

C-4

Development of in-situ Ultraviolet/X-ray Photoelectron Spectroscopy System for Heterostructures and Superlattices with Pseudo-perovskite Oxides Deposited by Pulsed Laser Deposition

Huaping Song¹, Yuta Watabe¹, Takaaki Inaba¹, Takahiro Oikawa¹, Keisuke Oshima¹, Chun Wang¹, Tomoko Nagata¹, Hiroshi Yamamoto¹, Nobuyuki Iwata¹

Abstract: Multi-functional oxides in particular ferroelectric and ferromagnetic multiferroic and magnetoelectric materials have been energetically investigated recently. To understand the electronic structures and magnetic ordering information in the multi-functional oxide films and heterostructures, we developed the in-situ ultraviolet/x-ray photoelectron spectroscopy (UV/XPS) system, which was connected to pulsed laser deposition system directly via a transfer chamber kept under ultra-high vacuum condition. It mainly consisted of a high resolution electron analyzer VG Scienta R4000 with 2-dimensional spin detector, a high intensity ultraviolet source and a dual Al/Mg x-ray tube as the alternative excitations. As an example, thickness-dependent electronic and spin structures in pseudo-perovskite oxide films deposited on SrTiO₃ (100) substrates will be studied by in-situ UPS/XPS.

1. Introduction

Ferroelectrics and multiferroics have recently intensively studied as perspective materials for information technology and data storage applications [1]. The remarkable properties are expected in the heterostructures and superlattices using the magnetic interaction at the interface. To understand the magnetoelectric interaction at the interface, the knowledge about electronic and magnetic ordering structures is of great importance. Photoemission spectroscopy (PES) is one of the most universal and powerful tools to investigate the chemical states and electronic structures of materials directly [2,3]. In our laboratory, we developed the in-situ ultraviolet/x-ray photoelectron spectroscopy (UPS/XPS) system, which was connected to pulsed laser deposition (PLD) system directly via a transfer chamber kept under ultra-high vacuum (UHV) condition. In this report, we will introduce the details of this UPS/XPS system.

2. Experimental

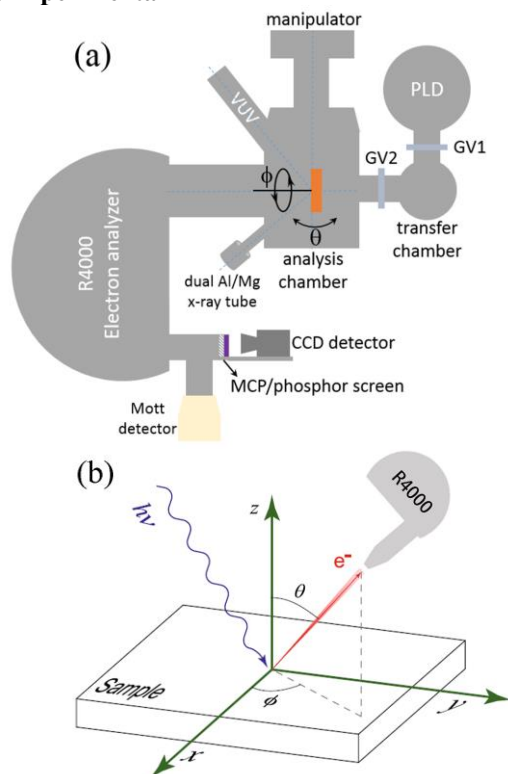


Fig. 1 Schematic drawing of in-situ UPS/XPS system.

Fig. 1(a) is the schematic drawing of the in-situ UPS/XPS system combined to PLD deposition chamber via a transfer chamber. There are two gate valves (GV1 and GV2) between PLD chamber, transfer chamber and analysis chamber successively, to isolate these chambers if without sample transfer. After the sample is prepared in PLD chamber, it will be transferred into analysis chamber via the transfer chamber by wobble sticks. The position of sample in analysis chamber is controlled by a two-axis manipulator. The rotation vertical to sample surface will change the incident angle (θ), which is designed for angle-resolved PES (ARPES) measurement [2]. While the rotation in the sample surface will change the azimuth angle (ϕ), which is necessary for x-ray photoelectron diffraction (XPD) measurement [4]. The definition of θ and ϕ is shown in Fig. 1(b). VG Scienta VUV-5000 provides high intensity non-monochromatized ultraviolet (UV) source (He I: 21.218 eV and He II: 40.814 eV) for UPS using plasma discharge in pure helium gas. X-ray tube (PSP TX400) contains dual Al and Mg targets, which provides alternative Al/Mg x-ray irradiation for XPS. A 2-dimensional (2D) spin detector is attached to VG Scienta R4000 electron analyzer. This combination allows us to detect electronic and spin structure alternatively.

3. Results and Discussion

The basic pressure in PLD chamber, transfer chamber and analysis chamber is 2×10^{-6} Pa, 3×10^{-7} Pa and 2×10^{-8} Pa, respectively. Keeping UHV condition in the transfer chamber and analysis chamber is extremely important for in-situ XPS and UPS measurements because of two reasons: the first one is to ensure the photoelectrons from sample surface have the inelastic mean free path large (IMFP) large enough to arrive the detector, and the second reason is to guarantee a clean and true 'as-grown' sample surface. The first reason is also the common requirement for other electron spectroscopy methods like scanning electron microscopy. The vacuum lower than 10^{-5} Pa is enough because the IMFP larger than 100 m under the vacuum in such level. The second reason is more rigorous, which is related to the adsorption on the sample surface. As we know, the residual gas in UHV chamber is mainly hydrogen and water molecules, which are very active for many semiconductor surfaces. The time to form monolayer

adsorbates (T_{ml}) on sample surface under UHV condition is decided by Eq. (1):

$$t_{ml} = \frac{4}{nvd^2} \quad (1)$$

where n is gas molecule density depending on the pressure, v is the speed of molecule and d is the diameter of gas molecule. According to calculation, T_{ml} in the vacuum of 1×10^{-6} Pa, 1×10^{-7} Pa, 1×10^{-8} Pa, and 1×10^{-9} Pa is about 4 min, 40 min, 7 hours and 70 hours, respectively. So the vacuum in the analysis chamber is extremely important for keeping the origin sample surface for in-situ XPS and UPS. The influence of vacuum in chamber is more obvious for UPS measurement, due to the extremely shallow probe depth in UPS^[5]. The probe depth (3λ) of PES in solid films is estimated by TPP-2M formula as shown in Eq. 2^[6]:

$$\lambda = \frac{E}{E_p^2 [\beta \ln(\gamma E) - \frac{C}{E} + \frac{D}{E^2}]} \quad (2)$$

where λ is the IMFP of photoelectrons in solid films (in Å), E is the electron energy (in eV), E_p is the bulk plasmon energy (in eV), and β , γ , C and D are parameters as described in the reference^[6].

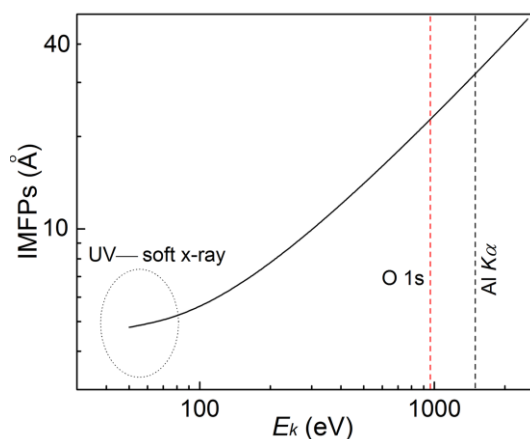


Fig. 2 The universal curve in SrTiO₃ calculated by TPP-2M formula.

The energy dependent IMFP in SrTiO₃ substrate (also called universal curve) calculated by TPP-2M formula is shown in Fig. 2. The probe depth of valence band in solid films is about 9 nm when Al K α ($h\nu=1486.6$ eV) source is used. However the probe depth of UPS locates at the bottom of universal curve, which is always below 1 nm. So UPS is more surface sensitive than XPS.

VG Scienta R4000 is a well-designed and widely used electron analyzer, which has an energy resolution of 1.8 meV in UPS measurement. The lens in R4000 can provide three different operation modes: transmission mode, spatial mode and angular mode. The first two are imaging modes and the third one is angular multiplexing mode for ARPES. This R4000 has an acceptance angle of $\pm 7^\circ$ and an angular resolution better than 0.4° when the light spot size is 1×1 mm². For the detecting system, there are two choices in our system. One is the standard multichannel panel (MCP)/phosphor screen with a charge coupled device (CCD) camera. The other one is Mott detector for spin

measurement using Au target^[7]. In principle, both PES and spin measurements can be carried out at the same time. It should note that the cross-section of Mott scattering is rather low, usually between 2×10^{-5} and 1.6×10^{-4} . So the counts of Mott spin detector are usually less than 1/10000 of regular ARPES. Therefore we should pay attention to guarantee the clean and stable sample surface during long time spin measurement.

Due to the difficulties in the improvement of vacuum, UPS/XPS system is still under optimization. After the optimization, we will study the thickness-dependent electronic and spin structures in pseudo-perovskite oxide films deposited on SrTiO₃ (100) substrates. The results will be reported at the conference.

4. Summary

An in-situ UPS/XPS system was developed in our laboratory. High resolution R4000 electron analyzer combining with 2D spin Mott detector enables us the possibility to perform standard PES and spin measurements in one system without changing any hardware. The alternative UV and x-ray excitation sources provide the ability to detect information with different probe depths. This in-situ UPS/XPS system will be very useful for the research in the electronic and magnetic ordering information in the heterostructures and superlattices with pseudo-perovskite oxides.

5. Reference

- [1] F. Manfred, J. Phys. D: Appl. Phys. **38**, R123 (2005).
- [2] C. S. Fadley, Nucl. Instrum. Methods Phys. Res., Sect. A **547**, 24 (2005).
- [3] Y. Segal, J. H. Ngai, J. W. Reiner, F. J. Walker, and C. H. Ahn, Phys. Rev. B **80**, 241107 (2009).
- [4] C. S. Fadley, Nucl. Instrum. Methods Phys. Res., Sect. A **601**, 8 (2009).
- [5] G. Liu, G. Wang, Y. Zhu, H. Zhang, G. Zhang, X. Wang, Y. Zhou, W. Zhang, H. Liu, L. Zhao, J. Meng, X. Dong, C. Chen, Z. Xu, and X. J. Zhou, Rev. Sci. Instrum. **79**, 023105 (2008).
- [6] S. Tanuma, C. J. Powell, and D. R. Penn, Surf. Interface Anal. **43**, 689 (2011).
- [7] D. J. Huang, W. P. Wu, J. Chen, C. F. Chang, S. C. Chung, M. Yuri, H.-J. Lin, P. D. Johnson, and C. T. Chen, Rev. Sci. Instrum. **73**, 3778 (2002).