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Principal Investigator: John C. Gregory

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ELECTRON SPECTROSCOPY ANALYSIS

Final Report

April 13, 1990 - April 12, 1992

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Surface Science Laboratories
The University of Alabama in Huntsville

UAH SURFACE SCIENCE LABORATORIES

The Surface Science Laboratories at the University of Alabama in Huntsville (UAH) are equipped with x-ray photoelectron spectroscopy (XPS or ESCA) and Auger electron spectroscopy (AES) facilities. These techniques provide information from the uppermost atomic layers of a sample, and are thus truly surface sensitive.

The XPS instrument is a Perkin-Elmer 5400 system. XPS provides both elemental and chemical state information without restriction on the type of material that can be analyzed. The sample (up to 1.00 inch in size) is placed into an ultra high vacuum (UHV) chamber and irradiated with x-rays which cause the ejection of photoelectrons from the sample surface. $MgK\alpha$ and $AlK\alpha$ are the standard sources available on the 5400 system, but a Zr $L\alpha$ anode may also be used on the UAH instrument. Since the kinetic energy of these emitted electrons is characteristic of the elements from which they were ejected, the position and intensity of the peaks in an energy spectrum provide the desired analytical information. The chemical state of an atom alters the binding energy of a photoelectron and thus its emitted kinetic energy. Thus, bonding information is derivable from these chemical shifts and also from the shapes of the peaks. Since x-rays do not normally cause charging problems or beam damage, XPS is applicable to a wide range of samples including metals, polymers, catalysts and fibers. Samples can be analyzed to as small an area as $200\mu m$ using the "small area" XPS system.

The AES instrument is a Kratos Analytical XSAM 800 system. AES uses a beam of high energy electrons as a surface probe. Following electronic rearrangements within excited atoms by this probe, Auger electrons characteristic of

each element present are emitted from the sample. As in the case of the x-ray photoelectrons, only those Auger electrons which emerge from the topmost atomic layers contribute to the spectrum, hence the high surface specificity of this technique. AES detects all elements other than hydrogen and helium usually to a sensitivity better than 1 atom percent of a monolayer. The main advantage of electron induced AES is that the electron beam can be focussed down to a small diameter and localised analysis can be carried out. The electron gun on the XSAM 800 can be focused to produce a beam of diameter 1000\AA , allowing high spatial resolution analyses, otherwise known as scanning Auger microscopy (SAM), to be performed. On the rastering of this beam synchronously with a video display using established scanning electron microscopy techniques, physical images and chemical distribution maps of the surface can be produced. Thus very small features, such as electronic circuit elements or corrosion pits in metals, can be investigated.

Facilities are available on both XPS and AES instruments for depth-profiling of materials, using a beam of argon ions to sputter away consecutive layers of material to reveal sub-surface (and even semi-bulk) analyses. Generally, AES is the preferable technique for such work, since its spatial resolution capacity is much better.

For further information on facilities available at the UAH Surface Science Laboratories contact Dr. J. C. Gregory at 895-6028 or Dr. G. N. Raikar at 895-6076.

Techniques Used:

X-ray Photoelectron Spectroscopy

Principles of the Technique

Surface analysis by x-ray photoelectron spectroscopy (XPS), more commonly known as Electron Spectroscopy for Chemical Analysis (ESCA), is accomplished by irradiating a sample with monoenergetic soft x-rays and energy analyzing the electrons emitted. Mg K α x-rays ($h\nu = 1253.6$ eV) or Al K α x-rays ($h\nu = 1486.6$ eV) are normally used. These photons have a limited penetrating power in a solid, of the order of 1-100 Å. They interact with atoms in this surface region by the "photoelectric effect", as shown in the upper part of Diagram 1, causing electrons to be emitted. The emitted photoelectrons have kinetic energies given by:

$$KE = h\nu - BE - \phi_s$$

where $h\nu$ is the energy of the x-ray photon, BE is the binding energy of a core electron (i.e. inner shell electrons), and ϕ_s is the spectrometer work function. The photoelectrons originating from K, L, M shells are designated as 1s, 2s and 2p, 3s and 3p (also 3d) etc in the figures.

After such a core electron is emitted, an inner shell ionized atom is left and this has two possible methods of relaxing. The most probable method of relaxation is via the radiationless emission of an electron (called the Auger effect) and is shown in the bottom part of Diagram 1. The inner K shell vacancy can be filled by an L_{II} electron whilst an L_{III} electron is emitted to remove the excess energy. The released electron is an "Auger electron" and in the above example it is designated as KL_{II}L_{III} Auger electron. The other relaxation process is via the well known "x-ray fluorescence

effect" in which an electron from an outer shell moves to fill the vacancy and a quantum of x-ray energy is released to remove the excess energy. However, the probability of such a process occurring is very low in comparison to Auger effect.

For the present analysis Mg source were used. Unless specifically noted within the text, survey scans were acquired using an analyzer pass-energy of 89.45 eV, whilst high resolution narrow/multiplex scans were acquired using an analyzer pass-energy of 35.75 eV. Analysis is done in the "large aperture" mode, i.e. the energy analyzer accepting electrons from an area of 1.0 mm².

For Scanning Auger Microscopy measurements, a 5 keV electron gun was used on the XSAM 800 system which provides excellent energy resolution. The principle of operation of this system is the same as described above.

The typical spectrometer (both ESCA and XSAM800) operating conditions include:

System base pressure: $\sim 10^{-9}$ Torr

X-ray gun power : 200 watts

Electron gun voltage: 3-5 keV and Filament Current = 2.8 Amps

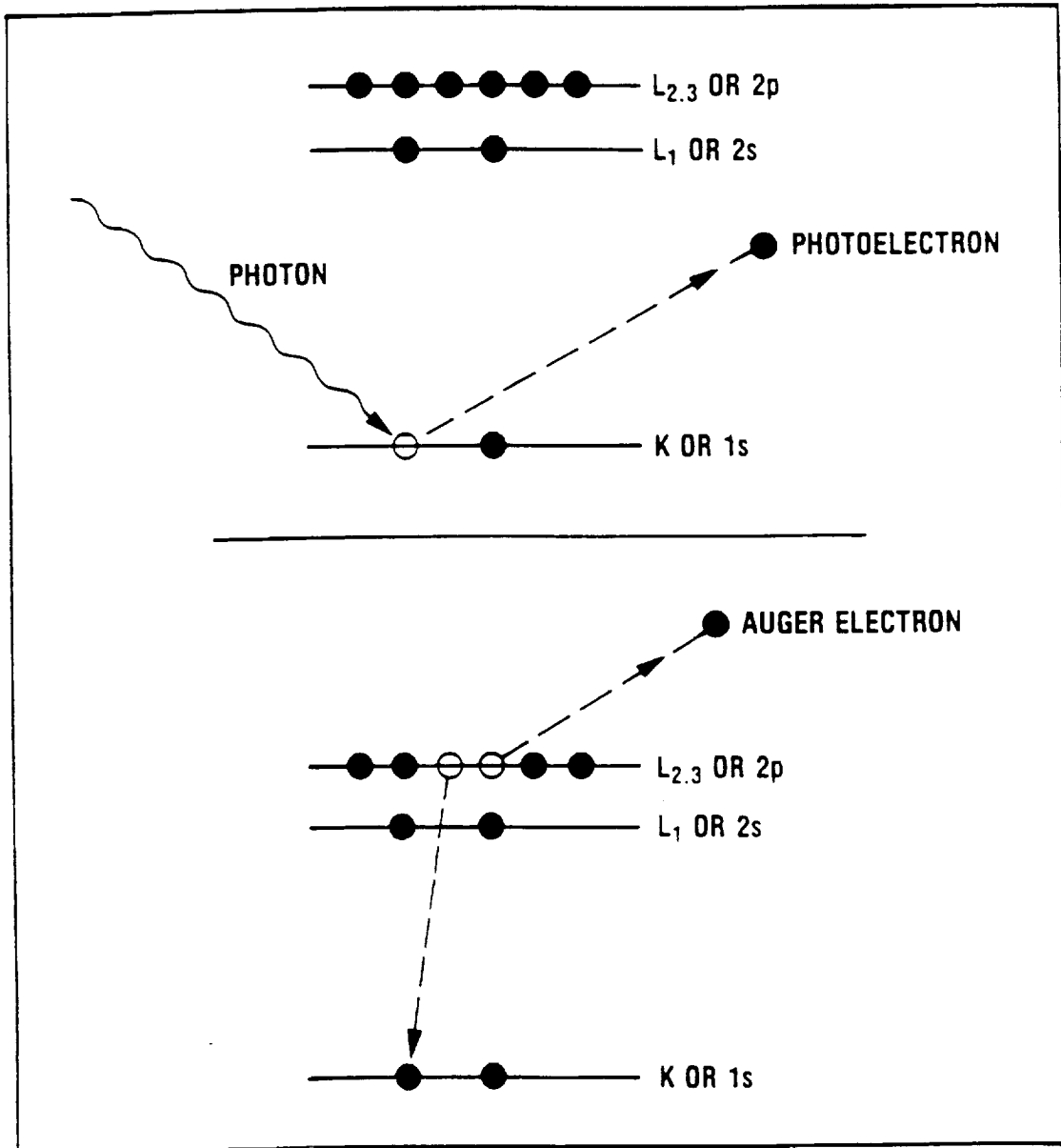


Diagram of the photoelectric process (top) and the Auger process (bottom).

Below is a summary of the samples delivered for XPS analysis. Detailed analysis reports were submitted when the samples were returned to MSFC. For each sample, the first page showed a wide survey scan. The next pages presented the quantitative chemical analysis in atomic percent followed by high resolution scans on each of the major component which showed the area used for the quantitative determination of atomic concentrations. Summary tables of atomic concentrations for the samples were appended following each report.

May - June, 1990

Two samples were delivered to UAH and XPS analysis was performed. The spectra and analysis were transmitted directly to EH12 personnel.

July - October, 1990

No samples were delivered and none analyzed during this reporting period. An upgrade of the XPS system was performed in September with the installation of an improved x-ray source cathode assembly.

January, 1991

Five samples were delivered in January by Dr. R. Linton from the Materials and Processes Laboratory at Marshall Space Flight Center. The polymer and silver samples were analyzed using X-Ray Photoelectron Spectroscopy.

- Tefzel - unexposed
- Tefzel - exposed
- Polysulfone - unexposed
- Polysulfone - exposed
- Silver - contaminated

May, 1991

The following materials were received from Marshall on May 10 for analysis. MSFC prepared some of the materials by cutting them into three peices each to facilitate sample mounting. Samples were mounted on May 13 and analysis was performed shortly thereafter. A total of nine (9) samples were analyzed.

1. Si-5658- analysis on central region of the material
2. S13GA- analysis on a central region of the disk that appeared brown in color
3. S13GB- analysis on an edge region of the disk that appeared white in color
4. H23A- analysis on the center of the bottom side of the halar material
5. H23B- analysis on the center of the top side of the halar material
6. H23C- analysis on the center of the edge side of the halar material
7. RTV511A- analysis on the center of the bottom (white) side of the polymer
8. RTV511B- analysis on the center of the top (brown) side of the polymer
9. RTV511C- analysis on the center of the edge (brown) side of the polymer

July 8, 1991

The following materials were received from MSFC for analysis:

- | | | |
|-----|---------|--|
| 1. | viton1u | viton 747 sample 1-10 unexposed (back) side |
| 2. | viton1x | viton 747 sample 1-10 exposed (front) side |
| 3. | viton2u | viton 747-1 sample psi#111 unexposed (back) side |
| 4. | viton2x | viton 747-1 sample psi#111 exposed (front) side |
| 5. | viton3u | viton sample 111L unexposed (back) side |
| 6. | viton3x | viton sample 111L exposed (front) side |
| 7. | si383a | silicon rubber sts 41 sample s-383(a) |
| 8. | si383r | silicon rubber baked out reference |
| 9. | halarr | halar reference sample |
| 10. | rtv511r | rtv511 reference sample |

November, 1991

The following materials were received from Dr. Roger Linton on Nov 7, 1991, for ESCA analysis. The requested area of interest was in the center of all the specimens and the information sought was the identification of foreign contaminants.

1. Gold film on quartz substrate, Specimen # 01-42
2. Aluminum disk, Specimen # 01-41
3. SiO/ Al / pyrex mirror, Specimen # 01-51
4. SiO/ Al / pyrex mirror, Specimen # 01-54

Please note that a high resolution scan (Pass energy =8.95 eV) on the valence band of Au sample was obtained to seek evidence for oxidation. When compared with the spectrum of "Auric oxide" (Au_2O_3) from literature, there appears to be NO evidence for oxidation on this sample. This spectrum was appended following the technical report.

November 14, 1991

The following materials were received from Dr. Roger Linton on Nov 14, 1991, for ESCA analysis. The requested area of interest was in the center of all the specimens and the information sought was the identification of foreign contaminants.

1. SiO/ Al / pyrex mirror, Specimen # 02-51
2. SiO/ Al / pyrex mirror, Specimen # 02-21
3. SiO/ Al / pyrex mirror, Specimen # 01-44
4. SiO/ Al / pyrex mirror, Specimen # 01-13

December, 1991

The following samples were received from Dr. Roger Linton on Dec 14, 1991, for ESCA analysis. The requested area of interest was in the center of the SiO/Al/Pyrex specimens and the X [Mo/ Au/ pyrex] and Y [Au/pyrex] regions of the Au thin film sample. The information sought was the identification of foreign contaminants.

1. Au thin film: X region [Mo/Au/ pyrex]
2. Au thin film: Y region [Au/ pyrex]
3. SiO/ Al/ pyrex mirror, Specimen # cm-01-45
3. SiO/ Al/ pyrex mirror, Control, Specimen # 2
5. SiO/ Al/ pyrex mirror, Control, Specimen # 5

The Au sample was thoroughly investigated in the two regions, called X [Mo/Au/ Pyrex] and Y [Au/ Pyrex]. It showed that there is more Au and Mo in the region Y than in X.

January, 1992

The following samples were received from MSFC for ESCA analysis.

1. MgF2 Mirror, PPPL: Exposed Region
2. MgF2 Mirror, PPPL: Unexposed Region
3. MgF2 Mirror, PPPL: Unexposed Region 2
4. MgF2 Control: Mirror side
5. MgF2 Control: Reverse side
6. Vanadium #1, PPPL: Exposed Region
7. Vanadium #1, PPPL: Unexposed Region
8. Vanadium #1, PPPL: Reverse side
9. Rhodium, PPPL: Exposed Region
10. Rhodium, PPPL: Unexposed Region

February, 1992

The following samples were received from Dr. Roger Linton for ESCA analysis. The requested area of interest was in the center of the SiOx/Al/Pyrex specimens. The information sought was the identification of foreign contaminants.

1. SiOx/ Al/ pyrex mirror, Specimen # cm-01-15
2. SiOx/ Al/ pyrex mirror, Specimen # cm-01-31
3. SiOx/ Al/ pyrex mirror, Specimen # cm-01-55

March, 1992

The following samples were received from Dr. Ann Whitaker for ESCA analysis. The requested area of interest was in the CONTROL (Unexposed) and Exposed Region. The information sought was the identification of foreign contaminants and possibly to identify Oxide/Oxides and determine thicknesses.

1. Sample # A0171-IV-66, HOS 875 (Exposed Region)
2. Sample # A0171-IV-66, HOS 875 (Unexposed Region)
3. Sample # A0171-IV-53, Mo (Exposed Region 1)
4. Sample # A0171-IV-53, Mo (Exposed Region 2)
5. Sample # A0171-IV-53, Mo (Exposed Region 3)
6. Sample # A0171-IV-53, Mo (Unexposed Region)
7. Sample # A0171-IV-52, Mg (Exposed Region)
8. Sample # A0171-IV-52, Mg (Unexposed Region)
9. Sample # A0171-IV-47, Nb (Exposed Region)
10. Sample # A0171-IV-47, Nb (Unexposed Region)

Please note that identifying the nature of oxide/oxides species on these surfaces and requires extensive curve fitting of the oxygen peaks. To determine the thickness of the oxide layer, depth profiling, which could damage the surface due to Ar ion etching, is recommended. Angle resolved XPS, which is non-destructive and quite time consuming, could be performed to get a rough estimate of the thickness.

April, 1992

The following samples were received from Dr. Roger Linton for ESCA analysis. The requested area of interest was in the center of the SiOx/Al/Pyrex specimens. The information sought was the identification of foreign contaminants.

1. Sample # cm-02-14, SiOx / Al / Pyrex
2. Sample # cm-01-24, SiOx / Al / Pyrex
3. Sample # cm-01-52, SiOx / Al / Pyrex
4. Sample # cm-02-55, SiOx / Al / Pyrex
5. Sample : SiOx / Al / Pyrex (Region 1)
6. Sample : SiOx / Al / Pyrex (Region 2)