface impurity concentrations, there is no way of determining whether the specimens used in this study were of higher surface purity or if the impurities were undetectable.

Sulfur dioxide was detected mass spectrometrically but only during the initial operation of the original silver leak which was several years old when installed. This impurity disappeared after a few thermal cycles of the leak and was not detected during subsequent thermal cycling of either the silver filaments nor a second permeation leak.

The oxides of carbon, CO and CO_2, were monitored mass spectrometrically during adsorption, desorption and cleaning cycles. The evolution of these oxides and other processes observed for these gases are lengthy and complicated; a complete, detailed analysis of the results for CO and CO_2 is presented elsewhere (*14*). Briefly, significant production of CO or CO_2 did not occur during adsorption at elevated temperatures nor during long adsorption times. The observed evolution of these gases during desorption and cleaning cycles is attributed to the coadsorption of CO (*15*, *16*) and the replacement chemisorption of oxygen of these gases from surfaces of the vacuum system (*14*). The amounts of CO and CO_2 evolved relative to the desorbed oxygen were, however, small.

With respect to surface impurities, it is important to note that the data in this paper were obtained only after the pretreatment procedures (Sec. II.3 below) produced a silver surface which would adsorb oxygen. Oxygen could not be adsorbed on the filaments following installation in the vacuum system, even after a 12 hr "anneal" at 773°K. The residual gas spectra during the anneal or during the pretreatment cycles were not abnormal, that is, unusual or large amounts of C, CO, CO_2, were not observed and SO_2 and Cl were not observed except for the isolated case concerning SO_2 as described above.

The silver samples were mounted in the UHV system using 304 stainless steel holders, designed to locate the filaments within the line of sight volume of the ionization region of the PPG. The stainless steel holders, with diameter 25 times that of the silver wire, were passivated prior to use; deleterious effects due to size or kind of material were not noted.

The potential probe method (*17*) was used to determine the sample temperature. The resistivity of the silver wire as a function of temperature, measured in a separate apparatus, agreed well with published values for high purity silver (*18*).

The thermally etched silver was prepared by heating a 15 cm length in air at ca. 1000°K for 12 hr. The resultant surface topography is shown in Fig. 1A. The enhanced grain growth, grain boundary grooving and facet features are typical of silver thermally etched in an oxygen-rich atmosphere (*19*). The thermally etched sample was cut from the center section of this wire. In contrast, the topography of a section of the cold-rolled silver wire in an "as-received" condition is shown in Fig. 1B. The topographical features are primarily die marks, produced when the silver is cold worked to size. This is the type of surface used for desorption studies from polycrystalline silver.

3. Pretreatment and Experimental Procedures

The silver filaments were conditioned *in situ* prior to the data runs using the cleaning procedures listed in Table 1. These cleaning cycles were repeated in the order given until oxygen was observed to desorb

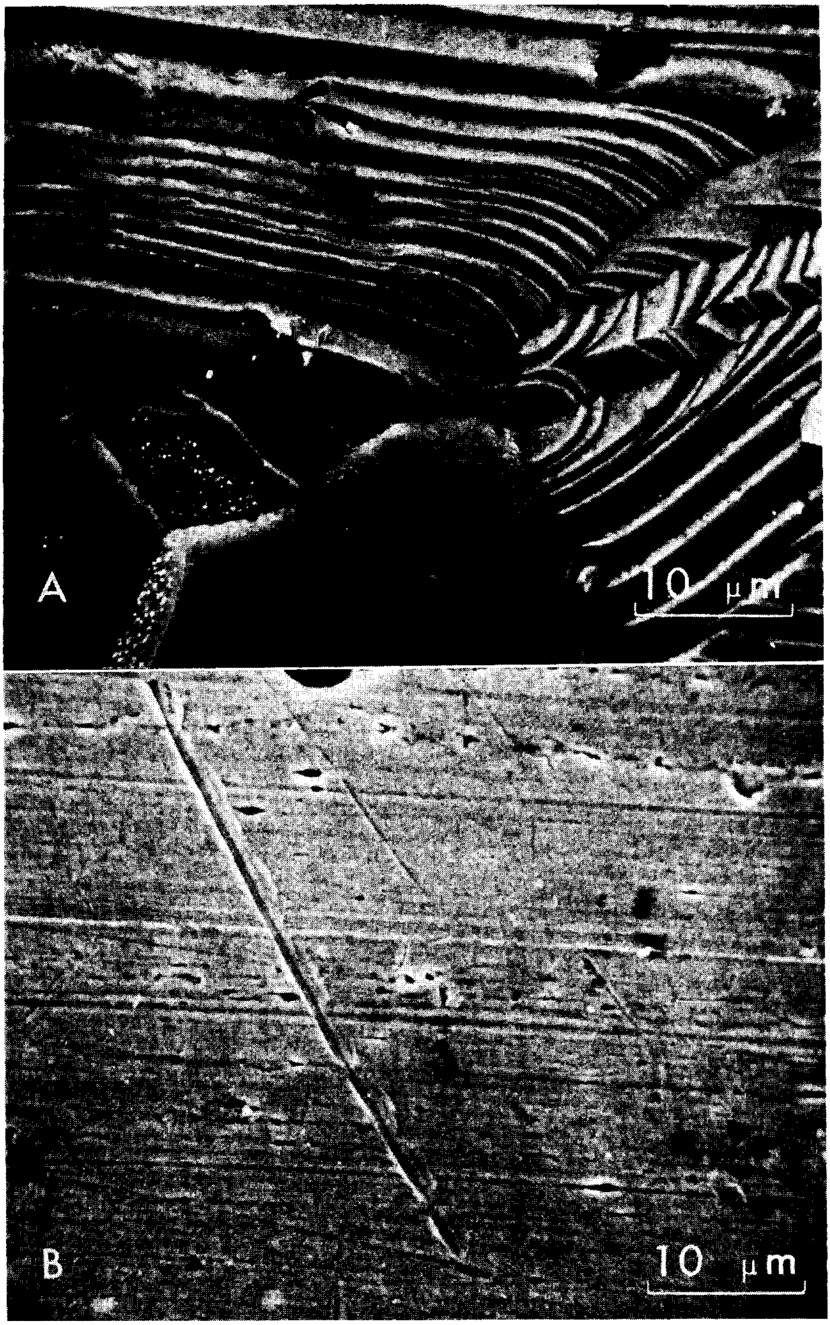

FIG. 1. Surface topography of (A) thermally etched silver and (B) polycrystalline silver.

with a maximum during the thermal desorption cycle (*20*); 15 to 20 complete cycles were typically required. These cycles are similar to those successfully employed at higher oxygen pressures and adsorption temperatures for powders (*2*) and monocrystals (*5*, *6*).

The subsequent data runs consisted of thermal desorption–oxygen adsorption–thermal desorption cycles without any pro-

TABLE 1

In Situ Cleaning Procedures for the Silver Filaments

Cycle	Pressure (Torr)	Duration	Sample temp (°K)	Heating rate (°K/min)
Outgassing	$\sim 5 \times 10^{-9}$	1 hr	773–873	—
Oxygen adsorption	$\sim 2 \times 10^{-6}$	1 hr	423–473	—
Thermal desorption	$\sim 5 \times 10^{-9}$	15 min	To 773	35

longed outgassing. The cleaning that occurred during a single thermal desorption cycle was adequate for subsequent oxygen exposure since further oxygen evolution could not be detected during repeated thermal cycling of the filament which followed the desorption to 773°K. After exposure of the filament to oxygen at the adsorption temperature, the filament was cooled to room temperature while the oxygen was being evacuated to 1×10^{-9} Torr or less. Prior to desorption, the ion pump was isolated from the vacuum system and the sublimation chamber was cooled with liquid nitrogen.

The thermally etched sample was heated during thermal desorption data runs using a constant current input. The resulting heating rate was nonlinear; the initial rate of about 50°K/sec decreased to less than 2°K/sec after about 15 sec. For the polycrystalline sample, a linear heating rate of about 4.5°K/sec was obtained by remotely programming the power supply with a capacitor-charging circuit. The heating current varied quasilogarithmically with time for the polycrystalline sample.

III. RESULTS

1. Thermally Etched Silver

Thermal desorption of oxygen from thermally etched silver is characterized by a single phase desorbing with the maximum desorption rate occurring at about 630°K. Typical thermal desorption spectra, plotted as a normalized change in the oxygen partial pressure versus temperature and time, are shown in Fig. 2. These evolution curves are proportional to the desorption rate; the asymmetrical shape is a result of the nonlinear temperature response (also plotted in Fig. 2a).

The amount of oxygen desorbing from thermally etched silver decreases with decreasing exposure. The previously well-defined maximum disappears after lower exposures, as is evident in the spectra of Fig. 2a. A desorbing phase persists over the same temperature range, however, even after exposures to only 500 L (not plotted). The evolution obtained after very low exposures is a mixture of a surface phase plus oxygen originating from absorption sites in the near surface or subsurface region. This mixed desorption is clearly evident in the inset to Fig. 2b where the desorption cycle was continued for an additional 50 sec to a final temperature of 750°K. Below 710°K, the desorbing phase is predominantly from the original surface layer. Above 710°K, the surface phase evolution is masked by absorbed oxygen diffusing to the surface

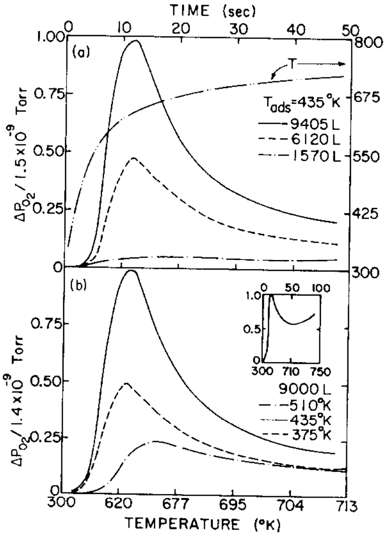

FIG. 2. Thermal desorption spectra of oxygen from thermally etched silver for (a) various exposures at 435°K and (b) various adsorption temperatures at an exposure of 9000 L.

and thermally desorbing. Transport of oxygen to the surface from absorption sites during thermal desorption occurs by the relatively slower process of diffusion. Diffusion is also enhanced above 710°K since the sample is at higher temperatures for longer times due to the diminishing heating rate. The monotonically increasing evolution above 710°K is characteristic of several experimental runs. This phase is similar to the one obtained from silver monocrystals by Rovida *et al.* (*6*) although a maximum desorption rate was not observed in our experiments, even up to 800°K.

Thermal desorption of oxygen from thermally etched silver after constant exposures of ca. 9000 L at various adsorption temperatures is shown in Fig. 2b. The maximum amount of oxygen desorbed was obtained after adsorption at 435°K. This general result obtained for several desorption runs is summarized in Fig. 3 but further studies are necessary to establish the exact temperature of the maximum. The exact temperature of the maximum was not pursued in detail because 435°K compares favorably with results obtained on silver powders (*1*) and single crystals (*5*, *6*). For low exposures, the amount desorbed, *q*, is essentially constant for all adsorption temperatures. However, a maximum in *q* occurs as the exposure is increased. This result is attributed to an activated adsorption of oxygen on silver, in agreement with previous results at much higher exposures on powders (*1–3*) and monocrystals (*5*, *6*).

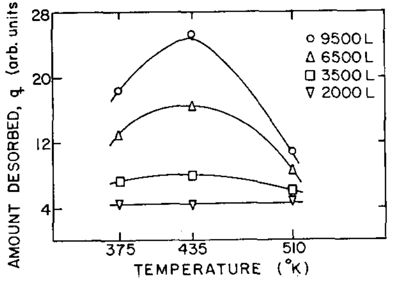

FIG. 3. Amount of oxygen desorbed from thermally etched silver after various exposures at different adsorption temperatures.

The singlet desorption spectra from thermally etched silver are also comparable to desorption spectra from silver powders and monocrystals. The maximum desorption rate occurs at approximately 630°K for thermally etched silver compared with 500–520°K for powders (*2*) and ca. 553°K for monocrystals (*5*). The differences in results can be accounted for by decreasing coverages of the same adsorbed state which desorbs by a second order process. The temperature for the maximum desorption rate varied only slightly with adsorption temperature in contrast to other work (*2*, *4*, *6*, *7*, *9*); this is because the variations in coverage were small in this work.

Accurate calculations of the kinetic parameters for the desorption from thermally etched silver were prevented by the nonlinear heating rate, which could not be reduced to any usable functional form. The activation energy for desorption, E_d, was estimated to be 32–36 kcal/mole by comparing experimental data to curves calculated using $\nu = 1 \times 10^{-3}$ cm^2 sec^{-1} for a second order process. Surface coverage, normalized to 7×10^{14} molecules/cm^2/monolayer (*21*) obtained from studies at much higher exposures, were between 0.014 and 0.023 monolayers (1.0 to 1.6×10^{13} molecules/cm^2) for exposures of 500 to 9000 L. Surface coverages for oxygen desorbing from metal filaments in ultrahigh vacuum can be in error due to an incomplete knowledge of the actual "emitting" area of the filament and a lack of a dynamic method of measuring the oxygen pumping speed *during* the thermal desorption cycle. The relative error in surface coverage due to these two parameters could be as high as 25% in our experiments.

2. Polycrystalline Silver

Two distinct pressure maxima are present in the thermal desorption spectra of oxygen from polycrystalline silver. Typical spectra

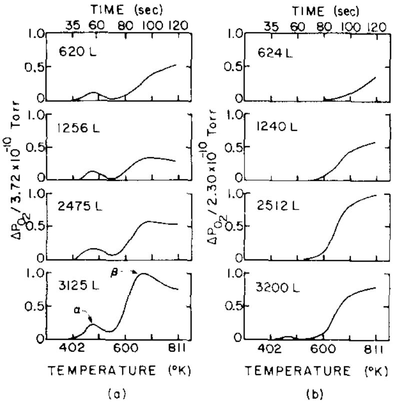

FIG. 4. Thermal desorption of oxygen from polycrystalline silver after various exposures at 1.7 × 10^{-6} Torr oxygen partial pressure and adsorption temperatures (a) 410°K and (b) 535°K.

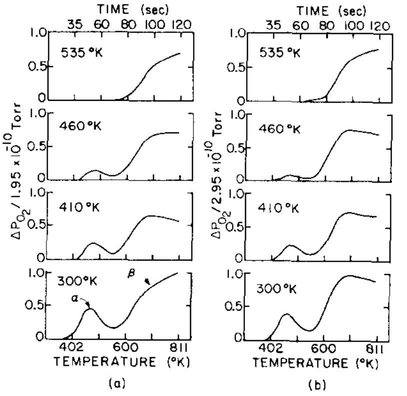

FIG. 5. Thermal desorption of oxygen from polycrystalline silver after exposures of (a) 1260 L and (b) 2500 L at 1.7 × 10^{-6} Torr oxygen partial pressure and various adsorption temperatures.

for constant adsorption temperatures and constant exposures are shown in Figs. 4 and 5, respectively. The consistency of the two-component, or doublet, spectra over the wide range of adsorption temperatures and oxygen exposures discounts any transient phenomena due to experimental conditions or procedures. The procedures used to obtain these data were similar to those procedures used for thermally etched silver. The only major change was the linear temperature response of the filament during thermal desorption. Absorbed oxygen is also observed to evolve from polycrystalline silver, preventing the appearance of a well-defined maximum for the second phase during some of the desorption cycles.

The intensity of the desorption from the low temperature desorbing phase, the α-phase, is a maximum at about 460°K. This temperature corresponds, for the observed second-order desorption, to an E_d of approximately 27 kcal/mole. The second desorbing phase, the β-phase, is similar to the phase desorbed from thermally etched silver, both in temperature-domain location and in the activation energy for desorption. The maximum of the β-phase desorption, when present in the spectra, occurs at about 650°K, E_d is approximately 37 kcal/mole for the second order desorption reaction.

The amount of oxygen, q_α, desorbed from the α-phase on polycrystalline silver is shown in Fig. 6. The integrated area under the α-peak is plotted in arbitrary units as a function of the exposure in Fig. 6a and as a function of the adsorption temperature in Fig. 6b. The decrease in q_α with increasing T_{ads} is typical for a weakly chemisorbed species. Similar areal integrations for the β-phase are not presented since they reflect the inconsistent spectral quality of the data for the β-phase, as is evident in Fig. 5. The β-peak at temperatures above 700°K contains oxygen evolving from sources other than the silver surface; the largest contribution to this evolution is probably absorbed oxygen (cf. the inset to Fig. 2b and

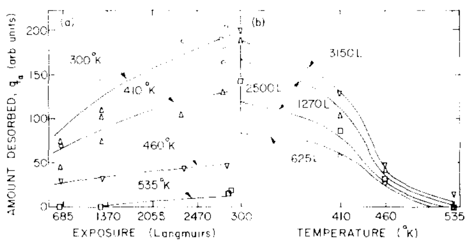

FIG. 6. Amount of oxygen desorbed from the α-phase on polycrystalline silver. Evolution data for (a) constant exposure and various adsorption temperatures and (b) constant adsorption temperatures and various exposures.

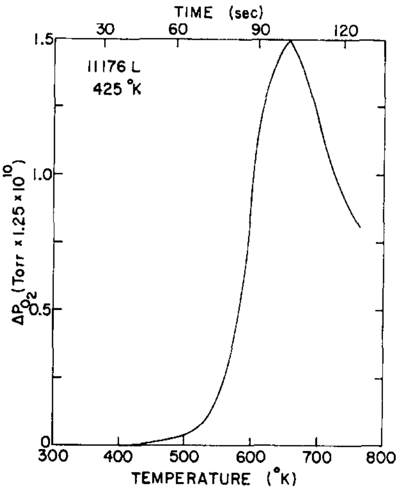

FIG. 7. Change in the thermal desorption from polycrystalline silver.

related discussion). These additional sources add an oxygen signal to the evolution at a critical point where the β-phase desorption is decreasing and thus distort the observed β-phase desorption. Sufficient evidence for the existence of a β-phase is, however, contained in several of the spectra in Figs. 4 and 5, where a distinct maximum occurred in the evolution.

Surface coverages for the α-phase desorbing from polycrystalline silver were calculated for all data runs and are not only subject to the same general comments made for thermally etched silver but also to the additional uncertainties that exist when calculating surface coverages for the α-phase. Since saturation of the α-phase did not occur during these experiments (cf. Fig. 6a) an adatom concentration for monolayer coverage could not be determined. Also, monolayer coverages of oxygen on silver previously discussed (*21*) are representative of a collective, *total* surface coverage obtained after higher exposures. The surface concentrations for the α-phase are between 1.8 and 3.5 $\times 10^{12}$ molecules/cm^2 for exposures of 500 to 6000 L. Similar calculations for the β-phase are not presented since coverages obtained from the data would not be representative of a pure surface phase.

A. Change in the thermal desorption from polycrystalline silver. A procedural change was made for the final desorption runs to test the effects of pretreating the silver filament with an oxygen adsorption at 773°K for 1 hr at 1.7 $\times 10^{-6}$ Torr (ca. 6000 L), followed by an outgassing *in vacuo* for 1 hr at 773°K. The remaining procedural steps for adsorption and desorption were identical to the steps used to obtain the previous results from polycrystalline silver.

The resultant thermal desorption spectra, as shown by a typical spectrum in Fig. 7, did not contain the α-phase desorption. Similar singlet desorption spectra were obtained for several combinations of the exposure parameters. Postexperimental observations of the surface showed that grain growth had occurred, as shown in Fig. 8 (cf. Fig. 1). The grain boundaries appear to be thermally grooved, as are the grain boundaries on a thermally etched silver surface. The oxygen partial pressure and filament temperature were not sufficient to promote observable faceting, but this does not preclude the existence of facets not resolvable by the electron microscope (typically less than 100 Å). In agreement with Kollen's (*22*) faceting study on polycrystalline silver at higher oxygen pressures from 573 to 673°K where no observable facets nor thermally grooved grain boundaries developed below 623°K, the topological changes of the polycrystalline silver filament occurred after prolonged exposure to oxygen after the adsorptions at 773°K.

IV. DISCUSSION

The thermal desorption spectra presented for both thermally etched and polycrystalline silver can only be described by second order kinetics. The data and computer-calculated curves generated for various combinations of the kinetic parameters are identical only in second order. Thus, the

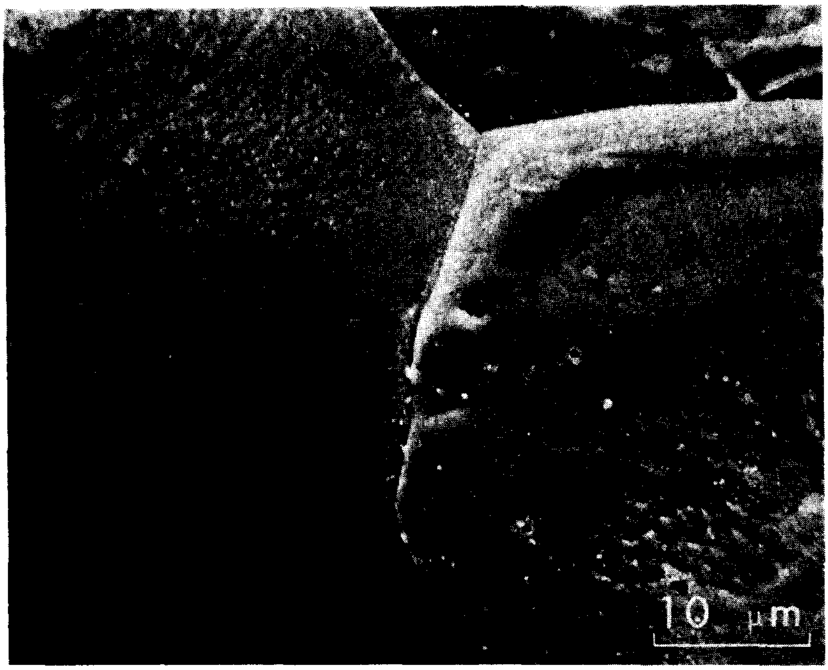

FIG. 8. Surface topography of polycrystalline silver altered by prolonged, periodic exposure to oxygen at 773°K.

standard interpretation of dissociated oxygen adatoms recombining to form molecular oxygen prior to thermal desorption can be applied to the results of these experiments. The dissociative chemisorption is, in fact, in accord with recent studies on (111) silver monocrystals (*6*) and silver whiskers (*8*), especially where lower surface coverages are involved.

The doublet desorption spectra obtained from polycrystalline silver is in contrast to the singlet spectra from thermally etched silver. The occurrence of desorption spectra consisting of two adsorbed phases of oxygen desorbing from silver could be either a surface structure effect or the result of adsorption on a surface where impurities below ISS detectability limits are present.

For the surface structure effects, the simplest explanation is to assume that those surface sites necessary for α-phase adsorption are not present in sufficient quantity on thermally etched silver. This assumption is plausible even though the thermally etched surface is comparatively complex, with exposed crystallographic planes of both low and high Miller indices (*20*) plus thermally grooved grain boundaries. The appearance of thermally grooved grain boundaries clearly shows sufficient silver surface mobility exists to eliminate unfavorable energetic arrangements.

Alternatively, the results obtained from an altered silver surface with discernible thermally grooved grain boundaries (derived from polycrystalline silver, Sec. III.2.A), may be considered a surface structural effect by allowing for adsorbate migration, for example, along grain boundaries. The migration to and along the grain boundaries would be followed by absorption at sites deeper in the grain boundary where a number of unsaturated surface silver atoms exist. Particles involved in this near-surface absorption would not be desorbed during the time required to complete a typical desorption cycle. The migration, enhanced at elevated temperatures, could occur during a tempering cycle of the filament. At elevated temperatures, absorption of mobile α-phase adsorbates into the grain boundaries could deplete this phase. This mechanism requires that the heat of adsorption of the α-phase (Q_α) be less than that for oxygen absorbed in a grain boundary. On the other hand, β-phase adsorbates could also be absorbed into the grain boundaries by a similar mechanism. The vacated β sites would then be available for replacement adsorption of mobile α-particles onto β sites. Again, the relative energies of the bound states must be appropriate. In either case, the α-phase would not appear in the desorption spectra, providing that sufficient mobility occurs to completely depopulate the α-phase and the oxygen adsorption energy in the β-state or in a grain boundary is greater than for the α-state, e.g., $Q_\alpha < Q_\beta < Q_{gb}$.

Adsorption of oxygen on impurity sites, such as carbon, sulfur, or chlorine, or a variance in the adsorption of oxygen due to the presence of surface impurities, must also be considered as possible causes of the doublet desorption spectra from polycrystalline silver. The change from a doublet to a singlet spectra from polycrystalline silver followed oxygen adsorption at 773°K, which is in accord with the temperature required to remove carbon and sulfur from silver in 10^{-3} Torr of oxygen (*6*). The impurities may prevent large scale migration of the oxygen adsorbates, giving rise to the doublet thermal desorption spectra. Once the concentration of impurities has been reduced, adsorbate migration could occur at a rate and in sufficient quantities to reduce the population of the α-phase below detectable limits. For the thermally etched silver, a substantial fraction of the impurities would have been removed from the surface during the thermal etch in air at ca. 1000°K. Based on these arguments, singlet desorption spectra are expected from thermally etched silver.

The exact mechanism causing the singlet desorption spectra cannot be discerned solely from the thermal desorption data. The processes of direct absorption or replacement adsorption as discussed above, cannot be quantitatively determined. The direct observation of adsorbate migration during adsorption and thermal desorption would be necessary in order to define the proper mechanism; this technique has yet to be applied to any gas–metal chemisorptive system.

V. CONCLUSIONS

1. Adsorption–desorption data were obtained from silver after pretreatment in high to very high vacuum by using repetitive exposures to oxygen while at elevated temperatures.
2. Slower heating rates were successfully used to modify the flash filament desorption technique to study gas–surface interactions of a metal with a low melting temperature without loss of resolution or sensitivity and without exceeding the melting point or causing the vapor pressure to become excessively high.
3. Oxygen adsorbed on thermally etched silver filaments to low exposures, thermally desorbed from a single adsorbed phase. On polycrystalline silver filaments, two adsorbed phases were initially observed in the desorption spectra. A singlet phase subsequently desorbed from the polycrystalline silver following pretreatment at 773°K with $\sim 2 \times 10^{-6}$ Torr oxygen.

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