Development of a Novel Elemental Analysis Method Based on NC-AFM in Combination with SR X-Rays

Scanning probe microscopy is one of the representative techniques used in modern surface science to observe surface structures at the atomic level; however it does not provide elemental analysis. Many attempts have been made to address this issue. We originally constructed a non-contact atomic force microscopy (NC-AFM) system in combination with a SR X-ray irradiation technique. We found the novel phenomenon that the force observed in NC-AFM was strongly affected by X-ray irradiation, especially when tuned to the energy of a sample surface. An important point is that the force change does not follow the absorption spectrum of the surface element. This finding can potentially lead to the development of a chemically sensitive NC-AFM.

Recent progress in the nanotechnologies shows that elemental analysis at the atomic level is a prerequisite for developing more precise nano-devices, nano-catalysts, and nano-sensors. Scanning probe microscopy (SPM) techniques such as scanning tunneling microscopy (STM) and non-contact atomic force microscopy (NC-AFM) are particularly powerful tools for observing surface structures at the atomic level. The evolution of these techniques is accelerating, and their application is expanding to liquid and electrolyte surfaces. Nevertheless, the techniques have the disadvantage that they do not provide chemical analysis. Recent successful progress in STM combined with synchrotron X-rays [1, 2] show prospects for the future acquisition of STM images of conducting sample surfaces at the atomic level with elemental information. But the story is still restricted to conducting samples, and there is no direct way to distinguish each atom with element-specificity on insulator surfaces such as oxides and nitrides.

In order to develop methods which can be applied to insulating surfaces, we proposed a new approach; X-ray Aided Non-contact Atomic Force Microscopy (XANAM) [3, 4]. The method combines NC-AFM with synchrotron X-rays. We have found a novel phenomenon during investigation of the interaction between the force of NC-AFM and the X-ray energy, which we expect to form the basis for a chemically-sensitive NC-AFM technique. Figure 1(a) shows the instrument installed at BL-7C, with a diagram of the system configuration given in Fig. 1(b). The instrument consists of two ultrahigh vacuum chambers; an AFM chamber and a pre-treatment chamber. The atomic force microscope is mounted on a high-precision mobile stage with three translational axes and a rotational axis to allow adjustment of the sample position relative to the X-ray pathway. All motion is controllable from outside of the X-ray protection hutch. The X-rays are focused along the sagittal direction by the monochromator crystal. After passing through a 1 mm diameter pinhole set in front of the I0 ionization chamber, the X-rays are introduced into the AFM chamber through a Be window and irradiate the sample surface at a glancing angle. The sample used was a Si wafer with Au islands.

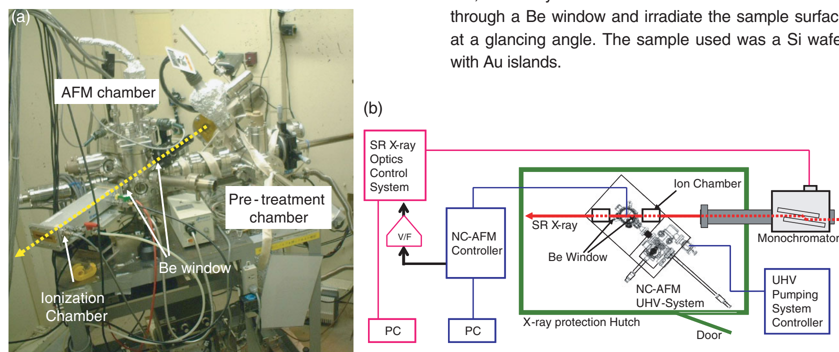

Figure 1
(a) Photograph of the XANAM chamber installed in the X-ray protective hutch at BL-7C of the PF. (b) Diagram of the experimental configuration.

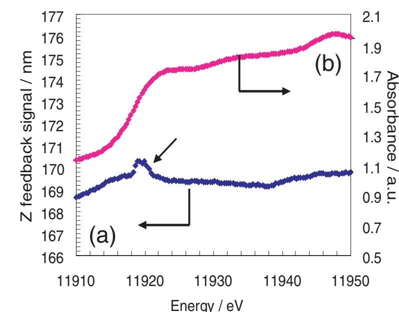

Figure 2
a) Spectrum of the attractive force (Z feedback signal) vs X-ray energy around the Au L_3 adsorption edge energy on a Au deposited sample surface b) Separately measured absorption spectrum of Au foil.

Figure 2(a) shows typical data in which a peak clearly appeared near the Au L_3 X-ray absorption edge energy (shown by an arrow in the figure). Such a change was not observed for a bare Si sample [3]. An important point is that the force change does not follow the absorption spectrum of the surface element. This finding is important for understanding this novel X-ray-induced phenomenon. We propose the mechanism that the X-ray-induced attractive force change involves a core electron transition to a bonding or an anti-bonding orbital of the covalent bond between the cantilever tip and the sample surface [5], and thus the attractive force between the tip and the sample changes around a certain X-ray energy. Further improvements have been made to establish more stable operation, which will contribute to uncovering the XANAM mechanism.

REFERENCES

[1] T. Eguchi, T. Okuda, T. Matsushima, A. Kataoka, A. Harasawa, K. Akiyama, T. Kinoshita and Y. Hasegawa, *Appl. Phys. Lett.*, **89** (2006) 243119.
[2] A. Saito, J. Maruyama, K. Manabe, K. Kitamoto, K. Takahashi, K. Takami, M. Yabashi, Y. Tanaka, D. Miwa, M. Ishii, Y. Takagi, M.A. Kasaya, S. Shin, T. Ishikawa, Y. Kuwahara and M. Aono, *J. Synchrotron Rad.*, **13** (2006) 216.
[3] S. Suzuki, Y. Koike, K. Fujikawa, W.-J. Chun, M. Nomura and K. Asakura, *Chem. Lett.*, **33** (2004) 636.
[4] S. Suzuki, M. Nakamura, K. Kinoshita, Y. Koike, K. Fujikawa, N. Matsudaira , W.-J. Chun, M. Nomura and K. Asakura, *J. Phys. Conf. Ser.*, **61** (2007) 1171.
[5] S. Morita, R. Wiesendanger and E. Meyer, *Non-contact Atomic Force Microscopy* (Berlin: Springer, 2002).

BEAMLINE

7C

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Evaluation Experiments of the Direct-sensing X-Ray HARP-FEA Detector

We have developed prototype X-ray high-gain avalanche rushing amorphous photoconductor (HARP) - field emitter array (FEA) detectors. Using beamlines at the Photon Factory, the basic properties of the prototypes were evaluated, including spatial resolution, image quality, sensitivity, and dynamic range. The results confirm that the X-ray HARP-FEA detector is an attractive candidate for the next generation of X-ray area detectors.

We have developed prototypes of the HARP-FEA detector, the principle behind which is shown in Fig. 1. Electrons and holes generated by X-rays in the HARP membrane (15 μm thickness) move toward the electrodes according to their polarity under the applied electric field, which has a magnitude of greater than 80 V/μm. Collisions with atoms within the membrane generate additional electron-hole pairs, eventually leading to avalanche multiplication. One of the attractive features of avalanche multiplication is that it offers a better signal-to-noise ratio than for example pre-amplifier amplification. Another benefit of the HARP detector is its direct-sensing feature, and it may be possible to develop an ideal detector satisfying all of the following requirements: high-sensitivity, high spatial resolution and high frame rate.

Accumulated charges at the HARP membrane are read out by electron beams from the FEA, which includes an active readout circuit. The FEA is compact (see Fig. 1) compared with conventional heat electron tubes. The HARP-FEA detector was assembled with an original camera, and the signals were fed into the camera control unit (CCU) which is equipped with an A/D converter. The digital signals were then recorded using original recording software. The frame rate is fixed to the NTSC-TV standard of 30 frames/sec. The pixel size is 20 μm (H) × 20 μm (V), and the number of pixels is 640 (H) × 480 (V). The effective area was small (12.8 mm (H) × 9.6 mm (V)), but this should be increased to more than 20 mm (H) × 20 mm (V) for applications such as medical imaging.

The evaluation experiments, as well as the application experiments reported in references [1] and [2], were performed at BL-5A and BL-17A for low X-ray energies (6-14 keV), BL-14B for medium energies (10-17 keV, see Fig. 2), and at BL-14C1 and AR-NE5A for high energies (20-80 keV). The results are the following:

(1) Spatial resolution was evaluated using an X-ray test chart. A 20-line pairs/mm slit pattern could be recognized, meaning that the spatial resolution of the HARP detector was 25 μm or better.

(2) As for image quality, initially there were many noise spots, termed “white damage”. Eventually these damage spots were reduced to only a few spots by improving the membrane manufacture technique.

(3) The sensitivity and dynamic range were compared to those of a CCD detector (Photonic Science XDI). The results are shown in Fig. 3. With an avalanche gain of 10, the sensitivity of the HARP detector was better than that of the CCD detector. However the dynamic range of the HARP detector was only about 9 bits, narrower than that of the CCD. Typically, a dynamic range of 13-14 bits is required for protein crystallography.

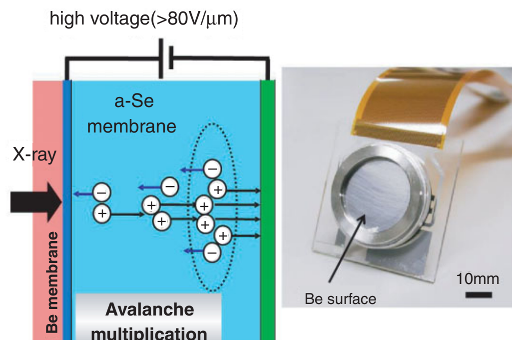

Figure 1
(Left) principle of the HARP detector and (right) photograph of a prototype HARP-FEA detector.

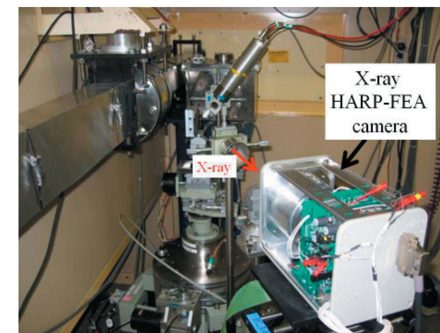

Figure 2
Experimental setup at BL-14B.

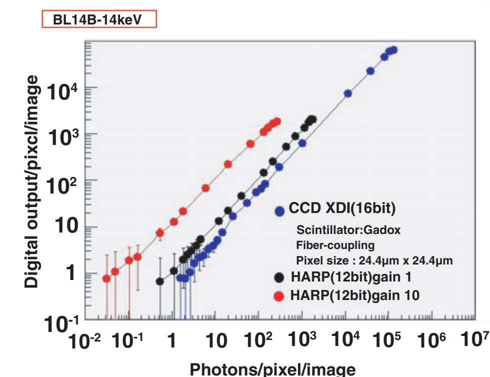

Figure 3
Relationship between the number of photons and the digital output of the detectors.

In summary, the series of evaluation experiments of the HARP detector revealed that the detector satisfies some of the requirements for next-generation X-ray detectors, namely high sensitivity, high spatial resolution, and a frame rate of 30 frames/sec. Although other properties such as dynamic range and effective area must be improved for various X-ray applications, we have confirmed that at the prototype level the HARP-FEA detector is an attractive candidate for a next-generation X-ray area detector.

This work was funded by the ‘Development of Systems and Technology for Advanced Measurement and Analysis’ program (FY2004-2007) of the Japan Science and Technology Agency (JST).

REFERENCES

[1] T. Miyoshi, N. Igarashi, N. Matsugaki, Y. Yamada, K. Hirano, K. Hyodo, K. Tanioka, N. Egami, M. Namba, M. Kubota, T. Kawai and S. Wakatsuki, *J. Synchrotron Rad.*, **15** (2008) 281.

[2] K. Hirano, T. Miyoshi, N. Igarashi, T. Takeda, J. Wu, T.-T. Lwin, M. Kubota, N. Egami, K. Tanioka T. Kawai and S. Wakatsuki, *Phys. Med. Biol.*, **52** (2007) 2545.

BEAMLINE

5A, 14B, 14C1, 17A and AR-NE5A

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Quick X-Ray Refelctometer in Simultaneous Multiwavelength Dispersive Mode

A new type of X-ray reflectometer has been developed, which will enable time-resolved X-ray reflectivity measurements of thin film and multilayer specimens as they undergo structural changes under external stimuli. The entire profile of the reflectivity curve of interest is measured at once as a function of X-ray energy using a convergent X-ray beam having a one-to-one correlation between its energy and direction. X-ray reflectivity curves from a rotating specimen were recorded successively every five-eighths of a second with an exposure time of 20 ms, demonstrating the potential of this method for sub-second to millisecond time resolved X-ray reflectivity measurements.

X-rays are specularly reflected when they are incident on surfaces of materials at a small glancing angle, typically less than 1 degree. Such X-rays penetrate into the material with a depth ranging from several to a few hundred atomic layers. Thus, by analyzing the X-ray reflectivity curve, atomic scale information is obtained on the surface layer thickness, the electron density distribution along the surface normal, and the surface and interfacial roughness for thin-film and multilayer samples such as semiconductor insulating layers, magnetic recording materials, and polymer films. The X-ray reflectivity curve is represented as a function of a quantity given by $q = 4\pi\sin\theta/\lambda$, where θ is the glancing angle and λ is the wavelength of X-rays. In the conventional method, the reflected intensity of monochromatic X-rays is recorded as a function of glancing angle, requiring step-by-step rotation of the sample and the detector. Typical data collection times using this method are from a few to ten minutes. In another method called the energy-dispersive method, a white X-ray beam is incident on the specimen at a fixed glancing angle and the spectrum of reflected X-rays is measured as a function of X-ray energy E (inversely proportional to λ) using an energy-dispersive solid-state detector. The data collection time is limited by the counting speed of the detector, and it usually takes from a few tens of seconds to a few minutes to collect the data. Hence, most applications of X-ray reflectometry to date have been limited to studies of specimens in static or slowly changing (minutes to hours) states, due to the lack of an appropriate technique quick enough for investigating structural changes on the sub-second to millisecond timescales or faster.

In order to realize time-resolved specular X-ray reflectivity measurements on the sub-second to millisecond timescales, a conceptually new method of measuring specular X-ray reflectivity curves was developed [1, 2]. The entire profile of the reflectivity curve of interest is simultaneously measured as a function of X-ray energy. A horizontally convergent X-ray beam which has a one-to-one correlation between its direction and energy is realized when a quasi-parallel white X-ray beam is incident on a curved crystal, as shown in Fig. 1. The X-ray beam is then incident on the surface of the specimen, which is placed at the focus in a geometry such that the glancing angle in the vertical direction is the same for all the X-ray components, which are reflected in the vertical direction by the surface and diverge in the horizontal plane. The perpendicular momentum transfer (q) continuously changes as a function of the horizontal ray direction even for fixed glancing angle since the wavelength (energy) changes. The X-ray intensity distribution across the beam direction measured downstream of the specimen using a one- or two-dimensional detector represents the X-ray reflectivity curve. Experiments were carried out on the AR-NW2A undulator beamline using a curved silicon crystal with a radius of curvature of 10 cm. With this reflectometer, specular X-ray reflectivity curves were measured with exposure times ranging from 2 ms to 1 s for a gold film of thickness 14.3 nm on a silicon substrate. Furthermore, the potential of this method for time-resolved measurements was demonstrated by recoding reflectivity curves successively every five-eigths of a second with an exposure time of 20 ms from the same specimen while it was rotated. Figure 2 shows the time dependency of the reflectivity curve. Development is still being continued to realize time resolved measurements from specimens which undergo structural changes upon external stimuli.

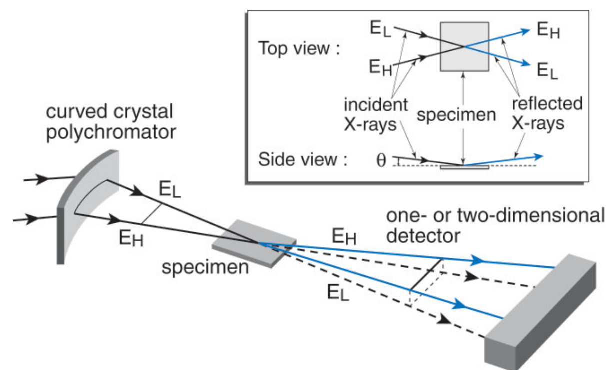

Figure 1
Geometry of the simultaneous multiwavelength dispersive X-ray reflectometer utilizing a curved crystal polychromator.

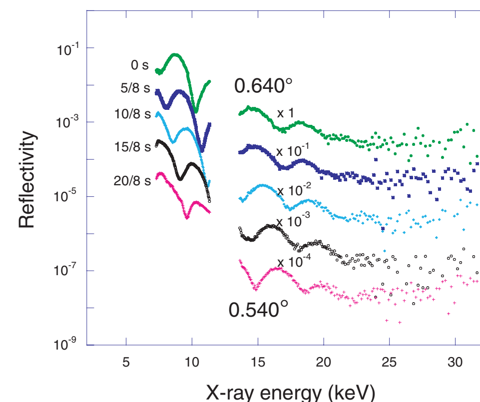

Figure 2
Time dependence of the specular reflectivity curve during the rotation of the specimen (14.3 nm thick gold film on silicon). The elapsed time is given at the left of each curve. For clarity, curves after zero elapsed time are shifted along the vertical axis. The glancing angle before and after rotation of the specimen is also indicated in the figure.

REFERENCES

[1] T. Matsushita, Y. Inada, Y. Niwa, M. Ishii, K. Sakurai and M. Nomura, *Journal of Physics: Conference Series*, **83** (2007) 012021.

[2] T. Matsushita, Y. Niwa, Y. Inada, M. Nomura, M. Ishii, K. Sakurai and E. Arakawa, *Appl. Phys. Lett.*, **92** (2008) 024103.

BEAMLINE

AR-NW2A

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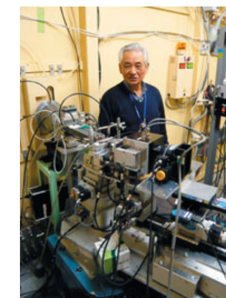

Development of Spectrally Matched Multilayer Mirrors for Use in VUV Microscopes

We have developed normal-incidence multilayer mirrors (photon energy: 92.5 eV) for use in transmission microscopes equipped with laser-produced plasma sources. The optics is composed of four spherical multilayer mirrors with radii of curvature ranging from +22.4 mm (convex) to –400 mm (concave). Mo/Si multilayers with 40 periods (period thickness: ~7 nm) were fabricated on mirror substrates. A spectral mismatch of no more than 1% is permitted for obtaining a high throughput. The spectral reflectances were measured at BL-12A. All the errors in thickness were found to be maintained within P-V value of 1.2%. This deposition system can be used for obtaining lateally graded multilayers for use in polychromators.

Soft X-ray microscopes have been developed mainly using Fresnel zone plates combined with synchrotron radiation sources. Normal-incidence multilayer reflective optics with high numerical apertures, such as the Schwarzschild objective, have the advantage of having a working distance longer than 10 mm, a field of view as large as 100 μm, and a high throughput for a laboratory soft X-ray source, which has a large angular divergence. We have developed multilayer mirrors (photon energy: 92.5 eV) for use in transmission microscopes equipped with laser-produced plasma sources. The schematic diagram of the optics is shown in Fig. 1. The optics is composed of four spherical multilayer mirrors — two of these mirrors illuminate the sample and the other two form a magnified image as a Schwarzschild objective.

The specifications of the mirrors are listed in Table 1. The period thickness is about 7 nm depending on the angle of incidence. A typical spectral reflectance of multilayer mirrors is shown in Fig. 2. A spectral mismatch of no more than 1% is permitted for obtaining a high throughput because the reflection bandwidth is FWHM 3.5%. In order to achieve intermirror spectral matching, we have stabilized our ion-beam sputtering deposition system to a thickness repeatability of RMS 0.1%. We have also developed a method to control the distribution of period thickness that involves the deposition shutter moving at a programmed speed [1]. This method is needed because the local angles of incidence vary across a spherical substrate. To achieve the exact spectral matching over the whole area of a substrate, the period thickness distribution has to be appropriately graded.

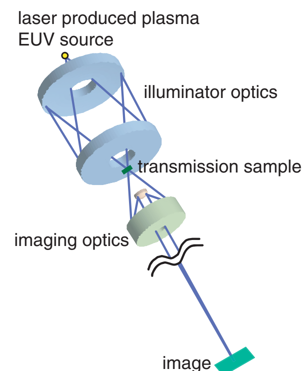

Figure 1
Schematic illustration of a transmission microscope using multilayer mirrors.

Thus, four 40-period Mo/Si multilayers with thickness distributions specified to allow exact spectral matching were deposited individually on four superpolished spherical mirror substrates. The period thicknesses were determined from the spectral reflectances measured at BL-12A [2, 3]. The results are shown in Fig. 3. The ordinate shows the difference in period thickness from the original design. The abscissa shows the position on the pupil; "1" and "–1" correspond to the edge point on the effective area and to the opposite end, respectively. The Schwarzschild concave mirror multilayer was first deposited, with a design energy of 91.9 eV.

Table 1
Spherical substrates for use in the transmission microscope.

use	size(mm)	center hole (mm)	radius of curvature(mm)	variation in period thickness from the center to the edge
illuminator 1	ϕ 100	ϕ 44	–400	+0.8%
illuminator 2	ϕ 100	ϕ 44	–400	+0.8%
imaging (concave)	ϕ 34	ϕ 20	–50	+0.5%
imaging (convex)	ϕ 9.6	—	+22.4	+4%

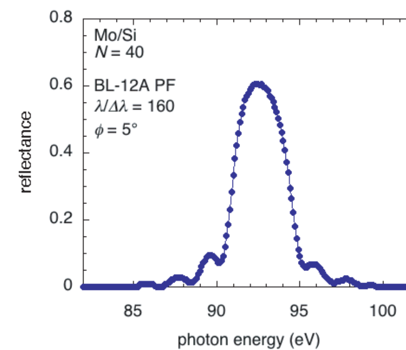

Figure 2
Spectral reflectance of a 40-period Mo/Si multilayer measured at BL-12A at PF.

Figure 3
Errors in period thickness of the four Mo/Si multilayer spherical mirrors.

After its thickness was found to be 0.6% smaller than the planned thickness, the design energy was changed to 92.5 eV for the other multilayers. All the errors in thickness were controlled to P-V value of 1.2%, which is precise enough given the Mo/Si multilayer bandwidth of 3.5%. The R–400 (concave) illuminator multilayers were successfully deposited with a matching accuracy of ±0.2%, which is sufficient even for a deposition of soft X-ray multilayer used in the carbon window region. A relatively large mismatch was found in the R+22.4 (convex) multilayer. A technique for deposition on small substrates is being improved to fabricate multilayers for use in soft X-ray microscopes.

The proposed deposition system can be utilized for the fabrication of multilayers for use in X-ray polychromators, which should be laterally graded from one end to the other along with a rectangular substrate. A graded-period multilayer with photon energy in the range of 5 to 33 keV was clamped to form an elliptic mirror on a shaped Cu block; this multilayer focuses X-rays horizontally to generate a convergent X-ray beam, which is polychromatic depending on the direction of convergence. The X-ray reflectance spectra of a sample mounted horizontally at the focus point in the configuration described above were observed [4].

REFERENCES

[1] T. Hatano, H. Umetsu and M. Yamamoto, *Precision Sci. and Tech. for Perfect Surfaces, JSPE Publication Series*, **3** (1999) 292.
[2] T. Hatano, S. Kubota, Y. Adachi, T. Tsuru and M. Yamamoto, *AIP Proc.*, **705** (2004) 839.
[3] T. Harada, T. Hatano and M. Yamamoto, *PF NEWS*, **25** (2007) 28.
[4] T. Matsushita, E. Arakawa, Y. Niwa, Y. Inada, T. Hatano, T. Harada, Y. Higashi, K. Sakurai, M. Ishii, M. Nomura and K. Hirano, *Eur. Phys. J. Special Topics (Proc. SXNS10)*, **167** (2009) 113.

BEAMLINE

12A

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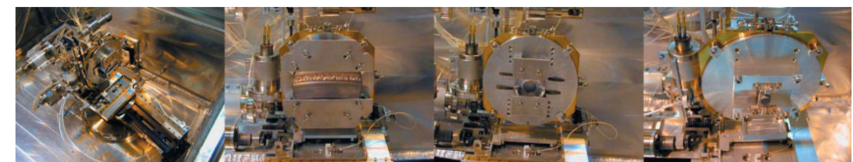

"VUV normal incidence multilayer mirrors"