

Multi-technique photoelectron spectrometer for micro-area spectroscopy and imaging

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In this note we present the new multipurpose photoelectron spectroscopy facility installed recently at the CSIR-Central Glass and Ceramic Research Institute, Kolkata. Apart from the possibility of performing conventional X-ray and ultraviolet photoemission spectroscopic measurements, this instrument is also equipped with the necessary sources facilitating the performance of macro- as well as micro-area spectroscopy at varying temperatures along with the possibility of X-ray beam-induced secondary electron and chemical state imaging. We present here the details of the instrument along with some experimental results from various samples assessing the system performance.

The technique of photoelectron spectroscopy (PES) has emerged as one of the most unique and versatile tools for materials characterization, especially in surface-related areas. It has widespread practical applications in various fields like surface chemistry or materials science, and has significantly contributed to the understanding of fundamental principles in solid state physics in general and in the context of strongly correlated electronic systems in particular^{1,2}. PES is established as the most powerful tool for providing direct information about the electronic structure of materials and with the additional advantage of its unique elemental sensitivity, the technique allows an accurate determination of chemical composition as well. Therefore, spatially resolved PES is ideal in its ability to simultaneously probe the chemical homogeneity and spatial variations in electronic structure of various systems exhibiting electronic/magnetic phase separations and grain boundary effects that may or may not have underlying chemical or electronic origin, like in manganites³, double perovskites⁴, etc. Such a technique can have an added advantage over other spectroscopy techniques like scanning tunnelling spectroscopy, which cannot provide any information concerning the chemical composition responsible for the specific electronic structure.

The main impediment in using spatially resolved PES has been to simultaneously satisfy the demands of energy resolution required to probe the relevant electronic structure, accessibility to probe a wide kinetic energy region to cover both the valence levels for the electronic structure information and core levels to obtain chemical information at the same time, deliver a sufficiently intense pho-

ton source focused on the sample and vary the temperature over a wide enough range to catch the phase transitions, if any. Recent developments in the synchrotron-based experiments and associated instrumentation have facilitated the possibilities of performing such investigations at various synchrotron sources across the world. But here the attempt is to perform such spatially resolved PES experiments at the laboratory level. The multipurpose photoelectron spectrometer discussed here has the additional advantage of performing imaging (scanning X-ray imaging and photoemission imaging) along with performing conventional spectroscopy measurements like X-ray photoemission spectroscopy (XPS), ultraviolet photoemission spectroscopy (UPS), depth profiling, etc.

Instrumental details

The spectrometer presented here is a PHI 5000 Versaprobe II scanning XPS microprobe manufactured by UL-VAC PHI, USA, customized for CSIR-Central Glass and Ceramic Research Institute. The system consists of load-lock and analysis chambers with various sources integrated into it. The mu-metal analysis chamber is designed with multiple ports aligned to the sample analysis position allowing multiple technique configurations and maintained at a base pressure of 4×10^{-10} mbar. The major components of the analysis chamber are the following.

Monochromatic scanning X-ray source

The system is equipped with a unique Al K_{α} X-ray source that provides a focused

monochromatic X-ray beam. The X-ray source utilizes a focused electron beam that can be electronically raster scanned upon an Al anode for X-ray generation. An ellipsoidally shaped quartz crystal monochromator refocuses the X-ray beam onto the sample surface. Therefore, when the electron beam is scanned on the anode surface the refocused X-ray beam is scanned on the sample surface⁵. The size of the X-ray beam can be varied from less than 10 μm to 200 μm and it also provides a high performance large area analysis capability where a 100 W–100 μm beam is scanned 1.4 mm in the non-dispersive direction of the X-ray monochromator at high speed, providing a rectangular analysis area with both high sensitivity and high energy resolution. The scanned X-ray beam excited secondary electron imaging of the sample surface is also possible, where in the energy analyser collects the X-ray excited secondary electrons and provides images that contain topographical as well as surface chemical contrast information. The use of the same hardware for secondary electron imaging and X-ray photoemission measurements ensures that the spectroscopic information comes from the areas selected on secondary electron images allowing a perfect correlation between the two while looking at small sample features for analysis.

Apart from the focused X-ray source, a twin anode providing non-monochromatized Al K_{α} and Mg K_{α} radiations for core-level photoemission measurements and a helium discharge lamp providing high-intensity He I and He II photon energies for performing ultraviolet photoemission spectroscopy measurements probing the valence band and Fermi edge are also available.

Ion gun

A FIG-5CE 5 kV floating argon ion gun is attached to the analysis chamber that could be operated between 5 eV and 5 keV range. This is designated to perform three different tasks: (i) sputter cleaning to remove the surface contamination, (ii) depth profiling and (iii) charge neutralization. The higher operating range between 1 keV and 5 keV is utilized for high etch rates required for the sample surface cleaning and depth profiling experiments. For ultra-thin films the floating column of the ion gun can be used to generate a high-current low-energy ion beam between 200 eV and 500 eV, which helps in enhancing the interface definition in ultra-thin films. Even lower beam energy of ≤ 10 eV is used along with a cool cathode electron flood source for the dual beam charge compensation system⁶, providing turnkey neutralization for all samples allowing the possibility of performing photoemission measurements even on insulating samples like glass and ceramics with ease.

Sample stage

A fully automated, five-axis (X , Y , Z , Θ and tilt) sample stage with compucentric zalar rotation and eucentric tilt compensation which can handle sample platens with 25 and 60 mm diameter is available. This facilitates: (i) designating a specific location as the centre of rotation, (ii) improving layer (interface) definition in multilayered films by minimizing the sputtering artifacts associated with sputtering at a fixed angle, and (iii) performing angular dependent XPS profiling with an angular range of 0° to 90° . Sample stage also provides the additional possibility to perform temperature-dependent measurements in the range -130°C to 500°C , with all five axis of motion and zalar rotation maintained. A microscope, camera and a light source for efficient sample positioning are also available.

Electron analyser

This is a 180° hemispherical analyser, model PHI 10-371, composed of two concentric hemispheres with a mean diameter of 280 mm which are surrounded by a magnetic shield optimized for energy resolution and high angular acceptance lens optimized for small-area

XPS sensitivity. The detection of electrons is through a unique multi-channel detector (MCD – a 16-position channel plate detector) and fast electronics for rapid data acquisition and maximum sensitivity in both the scanned and unscanned (snap shots) data acquisition modes is available.

Results and discussion

A schematic of the instrument highlighting the major parts is presented in Figure 1. Ag 3d core-level photoemission spectra acquired on a clean Ag foil using monochromatic Al K_α radiation yielded a resolution of 0.49 eV and the corresponding valence band spectra acquired using He I radiation yielded a resolution of 0.093 eV at room temperature. Also, spectra acquired with varying beam sizes from $9\ \mu\text{m}$ to $200\ \mu\text{m}$ confirmed the stability of the beams with the binding energy position and the resolution remaining almost constant with varying beam sizes, thereby affirming the capability of the equipment for performing conventional spectroscopy measurements. Apart from the conventional XPS and UPS experiments performed using laboratory sources, one can classify the additional three major highlights of this equipment as follows: (i) the patented turnkey dual charge neutralization capability, which renders photoemission measurements on electrically insulating samples easier in comparison to the traditional techniques, (ii) automated depth

profiling and (iii) scanning X-ray and photoemission imaging.

Dual charge neutralization

One of the major hurdles encountered while performing photoemission measurements on insulating/semiconducting samples is the charging effect. For metals and other conducting samples that are grounded to the spectrometer, electrons move to the sample surface continuously to compensate for those that are lost during the photoionization process, whereas semiconductors/electrical insulators cannot compensate this charge loss and eventually the sample picks up excess positive charges leading to the shifting/broadening of spectral features. Also, traditional electron flood gun charge neutralization is not effective in neutralizing the localized positive charge created by the X-ray beam because the surface static charge of the sample interferes with the low energy electron beam (Figure 2a). PHI's patented⁶ dual-beam charge neutralization method uses a low-energy ion beam to eliminate static charge of the sample, allowing the low-energy electron beam to reach the sample and neutralize the localized positive charge created by the X-ray beam (Figure 2b). This unique turnkey charge neutralization capability coupled with an automated sample stage of this system renders photoemission measurements on electrically insulating samples easier in comparison to the traditional techniques

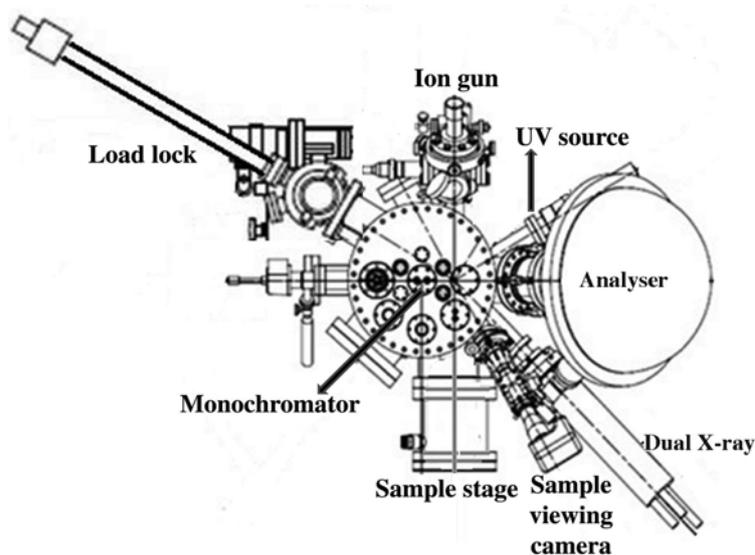


Figure 1. Schematic of the multipurpose photoelectron spectrometer.

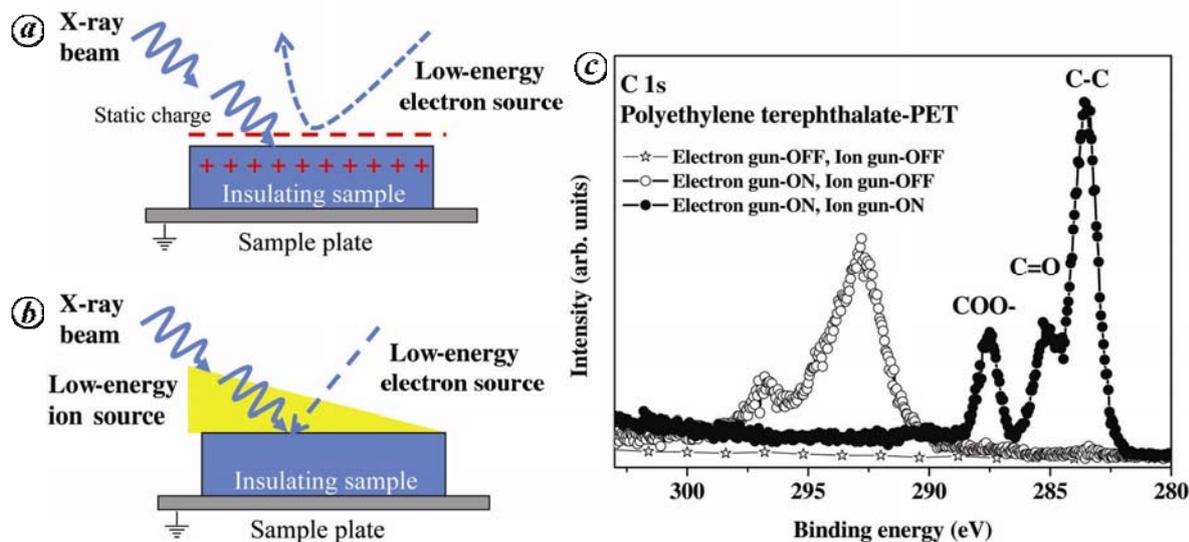


Figure 2. Schematic of the charge neutralization effects for an insulating sample using (a) conventional technique and (b) dual-charge neutralization procedure. c, C 1s core-level spectra from polyethylene terephthalate for various electron and ion gun settings.

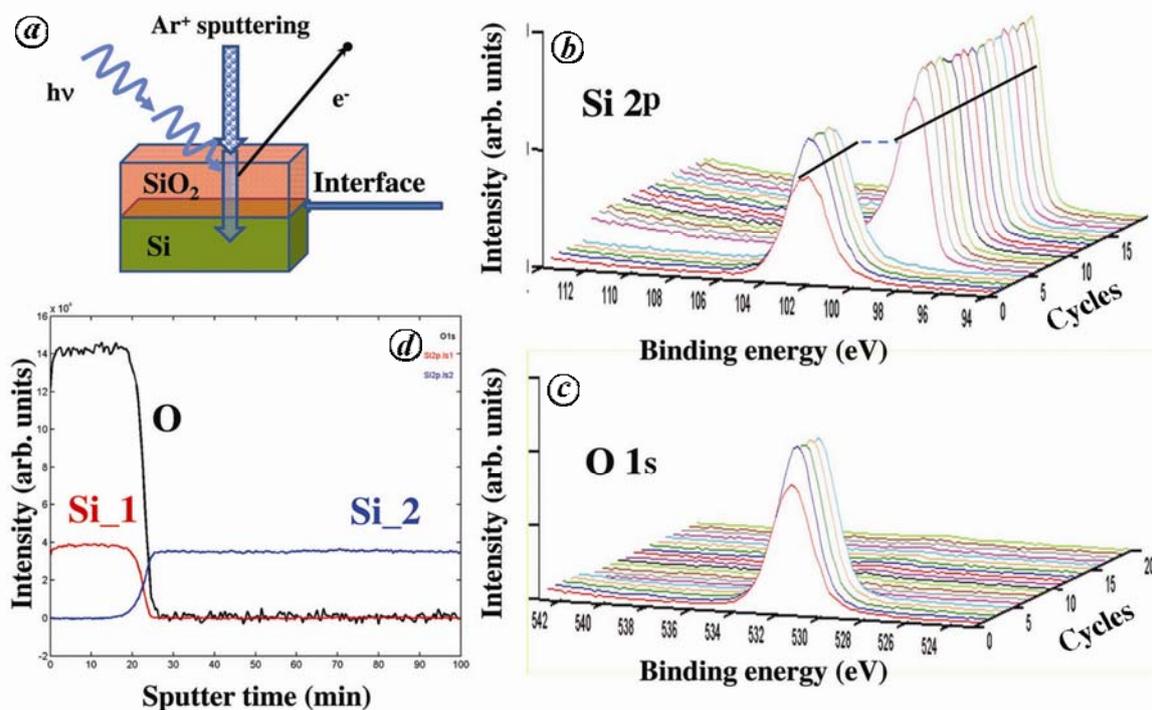


Figure 3. a, Schematic of the depth profiling mechanism across the SiO₂/Si interface. b, c, Evolution of Si 2p and O 1s core levels across the interface. d, Sputter depth profiles of O 1s, Si⁴⁺ and Si⁰, as extracted from the depth profile, plotted as a function of sputtering time.

by eliminating the requirement of any sample-to-sample tuning or operator intervention while analysing multiple insulating samples. This is demonstrated in Figure 2c, where the C 1s core-level photoemission spectra acquired from polyethylene terephthalate (PET) for various electron and ion gun settings using monochromatic Al K_α radiations are presented. With both the sources in

the ‘ON’ state, we could clearly reproduce the PET spectra with C=O, C–C and COO– contributions.

Automated depth profiling

While probing multi-layered films, apart from the information about the surface electronic structures, it is also important

to understand the evolution of electronic structures of and across the buried interfaces. This could be made possible by (i) tuning the surface sensitivity of the photoelectron by varying the emission angle⁷, (ii) varying the incident photon energies⁸ or (iii) performing a depth profiling – alternately sputtering out the surface layers and performing the spectral acquisition (schematic presented in

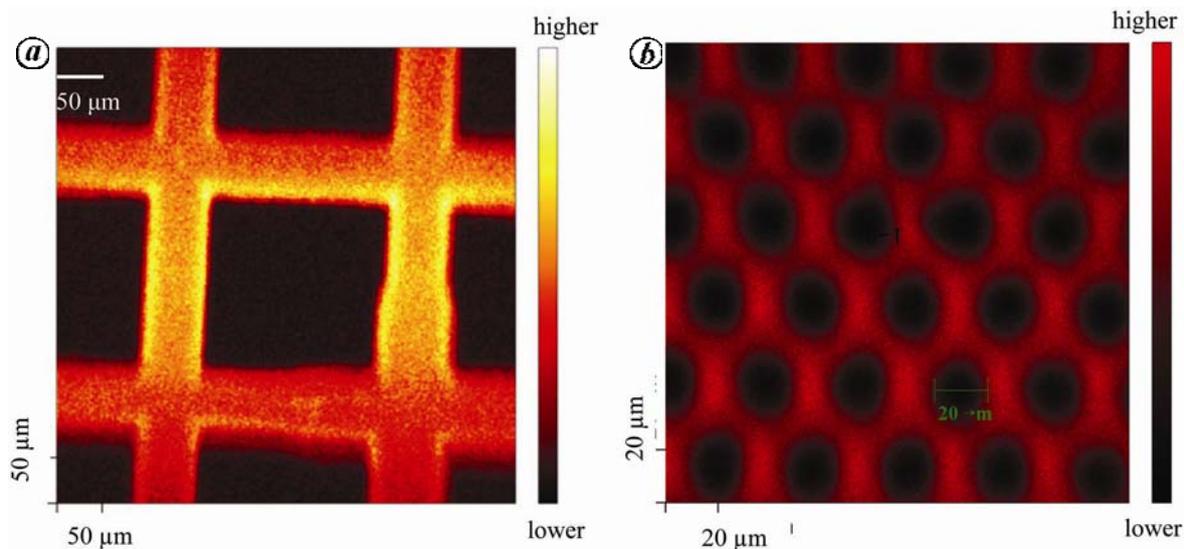


Figure 4. X-ray beam-induced secondary electron imaging from (a) Cu grid and (b) channeltron plate. Intensity colour code is presented.

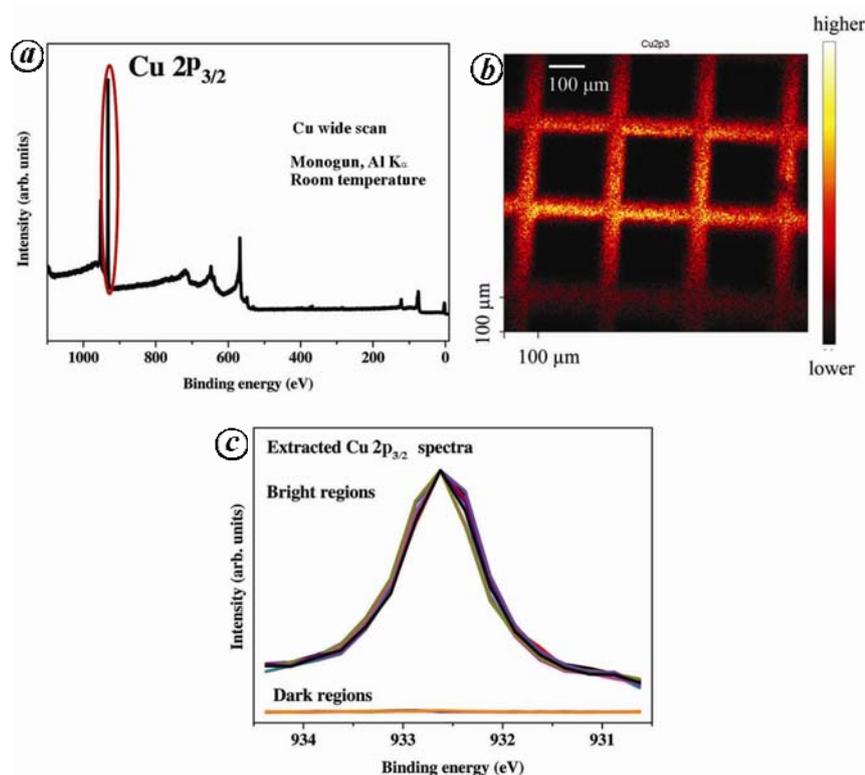


Figure 5. a, Wide scan acquired from a clean Cu grid. b, Image reconstructed from the elemental mapping performed using the Cu $2p_{3/2}$ core-level intensities. c, Spectra extracted from the brighter and darker regions of the image. Intensity colour code is presented.

Figure 3 a). In this spectrometer, the sputter gun, X-ray source and electron analyser are focused in such a way that one need not have to move the sample position while sputtering and data acquisition, thereby ensuring that the data are always acquired from the same sample

point. The sputter rate can be varied by tuning the ion gun voltage between 200 eV and 5 keV, and the ion gun can be used in spot mode or raster mode up to $10\text{ mm} \times 10\text{ mm}$ area, though for most XPS applications we use 1×1 , 2×2 or $3 \times 3\text{ mm}$ raster in order to create the

sputter crater 5–8 times the analysis area. The evolution of electronic structure across the SiO_2/Si interface in a 100 nm SiO_2 film grown on a Si substrate as probed by alternating Ar^+ ion sputtering and XPS spectra acquisition is presented in Figure 3. The sputter rate was set to an ion gun voltage of 2 kV with 5 min intervals and a total of 20 cycles (total sputtering time = 100 min). Figure 3 b and c correspond to the Si 2p and O 1s core-level spectra respectively, presented as a function of the number of sputter cycles. Si 2p undergoes clear chemical shifts of about 4 eV to the lower binding energy side, suggesting the evolution of Si^{4+} in SiO_2 to elemental Si across the interface. This is also confirmed by the complete absence of O 1s peaks after the same number of sputter cycles, wherein the SiO_2 layer is completely removed and only the substrate Si remains. The evolution of O and two different types of Si, marked as $\text{Si}_1(\text{Si}^{4+})$ and $\text{Si}_2(\text{Si}^0)$, with sputtering time reconstructed from their respective core level spectra is presented in Figure 3 d.

Imaging

One of the major highlights of this spectrometer is its imaging capabilities, including both scanning X-ray imaging (SXI) and photoemission imaging. As discussed in the previous section, the unique SXI capability of this spectrometer facilitates the rapid and confident location of small sample features for

XPS analysis. Figure 4a shows the SX image obtained using the focused X-ray source of Al K α radiation with a 9 μm beam from a Cu grid. Figure 4b shows the SX image from a channeltron plate used in the electron energy analyser revealing pore sizes of 20 μm . The elemental contrasts in the SX images together with the accessibility of various beam sizes ranging from 9 to 200 μm allows one to pinpoint and probe specific smaller sample features of interest.

The role of photoemission imaging in understanding the competing electronic phases, which critically influence the properties of strongly correlated systems, has been reported in recent years^{3,4}. One of the major highlights of this spectrometer is the possibility to perform such photoemission imaging creating elemental maps. Here the analyser is set to accept electrons of an energy characteristic of a particular element. The incident X-ray beam is rastered over the surface to be analysed. The resulting reconstructed image, with the intensity modulated by the peak intensity, will correspond to the distribution of that element over the surface. Figure 5a shows the wide scan acquired from a clear Cu grid and the intensity image reconstructed from the associated Cu 2p_{3/2} core-level spectra is shown in Figure 5b. The probe was a focused X-ray source of Al K α with 9 μm beam size. Colour distribution is such that black corresponds to lower intensities and red-yellow corresponds to higher intensities. The extracted spectra from various points in the dark and brighter parts of the image are shown in Figure 5c. As expected, the spectra from the brighter regions show Cu 2p_{3/2} intensities, whereas those from

the darker regions show a complete absence of Cu signals.

It is to be noted that this multipurpose spectrometer provides the same ultimate spatial resolution for spectroscopy and imaging. Detailed spectroscopy, depth profiling, imaging and angle-dependent measurements are available at all X-ray spot sizes from less than 10 to 200 μm . Even though the best guaranteed beam size is 10 μm for imaging, mapping and spectroscopy, we could recently tune the spot size to ~ 6 μm in our system.

Conclusion

We discussed here the newly installed multi-technique photoelectron spectrometer at CSIR Central Glass and Ceramic Research Institute. We have presented in detail the major components of the instrument and various experimental results demonstrating the versatility and capability of the equipment, which includes unique micro-area spectroscopy, high-performance macro-area spectroscopy, sputter depth profiling, angle-dependent XPS and depth profiling, turnkey insulator analysis, X-ray beam-induced secondary electron imaging and chemical state XPS imaging. This facility will be extensively used for investigating the core levels as well as the valence band photoemission studies leading to the understanding of the electronic structure of various systems of interest, both in the bulk and the nano regime.

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