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TIME-RESOLVED AUGER ELECTRON SPECTROSCOPY COMBINED WITH MODULATED MOLECULAR BEAM TECHNIQUES FOR GAS-SURFACE REACTION KINETICS STUDIES

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Abstract

An Auger electron spectrometer is combined with a modulated molecular beam system and the time-dependent concentration of adsorbed oxygen on a molybdenum surface subject to a chopped O_2 beam is measured and compared to predictions of a reaction kinetic model derived from modulated molecular beam spectroscopy alone.

Introduction

Although modulated molecular beam mass spectrometry is a useful technique for the study of gas-surface reaction kinetics(1), it is incapable of directly determining the identity and the time-dependent concentrations of reaction intermediates on the surface. Rather, this information is deduced from a reaction model constructed to fit the modulation frequency, temperature and pressure dependence of the reactant and reaction product signals measured by a mass spectrometer.

Recently Steinbach and Schütte(2) have shown that XPS and UPS used in conjunction with a modulated molecular beam are powerful tools for measuring the time-dependent behavior of surface species which is inaccessible by mass spectrometric detection. The purpose of the present work is to illustrate the use of modulated Auger electron spectroscopy (AES) to supplement modulated molecular beam spectroscopy in a relatively simple gas-solid reaction system. The low-spatial-resolution AES used here can detect the time-dependent surface element concentrations induced by the incident modulated reactant beam, but unlike XPS, can only with difficulty provide chemical identification of the adsorbed species. In addition the AES technique is more likely than XPS to disturb the reaction mechanism (by photon-stimulated desorption). On the other hand, the higher sensitivity and modulation frequencies achievable by AES represent significant advantages over XPS. Combination of time-resolved surface analysis by AES with conventional mass spectrometric molecular beam spectroscopy in principle permit both the surface concentration of the intermediate and reaction product emission to be measured in the same apparatus. Whether both techniques can be used simultaneously depends on the reaction conditions. Low temperatures

generally result in high surface concentrations and slow product desorption, a situation best suited to AES. At high temperatures, on the other hand, surface concentrations tend to be low and the reaction rapid. This combination is best exploited by mass spectrometric detection of the desorbed products. The AES and mass spectrometric measurements consist of both amplitude and phase, and because they probe different aspects of the reaction, provide complementary but independent data from which the mechanism can be deduced.

We demonstrate the utility of this combination by an AES study of a gas-solid reaction (molybdenum oxidation) which has previously been investigated by modulated molecular beam mass spectrometry(3). The approach is to measure the time-dependent surface intermediate concentration for this reaction (which is adsorbed oxygen) and compare the results with a theoretical prediction based solely on the kinetic parameters of the reaction determined in Ref. 3. No parameters of the reaction model are adjustable, so that the experiment constitutes a test not only of the applicability of the AES technique, but also of the validity of the reaction model presented in Ref. 3.

Experimental

The conventional mass spectrometric portion of the modulated molecular beam apparatus is shown in Fig. 1. To the basic system, which has been previously described in Ref. 1, a cylindrical mirror analyzer has been added inside the vacuum system and the electronics of the AES system have been added to the analogous electronic components for the mass spectrometer part. The gaseous reactant molecular beam is formed in the diffusion-pumped source chamber, where beam modulation and collimation take place. The solid reactant (the target) is located in the differentially-pumped target chamber in one of two possible positions. In the lower position (shown by the dashed

rectangle in Fig. 1) the reactant impingement spot is viewed by the mass spectrometer located in the differentially-pumped mass spectrometer chamber; this is the conventional configuration of the apparatus. When the target is moved in situ to the upper position (indicated by the solid rectangle), the reacting surface is exposed to the Auger analyzer which has been placed in the target chamber. The electron beam of the analyzer impinges on the center of the molecular beam spot on the target and the analyzer is tuned to the Auger peak of interest. The output signal from the analyzer (tuned to the 503eV peak of oxygen) consists of i) the periodic waveform from the surface species corresponding to the modulation frequency of the beam chopper (7 - 80 Hz), and ii) superimposed on this signal is the ripple due to the 10 kHz internal reference of the AES system. The total signal (shown schematically in Fig. 1) is not visible on an oscilloscope because it is swamped by noise. The type of output from the lock-in amplifier in the AES electronics (No. 1) due to this input signal depends on the time constant τ_1 selected for processing the input waveform.

To determine the steady-state component of the surface intermediate concentration induced by the incident modulated reactant beam, a 10 s time constant is used on this lock-in amplifier. The long time constant relative to the period of the input signal provides a temporal average of the latter as the output of lock-in No. 1 (denoted by V). This measurement, in conjunction with measurement of the steady-state AES signal from the substrate metal permits determination of the time-averaged coverage of the surface intermediate by the usual method(4). To measure the phase and amplitude of the first Fourier component of the time-dependent surface intermediate concentration, a time constant τ_1 = 1 ms is used on lock-in amplifier No. 1. The time constant τ_1 is much smaller than the periodicity of the input

signal, which means that in this case, the AES system output is the same shape as the input with only the 10 kHz ripple removed. This signal is routed to lock-in amplifier No. 2 where it is processed with the reference signal drawn from the chopper modulating the molecular beam. The time constant τ_2 of the No. 2 lock-in is set at 10 s to provide accurate measurement of the phase angle and amplitude of the first harmonic of the signal coming from lock-in No. 1. This signal contains the time response of the surface intermediate concentration on the reacting solid.

In order that the phase measured by lock-in No. 2 be properly referenced to reactant beam impingement on the target (so that it can be compared with the theory in absolute terms), the mechanical phase lag in the chopper motor and the phase lag due to beam transit from the chopper to the target in its upper position must be eliminated. This correction is achieved in separate experiments with the target in the lower position in Fig. 1, which scatters the incident reactant beam into the mass spectrometer (reaction product signals are not measured because this information is available from Ref. 3). The output signal is fed to lock-in No. 2. Because the beam path length when the target is in the Auger-measuring position is very nearly the same as the sum of the distances from the chopper to the target in the lower position and from here to the mass spectrometer, this measurement serves to eliminate the parasitic phase lags. However, no attempt has been made to determine the absolute amplitude of the first Fourier component of the surface intermediate signal because no convenient reference signal (such as was provided by the substrate metal signal for the steady-state determination) is available.

Results

To illustrate the AES technique, we investigated the oxidation of polycrystalline molybdenum, which has been studied by Ullman and Madix(3)

using modulated molecular beam mass spectrometry exclusively. The surface temperature (1800 K) and the incident oxygen beam intensity (1.2×10^{16} molecules/cm^2-s on the target in the upper position) were chosen because the AES signal was easily measurable with the oxygen beam on and disappeared immediately when the beam was turned off.

Using the 10 s time constant on lock-in No. 1, the steady-state spatially-averaged oxygen peak height was determined. This measurement, along with that of the molybdenum peak height, gave a time-averaged oxygen coverage of the surface of $\sim$ 5%.

The absolute phase lag and the relative amplitude of the first Fourier component of the oxygen surface concentration measured by the AES method described in the preceding section are shown in Fig. 2. Because the spot size of the incident electron beam is $\sim$1.5mm, these measurements represent spatial averages over local surface concentration distributions on individual grain faces. They are plotted as functions of the nondimensional frequency $\omega a^2/D$, where ω is the modulation frequency of the oxygen molecular beam (35 to 415 radians/s), a is the radius of the grains (measured from photomicrographs to be $\sim$ 5μm) and D is the surface diffusion coefficient of oxygen adatoms on the molybdenum surface. Although the phase lag shown in Fig. 2 is absolute (i.e., it is relative to the impingement of the oxygen beam on the surface), the lowest amplitude point has been matched to the theoretical prediction (described below) at an abcissa value of 1.5.

Comparison with the Ullman-Madix Model Predictions

Ullman and Madix(3) found that the rate-controlling step in the high-temperature oxidation of molybdenum is the diffusion of oxygen adatoms across the grain surface to the grain boundary where the product oxide(s) rapidly form and desorb. From their molecular beam data, they deduced the oxygen surface diffusion coefficient at 1800 K (6×10^{-6} cm^2/s as well as the temperature

dependent oxygen sticking probability (0.3) at 1800 K. We use these values in the following calculation of the spatially-averaged surface oxygen concentration, which is what the AES measured.

Following the usual procedure in molecular beam analysis(1), the oxygen adatom concentration in the grain surface is represented by the truncated Fourier expansion:

$$n(r,t) = n_o(r) + \tilde{n}(r)e^{i\omega t} \qquad (1)$$

where r is the radial position on the grain surface, which has been modeled as a circle. Applying the surface mass balance for oxygen adatoms on the grain surface as developed by Ullman and Madix, the steady-state component is found to be:

$$n_o(r) = \frac{1}{4}\frac{a^2\eta I}{D}\left(1 - \left(\frac{r}{a}\right)^2\right) \qquad (2)$$

where η is the O_2 sticking probability and I is the incident molecular beam intensity. Because the spatial resolution of the AES system is low, the measurement represents the average oxygen concentration over the surface of the grain, which can be obtained theoretically from Eq(2):

$$\langle n_o \rangle = \frac{a^2\eta I}{8D} \qquad (3)$$

Dividing $\langle n_o \rangle$ by the density of molybdenum atoms on the surface ($\sim 10^{15}$ cm^{-2} (4)) gives a theoretical coverage of $\sim$ 2%, which is in fair agreement with the experimental value of $\sim$ 5%.

The first fourier component of the surface concentration, $\tilde{n}(r)$, is given by:

$$\frac{\tilde{n}(r)}{\eta I/\omega} = A\,\{\tan\theta\ \mathrm{ber}(x) - \mathrm{bei}(x)\} - i\{1 - A[\mathrm{ber}(x) - \tan\theta\ \mathrm{bei}(x)]\} \qquad (4)$$

where $x = (\omega/D)^{\frac{1}{2}}r$, ber and bei are the Kelvin functions(5) and θ is the phase of the Kelvin function at $(\omega/D)^{\frac{1}{2}}a$. The coefficient A is:

$$A = \frac{4}{\pi}\ \frac{\cos^2\theta}{\mathrm{ber}[(\omega/D)^{\frac{1}{2}}a]} \qquad (5)$$

The average of Eq(4) over the circle representing the grain is obtained from:

$$\langle \tilde{n} \rangle = \frac{2}{a^2} \int_0^a r\, \tilde{n}(r)\, dr$$

which we do not explicitly display here.

The calculated phase and amplitude of $\langle \tilde{n} \rangle$ are shown in Fig. 2 as solid lines. Both the absolute phase lag prediction and the shape of the theoretical amplitude are in excellent agreement with the AES data over a a factor of 10 variation of beam modulation frequency.

We also show as the dashed curve in Fig. 2 the calculated value of the phase of the oxygen adatom concentration at the grain boundary (i.e., the limit of the phase lag of $\tilde{n}(r)$ as $r \to a$). Because reaction at the grain boundary and subsequent desorption are rapid compared with diffusion over the grain surface, this phase lag should be identical to the product desorption phase lag deduced theoretically by Ullman and Madix(3) - that is, the dashed curve in Fig. 2 is the same as the theoretical curve in Fig. 3 of Ref(3). Display of the dashed curve does not demonstrate further agreement of our data with the Ullman-Madix model. Neither does the difference between the phases given by the solid and dashed curves represent a discrepancy between the AES and the mass spectrometric analyses of this reaction. The difference between the two phase lag curves in Fig. 2 simply demonstrates that AES and mass spectrometry probe different aspects of the surface reaction. The application of these two techniques in the same vacuum system, although not necessarily simultaneously, provides a very potent tool for mechanistic studies of gas-solid reactions.

Conclusions

This investigation has shown how to measure the time-dependent concentration of a surface intermediate in a modulated molecular beam experiment by using Auger electron spectrometry and how these results are related to

reaction kinetic information obtained by detection of reaction product emission by mass spectrometry. The AES measurements also provided independent confirmation of the mechanism of the oxygen/molybdenum reaction proposed by Ullman and Madix.

It is apparent that an Auger system with high spatial resolution (microns rather than millimeters) would permit similar measurements to be made locally on the reacting surface. Such a capability could be very valuable in some reactions on heterogeneous surfaces.

Acknowledgement

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Figure Captions

1. Schematic of the modulated molecular beam reaction apparatus incorporating both mass spectrometric and time-resolved AES detection techniques.

2. Amplitude and phase of the first Fourier component of the oxygen adatom concentration averaged over the grain surface - measured by AES (points); calculated using reaction parameters from Ref. 3 (solid curves); phase lag of the reaction product oxide emission rate from Ref. 3 or equivalently of the oxygen adatom concentration at the grain boundary from Eqs.(4) and (5) (dashed curve).

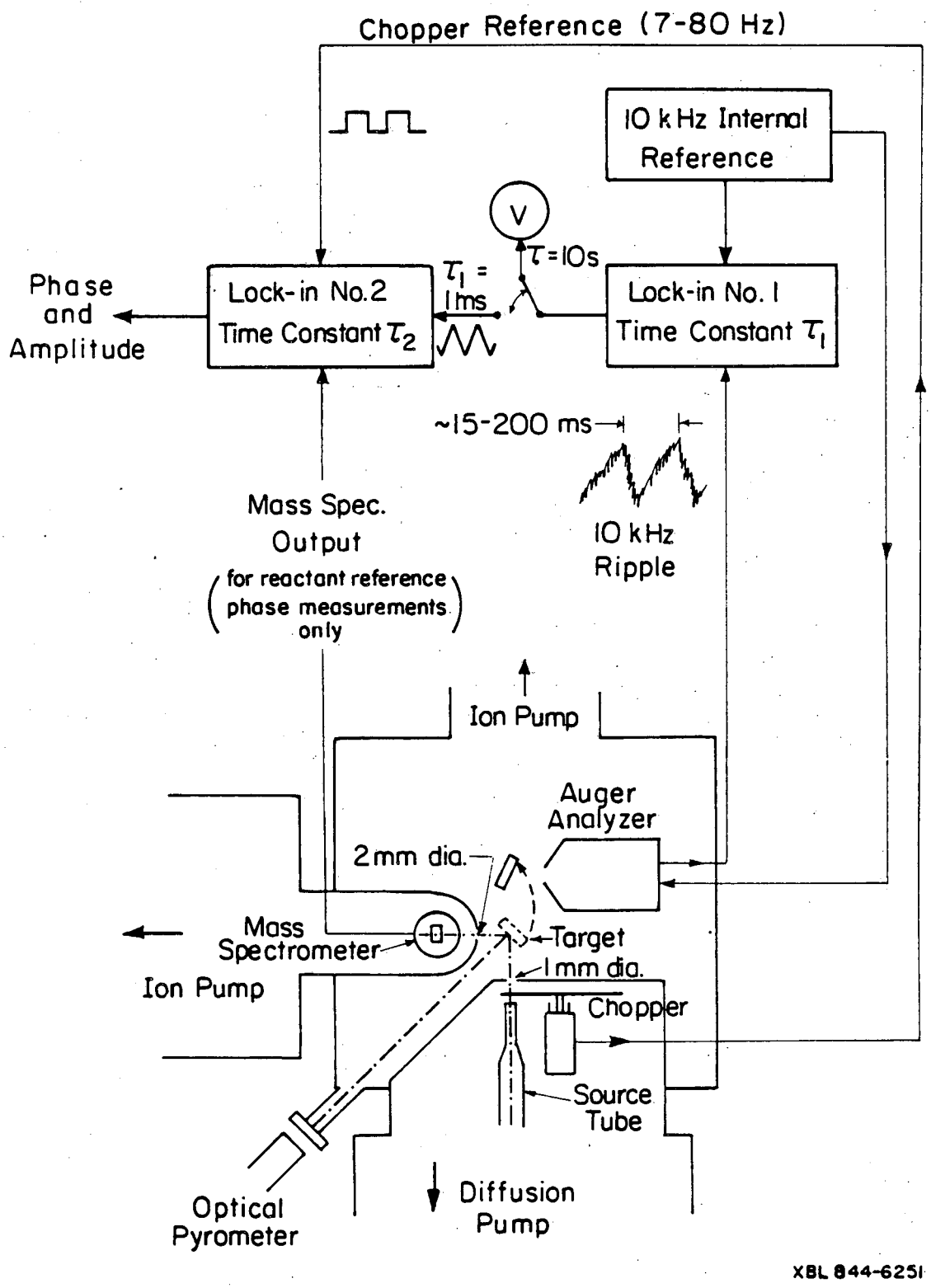
Chopper Reference (7-80 Hz)
10 kHz Internal Reference
V
τ=10s
τ1 = 1ms
Phase and Amplitude
Lock-in No.2 Time Constant τ2
Lock-in No. 1 Time Constant τ1
~15-200 ms
10 kHz Ripple
Mass Spec. Output
(for reactant reference phase measurements only)
Ion Pump
Auger Analyzer
2mm dia.
Mass Spectrometer
Target
1mm dia.
Ion Pump
Chopper
Source Tube
Optical Pyrometer
Diffusion Pump
XBL 844-6251

Figure 1

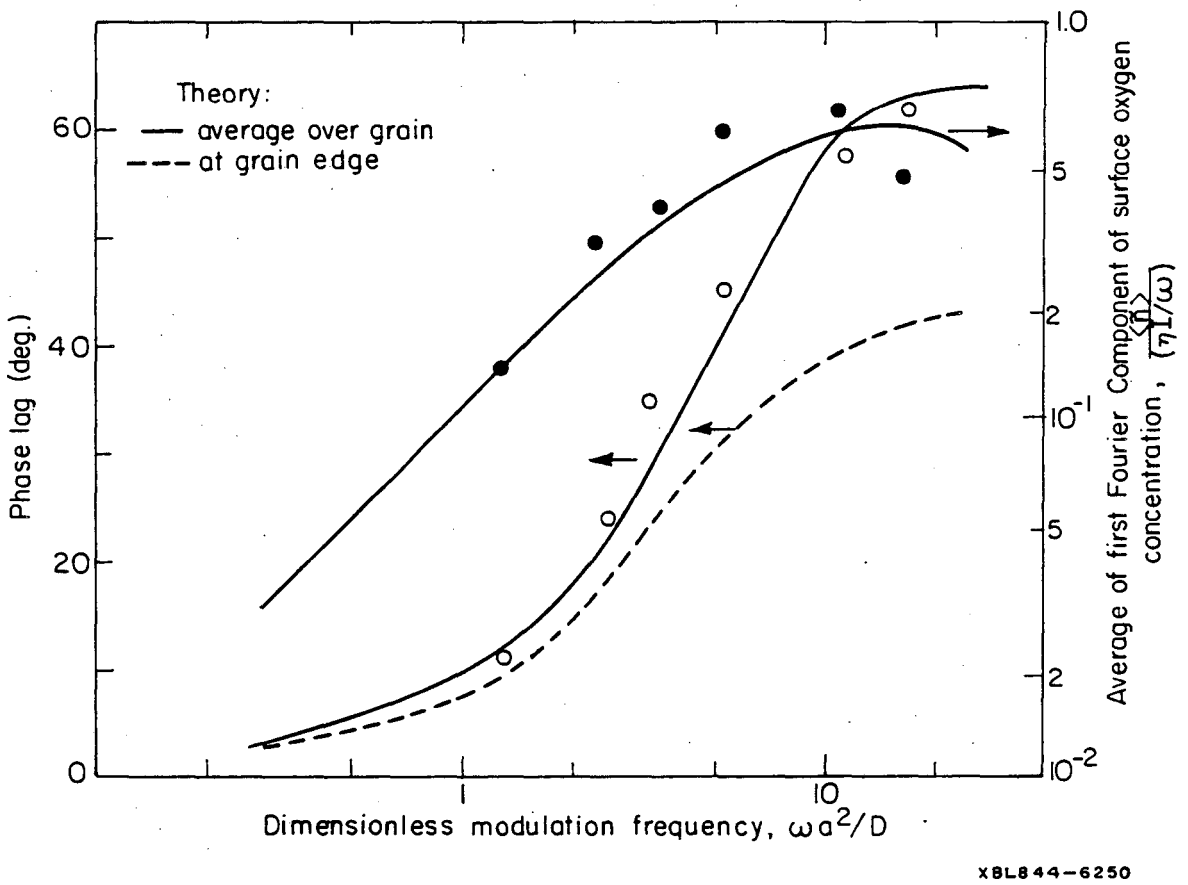
Theory:
average over grain
at grain edge
Phase lag (deg.)
0
20
40
60
1.0
5
2
10^{-1}
5
2
10^{-2}
1
10
Dimensionless modulation frequency, $\omega a^2/D$
Average of first Fourier Component of surface oxygen concentration, $\overline{\langle \eta \rangle / \omega}$
XBL844-6250

Figure 2

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