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A SCANNING PHOTOELECTRON MICROSCOPE (SPEM) AT THE NSLS

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Abstract

We are in the process of developing and commissioning a scanning photoelectron microscope (SPEM) at the X1A beamline of the National Synchrotron Light Source (NSLS). It is designed to make use of the Soft X-ray Undulator (SXU) at the NSLS. This high brightness source illuminates a Fresnel zone plate, which forms a focused probe, $\leq 0.2\mu$m in size, on the specimen surface. A grating monochromator selects the photon energy in the 400 - 800 eV range with an energy resolution of better than 1 eV. The expected flux in the focus is in the $5 \times 10^7 - 10^9$ photons/s range. A single pass Cylindrical Mirror Analyzer (CMA) is used to record photoemission spectra, or to form an image within a fixed electron energy bandwidth as the specimen is mechanically scanned.

As a first test, a 1000 mesh Au grid was successfully imaged with a resolution of about 1μm and the CMA tuned to the Au 4 f photoelectron peak. Once it is commissioned, a program is planned which will utilize the microscope to study beam sensitive systems, such as thin oxide/sub-oxide films of alumina and silica, and ultimately various adsorbates on these films.

I. Introduction

Our experimental knowledge of the physics of surfaces has been based generally on data gathered from single crystal surfaces, both in the clean state and with thin layers of gaseous or solid adsorbates. The often heroic efforts required to prepare pure single crystals for these studies arise in part from the fact that in most cases both the excitation source (photons, electrons, ions) and the detector (photons, electrons, ions) spatially average over an area ranging in size from 1 to a few mm^2. The ability to produce either a source or a detector that spatially averages over a much smaller area of the surface (e.g. less than 1 μm^2) opens up a whole new area of the solid state physics of 'real' surfaces: polycrystalline surfaces, nonuniform adsorbates, impurities, grain boundaries, small particles, etc.

To date, of the mainstream surface science techniques only Secondary Ion Mass Spectroscopy (SIMS) and Scanning Auger Microscopy (SAM) have achieved spatial resolution of about 50 nm, whereas the spatial resolution of photoelectron spectroscopy has been limited to tens of μm, due to the lack of focusing optics and/or appropriate sources. In addition to our instrument, other efforts are under way to achieve high spatial resolution photoelectron spectroscopy, using various techniques in several laboratories [1] [2] [3] [4].

II. XPS Microprobe

Our instrument uses a Fresnel zone plate to provide a finely focused beam of X-rays. The zone plate (ZP) is a circular diffraction grating that acts like a lens for its various diffractive orders. The size of the diffraction limited focus depends on the outermost zone width and is therefore determined by practical fabrication limits. Presently spots as small as 50 nm have been achieved with ZPs with 40 nm outermost zone width [5] [6]. However, we do not use the highest resolution ZPs available to us, since their focal lengths are too short and do not allow enough working distance. We therefore employ a ZP with a diffraction limited resolution of 120 nm and about 8 mm focal length, and will soon upgrade to a ZP with 85 nm resolution and 5.5 mm focal length. This corresponds to a working distance of about 2 mm. The ZP is illuminated by the output of a Spherical Grating Monochromator (SGM), which in turn is illuminated by the Soft

X-ray Undulator of the National Synchrotron Light Source. The SPEM will operate in the photon energy range of 400 to 800 eV, with $\frac{E}{\Delta E}$ as high as 1200, and an expected flux of 1×10^8 photons/s/0.1%BW/200mA into the focus for diffraction limited imaging. This flux can be increased by decreasing spatial and energy resolution. For example, if we use the ZP with 85nm spatial resolution and relax it to 0.25 μm we gain almost an order of magnitude in flux.

The schematic diagram of the apparatus is shown in Fig.1. The ZP is coaxially mounted on the front of a Cylindrical Mirror Analyzer (CMA) such that both foci coincide. This allows a photoelectron spectrum to be taken with the CMA for a fixed spot on the sample, or the sample can be mechanically scanned through the focus at a fixed electron energy to form an image. Details of the beamline and the apparatus will be described elsewhere [7].

By operating in the VUV/soft x-ray photon energy range from 400 to 800 eV, the K-shells of elements up to fluorine can be reached, including the elements carbon, nitrogen and oxygen. In addition, the L-shells up to cobalt can be explored, including silicon and most of the third row transition metals. In particular, access to the K-shells of oxygen and carbon allows us to measure their chemical shifts in various materials. This leads to the possibility of investigating easily damageable oxides and polymers with high lateral resolution.

III. Initial Tests and First Results

The principal components of the instrument underwent tests separately prior to installation in SPEM. The mechanical stage was tested on a bread board with a laser interferometer. It showed a resolution of 16 nm and a repeatability of 60$\pm$15 nm during a time span of a few hours over a field of view of 140μm. A ZP with a nominal zone width of 100nm was tested at the Scanning Transmission X-ray Microscope at X1A with 354 eV photons and found to be close to expectations: a 7% efficiency and a resolution better than 150 nm. The CMA was modified to allow the photons free travel through its center and was successfully operated in retarding mode. A more detailed description of the stage and the modifications to the CMA is given elsewhere [7].

To test the ZP at the photon energy we anticipate to use most frequently (680 eV)

together with the scanning stage, we imaged a thin sample masked by a 50μ pinhole. The transmitted flux was used to form the image. As the line scan across the edge of the pinhole in Fig.2 shows, images in transmission already demonstrate a spatial resolution of 0.5μm, as determined by the 25-75% rise in intensity across the edge. The efficiency of the Zp was determined to be about 8%.

To include the CMA in the tests, we mounted a partially backed grid as the specimen. This way, both X-rays transmitted through the openings and electrons photoemitted from the specimen and the sample mount could be used to determine resolution, flux and contrast. Fig.3 shows the mesh as viewed in transmission, with the dark part to the left being the mount totally blocking the photons. Fig.4 is our very first photoelectron micrograph. It shows the part of the same mesh that is supported by the stainless steel mount. The CMA was used to select primary photoelectrons to form the image. The resolution demonstrated by these images is only on the order of 1μm. They were taken without vibration isolation, and without optimizing the throughput of the system. We are confident that we can improve the performance significantly. In particular, the implementation of active vibration isolation should bring the spatial resolution below the 0.2μm level.

IV. Future Experiments

Once we are satisfied with the performance of the microscope we intend to turn our attention to thin film aluminas. This system has both enormous complexity in the chemistry of its various phases, and even greater technological significance. In keeping with its relevance, the field has been the subject of intense experimental and theoretical investigation with an extensive literature reviewed by several authors [8] [9] [10], yet little is known about the details of the electronic and geometric structure of these materials.

The field is steeped in a lore which is related to the presence and function of surface hydroxyls in mediating various reactions. The pioneering theoretical work of Knozinger, et al. [10] suggested that specific types of hydroxyl sites should be the dominant structures on particular alumina phases. These sites are related not only by the coordination of the hydroxyls with respect to the aluminum atoms (tetrahedral

vs. octahedral) but by the relationship of these groups to each other and to cation vacancies.

As a practical matter it is difficult, if not impossible, to prepare a completely uniform alumina surface. To date, the inhomogeneity of these surfaces has not been directly examined for the various alumina phases in their native growth habit. TEM investigations of films removed from their substrates have generated interesting data [11] which reveal crystalline domains joined by amorphous material, but measurements of this nature cannot provide direct chemical information about these different phases or interface regions between phases. They do, however, show that the scale of these microcrystalline regions is on the order of 500 nm and can be increased by various sample preparation methods [12]. Information about the chemistry of these distinct regions has not been obtained by electron microscopic examination for two major reasons: First, the specimen preparation for transmission techniques requires the removal (by amalgamation) of the aluminum substrate from beneath the alumina film, which severely distorts the chemistry of the alumina film. Second, there is a demonstrated tendency for electron beams to modify the structure and chemistry of alumina surfaces [13] [14]. Both problems will be eliminated with SPEM, since we will use photon excitation and detect electrons emitted from the alumina surface on a thick substrate.

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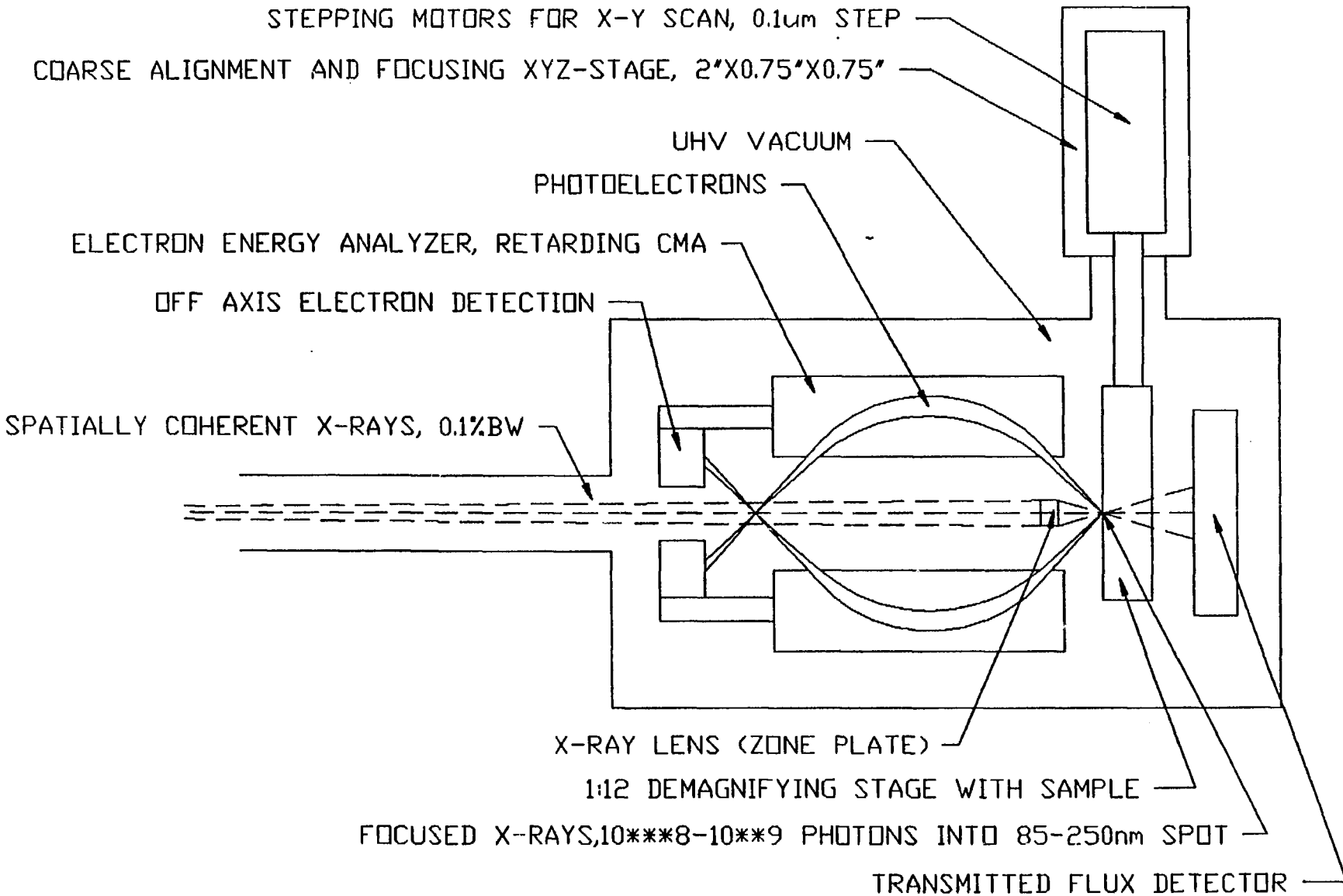
Figure Captions

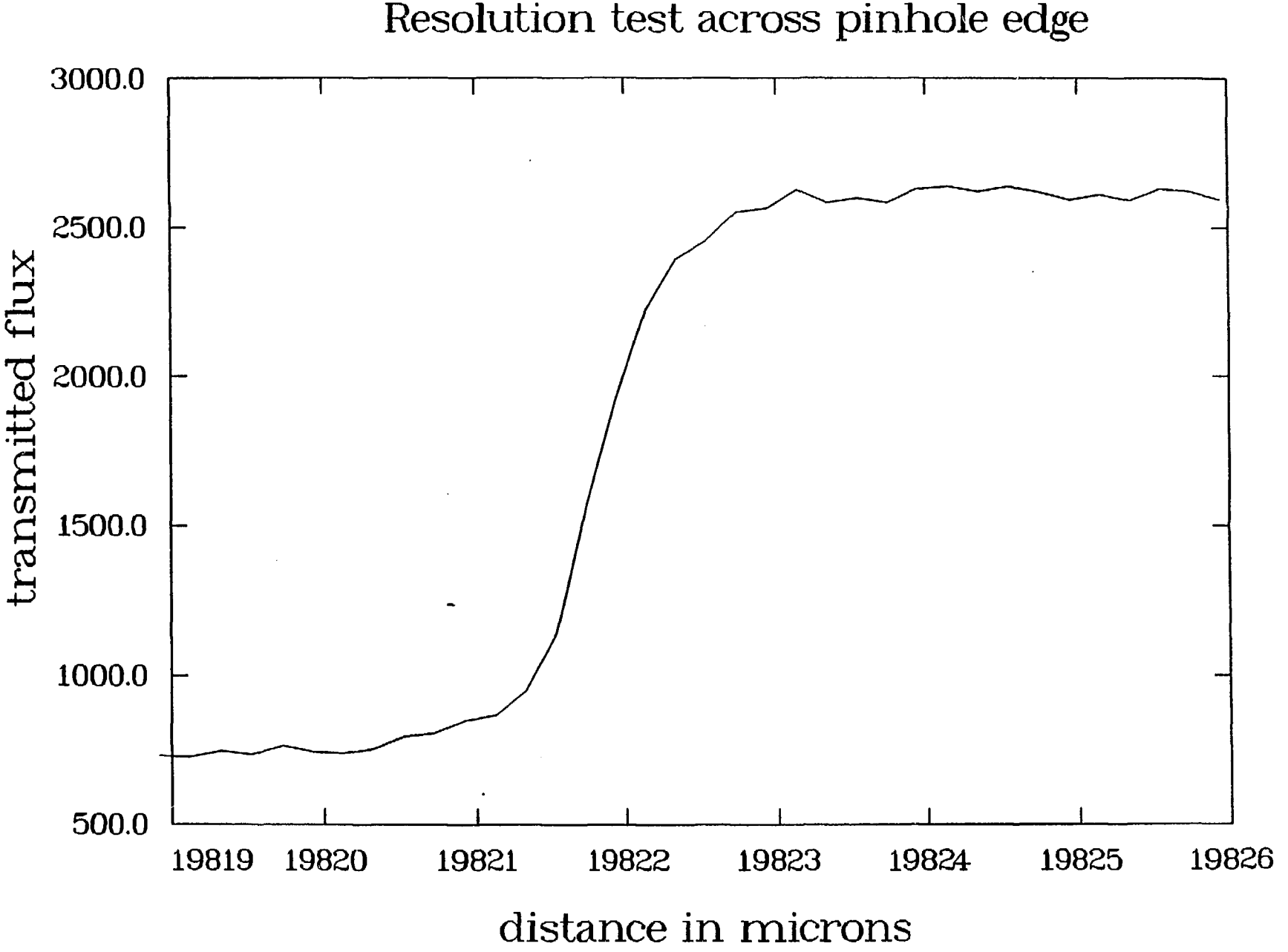
Fig1.: Schematic of the Scanning Photoelectron Microscope. X-rays in the energy range of 400-800eV are focused by a zone plate to a small spot on the sample. The energy of the generated photoelectrons is analyzed by a CMA electron spectrometer.

Fig.2. Line scan of transmitted flux across the edge of a pinhole. From the sharpness of the edges as determined by the 25-75% rise in intensity, we determine the resolution to be about 0.5μm.

Fig.3: Picture of a 1000 mesh Au grid taken in transmission just prior to the image shown in Fig.4. From the sharpness of the edges and the power spectrum of the image, we determine the resolution to be about 0.8μm. The opaque region to the right is the sample mount.

Fig.4: First core photoelectron micrograph of the same Au mesh as in Fig.3 and the same optical configuration, taken in the sample region where the mesh was backed by the stainless steel mount. The CMA was tuned to the Au 4f core lines and the photon energy was 680 eV. The pixel size is 1μm.


STEPPING MOTORS FOR X-Y SCAN, 0.1um STEP
COARSE ALIGNMENT AND FOCUSING XYZ-STAGE, 2"X0.75"X0.75"
UHV VACUUM
PHOTOELECTRONS
ELECTRON ENERGY ANALYZER, RETARDING CMA
OFF AXIS ELECTRON DETECTION
SPATIALLY COHERENT X-RAYS, 0.1%BW
X-RAY LENS (ZONE PLATE)
1:12 DEMAGNIFYING STAGE WITH SAMPLE
FOCUSED X-RAYS,10***8-10**9 PHOTONS INTO 85-250nm SPOT
TRANSMITTED FLUX DETECTOR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2500.0
2000.0
1500.0
1000.0
500.0
transmitted flux
19819
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distance in microns