X-ray Photoelectron Spectroscopy and its application in phase-switching device study

Xinyuan Wang
A53073806

I. Background

X-ray photoelectron spectroscopy is of great importance in modern chemical and material science, which is also known as electron spectroscopy for chemical analysis (ESCA) for learning the surface elemental composition and speciation of solid substrate within 10nm depth. The surface of solids plays a crucial when perceiving with the outer environment as it is often quite different from the underlying material, thus making the physical properties varies such as adhesion, biocompatibility, and interfacial electrical properties and so on. If the composition and speciation of solid surface can be figured out, we are able to understand the inner principles of how they interact with external forces and explore material mortification methods to satisfy further application.

ESCA, first introduced by Kai Seigbahn, is the origin of XPS technology. By irradiating materials with x-ray beam, the electrons are kicked off and their kinetic energy and numbers are analyzed. Its abilities in identifying and quantifying the elemental composition of the outer 10 nm or less of any solid surface with all elements from Li–U detectable and revealing the chemical environment where the respective element exists in are realized since then.

In this paper, we mainly talk about the basic physics of XPS and how measurements are made with instruments. Then a simple example is given which shows the procedures of analyzing XPS data results focusing on Tantalum oxide. After that figures in the reference paper are further introduced revealing the significant role of XPS to understand semiconductor fundamentals.

II. Basic Principles

XPS is based on photoelectric effect which was first noted by Heinrich Hertz and explained by Albert Einstein. He showed that this induced electron emission from metallic objects if the energy transfer was greater than the biding energy between the electron and the respective metal atom, and creatively introduce the concept of the photon – a massless particle with no charge which is the quantum of electromagnetic radiation in quantum field. Its energy and momentum can be expressed with

$$E = h\nu$$

$$\boldsymbol{p} = \hbar\boldsymbol{k}$$

where h is Plank's constant, v is its frequency and $\boldsymbol{k}$ is its wave vector.

When a photon hits the material which cause electrons from atomic orbitals or bands moving out to the vacuum level, the photoemission process happens. This process require energy high enough to overcome the attraction from nuclei, in other words the initial energy of photon should be larger than the emitted electron's binding energy. Following the energy conservation rule,

$$h\nu = E_b + E_{kin}$$

$h\nu$ is the photon energy, E_b is the electron binding energy with respect to vacuum level prior to ionization and E_{kin} is the kinetic energy of photoelectron. Generally E_b is taken place by $E_b + \phi$ relative to Fermi level. Here is a schematic figure showing how the photoemission process takes place,

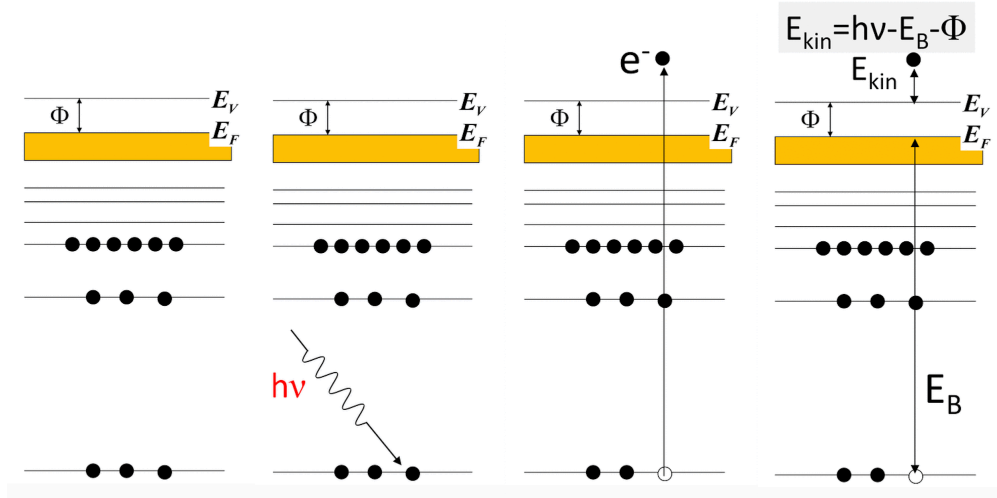

Figure 1. The photoelectron emission process

Subsequently, as the emitted electron leaves a hole in lower energy level, electrons from upper levels will drop to its nearest lower level which also results in photon emission, called Auger process.

With the above description, X-rays are found ideally suited to probe the core levels of a solid, which generally show no dispersion due to their highly localized atomic-like character. Two crucial parameters to describe the XPS ability are surface specificity and sensitivity. An electron has a limited flight mean path in solid before losing part of its energy. When X-rays penetrating the solid, almost all the photoelectrons will lose energy at the depth above 10nm, leading to that the signals only exist at the surface

region. Sensitivity is dependent on the photoelectron cross section and the spectral background. The photoelectron cross section describes the yield of electrons produced as a function of the impacting photon energy. This also gives the reason why Hydrogen and Helium are not detectable in solids because of their low photoelectron cross sections.

III. XPS Instrumentation

A XPS instrument primarily contains three parts,

1) An X-ray source
2) Extraction optics and energy filter (energy analyzer)
3) A detection system

And within the instrument the environment should keep the photoemission process not affected by external electric or magnetic fields. Besides the emitted electrons should be able to traverse from the sample to detector and not modified during the analysis. Thus a vacuum condition is necessary in XPS to satisfy the above requirements.

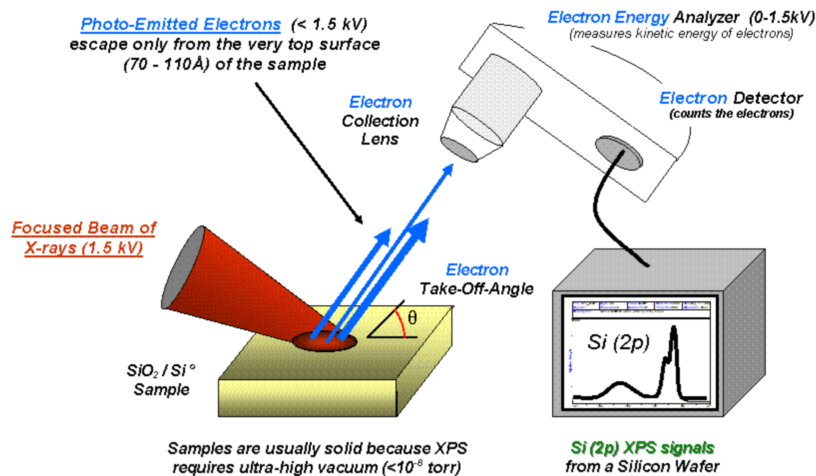

Figure 2. The schematic system of SPS instrument

The above figure shows a schematic system of XPS. The source is the unit from which X-rays are produced/directed onto the sample. There are generally two options of sources in self-contained XPS instruments, the standard and monochromatic. Monochromatic source with Al-Kα1 emissions are increasingly popular due to the ability to produce a focused X-ray beam without the requirement of the source being in close proximity to the sample and the narrower energy spread of the resulting X-rays. X-rays of narrower energy spread than this can only be produced in synchrotrons. The energy resolution in XPS is primarily dependent on the source.

Energy filters used in XPS tend to consist of CHAs. These are heavily favored over CMAs due to their superior energy resolution and the fact that when operated under the CAE mode, these provide a constant energy resolution over the entire B.E.XPS range of interest. In addition, little variation in B.E.XPS values is noted once the sample–analyzer distance is optimized. CHAs also allow for the incorporation of transfer lenses. SMAs, a variant of the CHA, are also used in imaging.

Detectors are comprised of some form of EM. The type used depends on the information of interest. If counts over some large area are required, multiple channeltrons placed along the energy-dispersive axis of the energy filter are the best option. Additional information that is, imaging of the spatially dispersed and/or angularly dispersed data can be acquired using an MCP detector when combined with CHA or SMA. Imaging can be carried out in one of several modes, with the parallel mode providing the best spatial resolution.

IV. XPS Data Analysis

XPS requires little in the way of sample preparation. Indeed, all that is generally required is that

(a) The sample be of a size amenable to that of the instrument

(b) The surface of interest remains clean before and during analysis

(c) The surface of the sample be ultrahigh vacuum (UHV) as well as X-ray compatible

To better understanding the data analyzing process in XPS, I refer to the data measured during my undergraduate study on bilayer Tantalum oxide based resistive-switching memory device. The device consists of two layers of different compositional tantalum oxide. About 40nm-thick TaO_y was deposited by RF reactive magnetron sputtering at pressure of 6.3×10^{-3}Torr with 3.3% O_2 partial pressure in Ar and O_2 ambient. Next, 25nm- thick Ta_2O_{5-x} was deposited at the pressure of 2×10^{-2}Torr with 6% O_2 partial pressure.

First we get a wide-scan or survey spectrum of a somewhat dirty silicon wafer, showing all elements present. A survey spectrum is usually the starting point of most XPS analyses because it shows all elements present on the sample surface and allows one to set up subsequent high-resolution XPS spectra acquisition. The following figure shows a quantification table indicating all elements observed, their binding energies, and their atomic percentages, from which obvious peaks of O and Ta are observed.

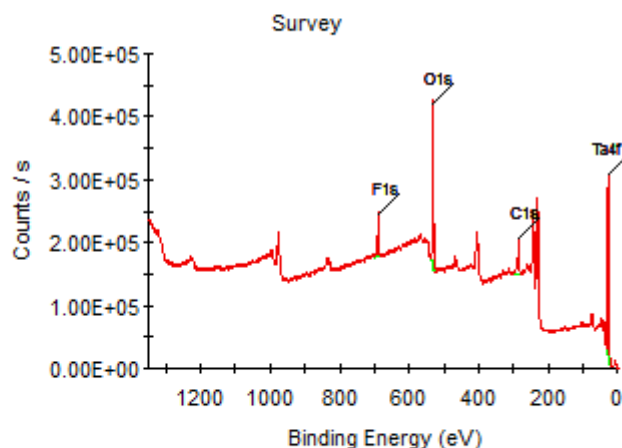

Figure 3. The survey spectrum of bilayer tantalum oxide

Notice here there exists a C-1s peak which is used as ensuring accurate calibration of the gap ϕ between two energy references E_{vaccum} and E_F in insulator. The C-1s peak arising from adventitious carbon. Adventitious carbon arises from the adsorption of aliphatic hydrocarbons from the atmosphere, which includes that present under UHV. These are useful since they can provide an effective internal reference check but only if the C-1s from these adsorbates on the respective surface is well-known to within 0.1 eV.

XPS depth analysis was done to study the element composition and structure in the surface of tantalum oxide of which the thickness is within 10nm. The figure below shows the atomic percentage of O1-s and Ta4-f. The concentration of Ta rises after 600s etching, which indicates a transform from oxygen-rich layer to oxygen-deficient layer.

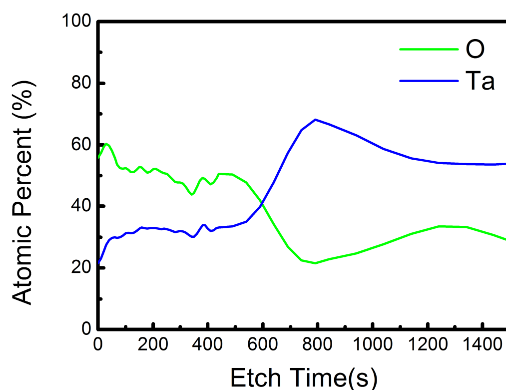

Figure 4. The atomic concentration of Ta and O along depth

High-resolution spectrums of two elements in the bilayer strucutre are separately displayed at different etching times. The choice of 200s and 1040s is dependent on the above concentration comparison between O and Ta, in order to show the difference of

two tantalum oxide layers. The raw data spectrum (black) is fitted with several components or chemical states.

At 200s etching time, the more oxidized forms of Ta (Ta_2O_5) appear at higher binding energies at about 28.9eV and 27.2eV, which are $Ta4-f_{5/2}$ and $Ta4-f_{7/2}$. Besides the typical Ta 4f two peaks at the surface, the profile spectra can be decomposed into many other peaks indicating tantalum suboxides. When look at the O1-s spectra, it can actually be fitted with two Gaussian components centered between 531~532eV.

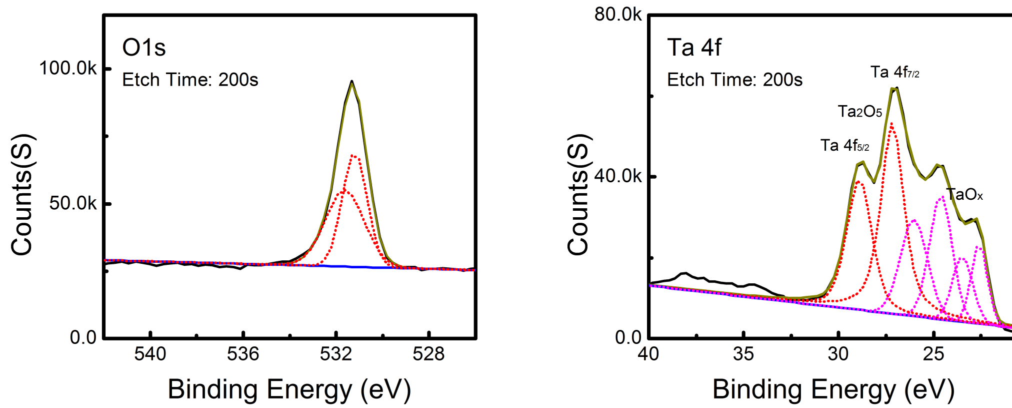

Figure 5. O and Ta spectrum at etching time 200s

In the 1040 etching time spectrums, the so-called metallic form of Ta exhibits a set of doublet peaks at around 22±0.2eV. Also new strong doublet attributed to Ta suboxide forms clearly, and the Ta 4f doublet changes its typical form to a shallow peak with significantly increased intensity. The variation of the intensity of the different peaks indicates that tantalum suboxides and metallic Ta dominate in the oxygen-deficient layer.

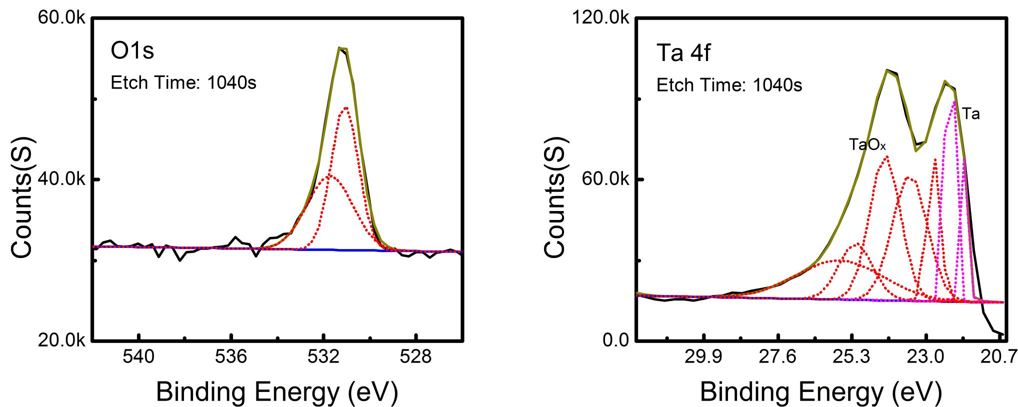

Figure 6. O and Ta spectrum at etching time 1040s

V. Application in the paper

The reference paper uses similar method to analysis its device structure and composition. Figure 7 shows the atomic percentage by fitting O-1s, Al-2p, and W-4f peaks. The concentration of O rises after 2000s etching time and declines after 4000s, which indicates an existence of oxygen-rich layer.

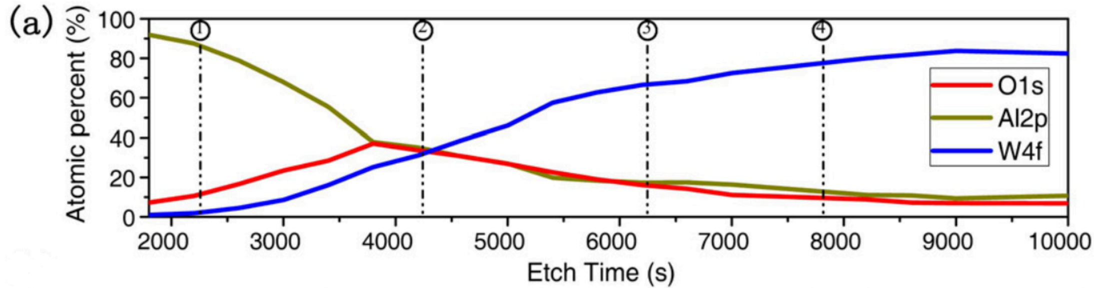

Figure 7. XPS depth profile of Al/W:AlOx/WOx/W/Al stack

In order to distinguish this oxide layer, O 1s peaks were analyzed as shown in Figure 8. Four etching times 2200s, 4200s, 6200s, and 7800s with distinct compositions were chosen for analysis. The O-1s spectra at the points 1 and 4 show a singlet peak at 532:1±:5eV and 530:8±:5eV which correlate to AlOx and WOx seperately. The O-1s peaks at points 2 and 3 are the combination of these two peaks. The separating curves confirm the oxide layer transformed from AlOx to WOx. The spectra of Al-2p and W-4f shows peaks at different binding energies which are correlated to different chemical state.

This work is of much importance to study the device structure and to further modify the parameters in fabricating process aiming to improve its properties. First of all, it helps us to understand the inner mechanism of how the device works. The metal oxide based resistive-switching memory is a good example to display the mentioned importance. As the electrical characteristics of layers with different composition varies and may even lead to some unexpected results. The XPS analysis offers confirmation or correction on previous guess as well as arouse new conceptions.

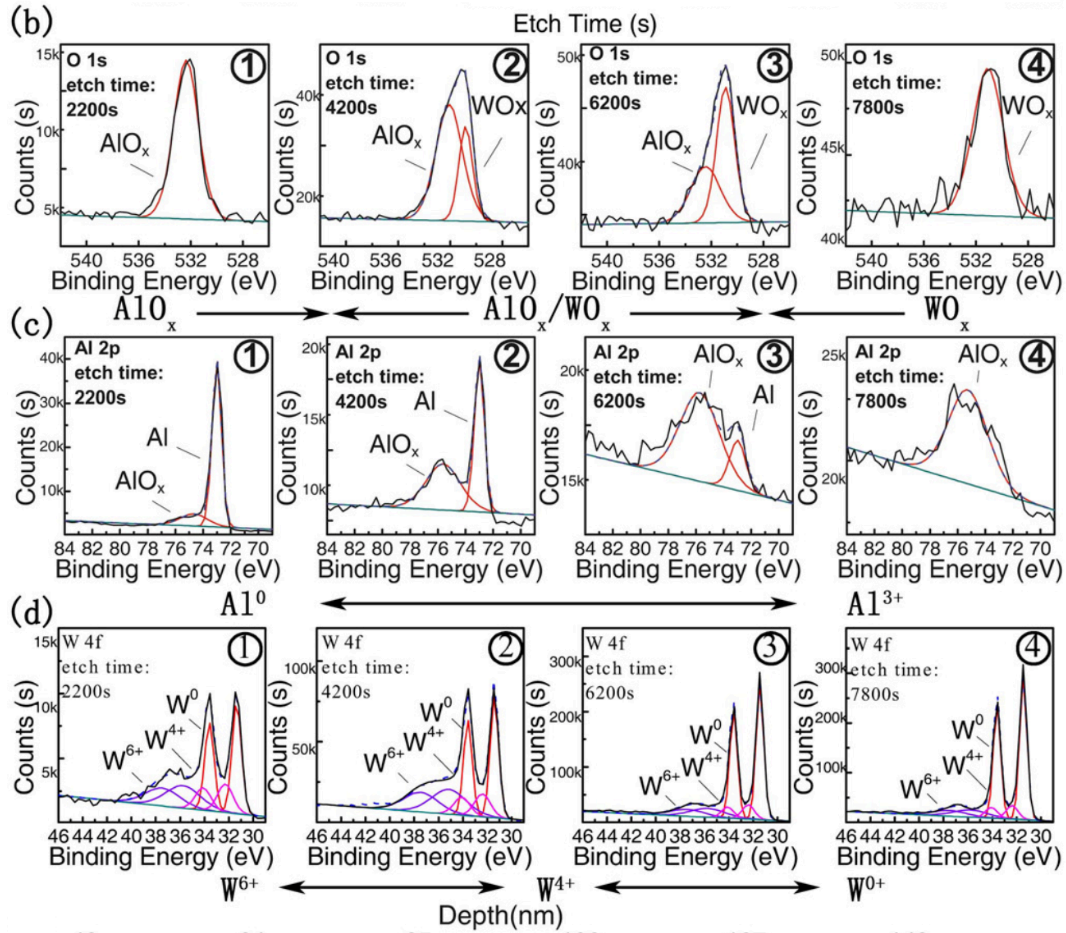

Figure 8. O 1s, Al 2p, and W 4f XPS spectra

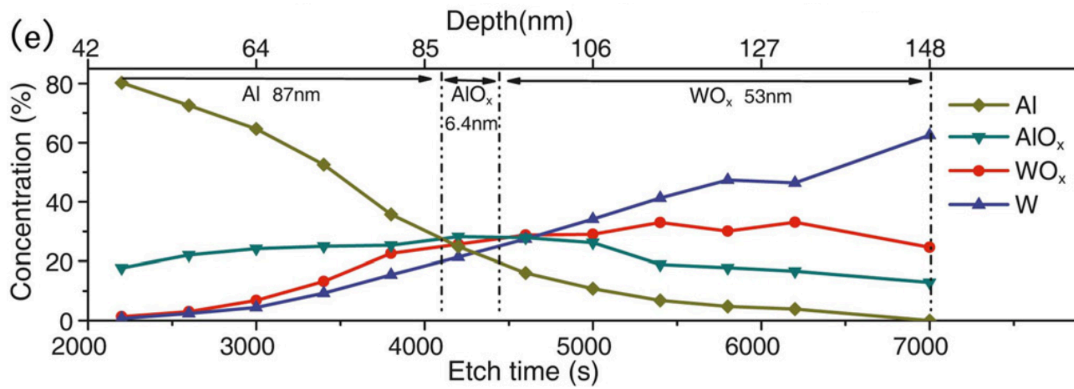

Figure 9. Summary of the concentration