

ESDIAD

(ELECTRON STIMULATED DESORPTION IN ION ANGULAR DISTRIBUTIONS)

INTRODUCTION:-

ESDIAD is the new surface science technique that has been worked on and developed mainly by two surface scientists namely John T. Yates (University of Pittsburg) and Theodore E. Madey (University of Rutgers).

This technique has permitted the imaging of the rotation and translational vibration of small adsorbate molecules chemisorbed on metallic crystal surfaces. In this technique, electronic excitation caused by a focussed beam of low energy electrons, results in ejection or desorption of ions in discrete directions determined by the orientation of the chemical bonds which are ruptured. ESDIAD records a snapshot of the direction of the chemical bond (between adsorbate and surface) being ruptured, on a very short and precise timescale of subpico seconds and by superimposing a number of these snapshots, it gives the details of the azimuthal orientation and the polar angle of the chemical bonds being broken. It also provides us with an opportunity to observe molecular rotation of the adsorbate molecules as well.

A new method has also been developed by coupling ESDIAD with TOF (Time of Flight) selection of desorbing ions in order to directly image the molecular dynamics. It is expected to give an insight of the first step in a surface chemical reaction.

Basic mechanism:

The basic principle is the same as that of ESD (Electron Stimulated Desorption) technique. The adsorbate layer on a crystal surface is bombarded with low energy electrons (less than 500 eV) and the physical and chemical changes occurring due to electronic transitions are studied.

These electronic transitions occurring in molecular states lead to dissociation of metal-adsorbate adbond or a molecular bond. These transitions are characterized as thermal desorption, conversion from one binding state to another (including dissociation) or desorption of ground state and excited neutral as well as positively and negatively charged molecular or atomic species. The positive ions being easily detectable are mainly studied.

The exact mechanism of these transitions is not well understood though the inter-atomic and intra-atomic Auger mechanisms are thought to play substantial role in these transitions.

Many theories have been proposed to explain the desorption process. The one, which is widely accepted is the MGR (Menzel- Goomer- Redhead) model. It also follows the Frank Condon principle, which states that the electronic transition takes place quickly, compared to the time required for a nuclear motion (i.e the velocity and internuclear separations remain unchanged). The MGR model proposes a diatomic system of a metal substrate atom M and the adsorbate A. The potential energy of interaction of the two atoms is shown by the lower curve in Fig 1. E_a is the binding energy of the system.

Fig 1:- Schematic potential curves for interaction of M and A (lower) and M and A^+ (upper).The shaded region shows the possible electronic transition due to ESD.

The upper curve represents the $M + A^+ + e^-$ state. The two curves are separated by an energy equal to the ionisation potential of A i.e $E_i(A)$. The incident low energy electrons induce transitions from the lower curve to the repulsive portion of the upper

curve. This is shown as the Frank Condon region representing the range of internuclear separations (unchanged). The A^+ ions thus formed may desorb with a certain kinetic energy.

The neutralisation and recapture of these ions can reduce the number of ions, as compared to the number of desorbing neutrals.

There are other possible potential curves for the excited neutral state of adsorbed species or an antibonding neutral state which can hinder direct transition to the upper curve and hence desorption cannot take place. The separation distance substrate and the adsorbate lies in the order $d_{\text{ion}} < d_{\text{ground state neutral}} < d_{\text{metastable}}$.

The rate of ejection of ions, is found to be linearly related to number of incident electrons.

In this technique the electronically induced ionic emissions are detected in all three dimensions, not just in direction normal to surface, as is done in ESD.

TOF_ESDIAD combination is even more informative. By varying the pre-acceleration voltage (for fixed energy) at constant flight time gating, the energy distribution of a particular species can be measured, while a mass spectrum at fixed energy can be obtained from a time of flight spectrum.

It is also possible to take a very narrow TOF window (corresponding to the width of incident electron beam) and to analyze the corresponding angular distribution. The TOF distribution of a certain species can also be analyzed by focusing on an integrated ESDIAD pattern.

INSTRUMENTATION:

Digital Acquisition ESDIAD System

The whole system is installed inside a stainless steel chamber that is pumped with an ion pump, turbo pump, titanium sublimator, and a liquid nitrogen cryobaffle. With just the turbopump and ion pump operating and a fresh titanium layer, the ultimate system pressure is about 3.0×10^{-11} Torr.

The crystal is mounted on a differentially pumped rotatable feed which permits the crystal to be positioned in front of (1) a calibrated glass microcapillary array dosing source; (2) an ion sputtering gun for surface cleaning; (3) a quadropole mass

Fig 2:- Schematic Digital Acquisition ESDIAD system.

spectrometer for mass identification of desorbing species or for temperature programmed desorption(TPD); (4) a cylindrical mirror analyzer for Auger analysis (AES). The single crystal is mounted on tungsten leads, which are used for resistive heating of the crystal. The Ni(110) crystal is typically flashed to 980 K for cleanup between experiments or after sputtering to anneal the sputter damage. The tungsten leads are also nitrogen cooled so that the sample can be cooled to about 83 K, to reduce the chances of thermal desorption.

The electron gun directs a focused beam of low energy electrons towards a metallic single crystal surface containing the adsorbate. The electron stimulated desorption results in positive ions emission in specific angular directions depending on the adsorbate's bonding geometry. These positive ions pass through hemispherical grids and planar grids. The ions then go to the pair of microchannel plates MCP and produce electron pulses. These electron pulses are amplified by a factor of 10^6 and drawn to a resistive anode. Each electron pulse propagates as an expanding ring of charge through the conductive film. This ring of charge is detected as it reaches at each of the four corner of the anode. Since the amplitude of the expanding ring falls off as r^{-1} in a properly edge-terminated thin conductive film detector, the pulse height arriving at each of the four corners is used to calculate the coordinates of the point of impact.

The pulses at the four corners are coupled into four pre-amplifiers labeled A,B,C and D. These amplified pulses then go to the position computer. The position computer then

generates a pair of pulses whose heights are proportional to the x, y coordinates of the impact point of the initial electron pulse on the anode. These x, y pulses are then sent to a pair of the analog-to-digital converters (ADC) that form the dual parameter input to a Nuclear Data 76B multichannel analyser(MCA). The MCA has the capability of displaying the three dimensional ion angular distribution data in a projection on a screen that shows the number of events as a function of the x, y position, yielding the visual and quantitative information with the best achieved resolution of 0.3° .

EXAMPLE:-

The ESDIAD technique has been shown to be direct method for the adsorbate orientation and dynamics. The study of striped oxidized Cu(110) surface showing formation of self organized nano structures was done by John T.Yates, Dan Mocuta, Joachim Ahner, Jae-Gook Lee, Sava Denev at University of Pittsburg in 1999.

The yield and angular directions of the O^+ desorption from the oxide strips on the copper surface, give us the ESDIAD patterns that enable us to get information about the growth and structure of the oxide strips. It even suggests consideration of different parameters in the preparation of theCu-O-Cu-O.... super lattice.

EXPERIMENTAL DETAILS::

The Cu single crystal oriented in the $\langle 110 \rangle$ was taken and cleaned and checked for surface impurity. The experiment was performed in a ultra high vacuum chamber. The crystal could be cooled down 80 K using liquid Nitrogen, and heated up to 900 K by resistive heating. The crystal was exposed to O_2 for adsorbate layer formation.

The crystal surface was exposed to Oxygen and the O^+ ions desorption was stimulated by 10 ns pulses of 0.5mm beam of electrons having ~ 182 eV. The data was collected in three dimensions (x, y, t) where x, y are the co ordinates for the position-sensitive detector while t is the time of flight of the desorbing ion to the detector. This combines ESDIAD with TOF to get more information. A compressing accelerating voltage of 10V is applied between crystal and detector, while angular measurements for the desorbing directions were made under field free conditions.

RESULTS:

The clean crystal at 80 K, was exposed to various amounts of oxygen to observe coverage dependency. And then the surface was heated for higher annealing temperatures up to 773 K, in steps of 25 K and ESDIAD spectra are taken.

Fig 3: The results for different annealing temperatures for the surface with coverage 0.1 ML.

Fig 4:- ESDIAD patterns for O/Cu(110) for increasing O coverage at 80 K.

DISCUSSION:

The dissociative adsorption of oxygen even at 80 K was observed by ESDIAD as well as STM, HREELS, and UPS and it is established that the adsorbed oxygen atoms are most stable at the hollow sites. It has also been well studied fact that at high temperature, the adsorption of oxygen is characterized by forming chains of $\ddot{O}\cdot\text{O}-\text{Cu}-\text{O}-\text{Cu}-\text{O}\ddot{O}$. with the Cu atoms liberated from the defect sites, on top of metal surface.

Fig 5:- The nano structure model for the beam assignment of the ESDIAD patterns.

From the ESDIAD patterns shown in figure 3 we see that at constant coverage the O^+ signal increases linearly with increasing temperature up to about 700 K. But afterwards O^+ desorption starts to decrease with increasing temperature. This is because the chains of ..O-Cu-O.. bonds start to form stripes and become longer and hence immobile on the surface, limiting the rate of escape of Cu atoms from the surface. And also due to constant oxygen coverage, the O^+ desorption signal goes down.

It can be seen from the results (Fig 4) that with increasing oxygen coverage the initial O^+ beam at (≈ 0.02 ML (Fig B (a)) changes into three beam pattern at (≈ 0.05 ML (Fig B (c)) and then to four beam pattern at coverage of 0.1 ML. The four beams represent A and B beam for the oxygen atoms at the edges of the stripe, while the two middle beams C and D for the oxygen atoms in the center of the stripe. As the coverage increases, the width of the stripes increases, and the oxygen atoms at the edges represented by A and B peaks become relatively smaller or remain same, while C and D peaks representing oxygen atoms in the center of stripes become bigger.

The C and D peaks keep growing at higher coverage as the oxygen atoms in the center of the stripes are surrounded four Cu atoms hence experience greater repulsive forces to get easily desorbed.

The ESDIAD-TOF results showed that (a) the oxygen atoms in the stripes have a ten fold greater cross section for the ESD, as compared to the oxygen atoms in the hollow sites. And (b) within the stripes, the oxygen at the edges, have four times greater desorbing probability due to the unbalanced attractive forces. (c) The width of stripes is related linearly with the coverage.

This model of nano structure will be helpful in understanding desorption patterns for other metal adsorbate systems.

ADVANTAGES AND DISADVANTAGES:

ESDIAD is a good technique to study stepped metal surfaces. It gives information about structure of step sites even in the presence of adsorbate layer. Moreover, PSD and SEXAFS can also be used on the same site to obtain further structural information from these sites.

The off-normal emission beams are easily seen in ESDIAD but some high symmetry sites like atop, four fold hollow, or two fold (symmetric) bridge site, eject ions preferentially

along surface normal and this high beam signal along surface normal is not easily distinguished in ESDAID.

The digital ESDIAD apparatus can also be used to perform digital LEED measurements.

BIBLIOGRAPHY AND REFERENCES :

1. The Chemical Physics of Solid Surfaces And Heterogeneous Catalysis ; Vol 2, edited by D.P. Woodruff and D.A. King.
2. Surface Electron Transfer Processes; written by R.J. Dwayne Miller, George L. Mclendon, Arthur J. Nozik, Wolfgang Schmickler, Frank Willig.
3. Chemistry And Physics Of Solid Surfaces; Vol 3, edited by Ralf Vaneslow, Walter England.
4. Desorption Induced by Electronic Transitions DIET I ; edited by N.H. Tolk, M.M. Traum, J.C.Tully, T.E. Madey.
5. "Self Organised nanostructures: an ESDIAD study of the striped oxidized Cu(110) surface"; Dan Mocuta, Joachim Ahner, Jae-Gook Lee, Sava Denev, John T. yates Jr.; Surface Science 436 (1999) 72-82.
6. "Enhancement of the ESDIAD method for imaging the bond directionality in chemisorbed species."; M.D. Alvey, M.J.Dresser, J.T.Yates; Surface Science 169 (1986) 91-103.
7. " Structure of W(111) for NO And O₂ coadsorption studied by ESDIAD."; H.Miki, K. Irokawa, M. Nitta, K. Takeuchi, T.Kioka.; Surface Science 433-435(1999) 272-277.
8. "Measuring Dynamical Behavior Of Admolecules- ESDIAD studies near the zero point";
"; Dan Mocuta, Joachim Ahner, John T. yates Jr.; Surface Science 59 (1998) 167-175.
9. "TOF_ESDIAD measurements of a coadsorbate system: CO on an oxidized Cu(110) surface."; Dan Mocuta, Joachim Ahner, John T. yates Jr.; Surface Science 390 (1997) 126-131.
10. "Dynamical studies of surface species - observing librational motions of adsorbates."; Dan Mocuta, Joachim Ahner, John T. yates Jr, Rex D. Ramsier; Surface Science 386 (1997) 1-9.
11. "Oxygen Chemisorption on Cr(110)"; Theodore E. Madey and Niel D.Shinn; Surface Science 173 (1986) 379-394.

12. "Transmission of low energy (>10 eV) O^+ ions through Au films on TiO_2 (110).";
B. Yakshinsky, M. Akbulut, T.E. Madey; Surface Science 390 (1997) 132-139.

13. Modern Techniques of Surface Science- Second Edition by D.P. Woodruff and T.A. Delchar.

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Assignment by:-

ASMA ZIA

CEM 924

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