Determination of Ti to N ratio of Titanium Nitride coating by Auger Electron Spectroscopy and X-ray Photoelectron Spectroscopy

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Physical vapor deposition (PVD) is a coating process used in manufacturing of items which require thin films for mechanical, optical, chemical or electronic applications. Common industrial coatings applied by PVD are titanium nitride (TiN), zirconium nitride (ZrN), chromium nitride (CrN), titanium aluminum nitride (TiAlN)

Take TiN as an example. TiN is a ceramic-type material having many attractive characteristics such as low electrical resistance, good corrosion resistance, and considerable hardness, often used as a thin coating on steel and carbide to incorporate corresponding properties on the substrate's surface. It could be used as a hard coating for machine tools and as a protective coating in watchcase, It is also used for decorative purposes due to its gold appearance.

In order to control deposition processes and relate them to material properties, it is necessary to characterize the Ti to N ratio of the applied coating. In most applications a TiN coating of less than 5 microns is applied but sometimes even less than 1 micron. It is difficult to quantify the TiN content by EDX and XRF as both analytical techniques have relatively large analysis volume and less sensitive to low atomic number elements such as Carbon, Oxygen and Nitrogen. Therefore, more surface sensitive analytical techniques such as Auger Electron Spectroscopy (AES) and X-ray Photoelectron Spectroscopy (XPS) are particularly suited for thin film analysis.

TiN analysis by Auger Electron Spectroscopy (AES)

Auger Electron Spectroscopy (AES) is a quantitative analytical technique that utilizes a finely focused high energy electron beam (up to 20keV) as an excitation source to eject Auger electrons from the surfaces of solid materials. The in-situ electron energy analyzer is used to measure the kinetic energy (KE) and number of electrons that escape from the surface. From the kinetic energy and intensity of an Auger peak, the elemental identity and quantity of a detected element can be determined. The average analysis depth of Auger electrons approximately 5 nm which make AES is extremely surface sensitive. The following TiN analysis is done by PHI 680 Scanning Auger Nanoprobe (figure 1)

Figure 1. PHI 680 Scanning Auger Nanoprobe

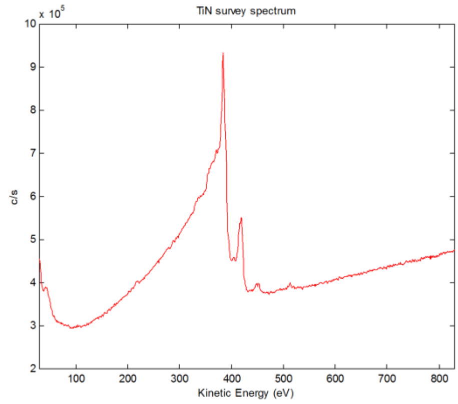

Figure 2. Survey spectrum of TiN coating by AES

Firstly, a survey spectrum is acquired to determine the elements existed on the TiN coating (figure 2). For quantification, it is required to obtain the derivative spectrum, the relative atomic % of the detected elements are related to the peak to peak height of the Ti and N signals (figure 3).

The quantification of TiN by AES is a somewhat a tricky issue as the major N1 peak overlapped with the Ti1 peak at ~390eV (figure 4). Direct quantification of Ti:N ratio using the major peaks will lead to overestimation of N content (Ti2 : N1 = 1 : 3.5). In this case, using a minor N2 peak (no direct overlap with Ti1 peak) to determine the N content could obtain approximate stoichiometric Ti to N ratio (Ti2 : N2 = 1 : 1.1).

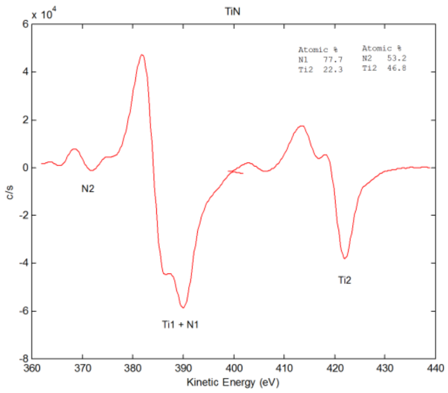

Figure 3 Derivative spectrum of Ti and N in TiN coating

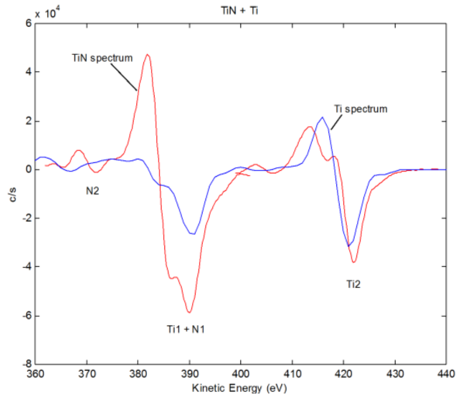

Figure 4 Overlapped spectra of TiN and Ti reference

TiN analysis by X-ray Photoelectron Spectroscopy (XPS)

X-ray Photoelectron Spectroscopy (XPS) is a quantitative spectroscopic technique that measures the elemental composition and chemical states of the elements that exist in a material. XPS spectra are obtained by irradiating a material with a beam of monochromatic Aluminum X-ray (Al Kα) causing photoelectrons to be emitted from the sample surface. The in-situ electron energy analyzer is used to measure the kinetic energy (KE) and number of electrons that escape from the top 5 nm of the material. From the binding energy (deduced from KE) and intensity of a photoelectron peak, the valuable information about the elemental identity, chemical state and relative amount of the detected elements can then be determined. The following TiN analysis is done by PHI Quantera Scanning X-ray Microprobe (figure 5)

Fig 5. PHI Quantera Scanning X-ray Microprobe

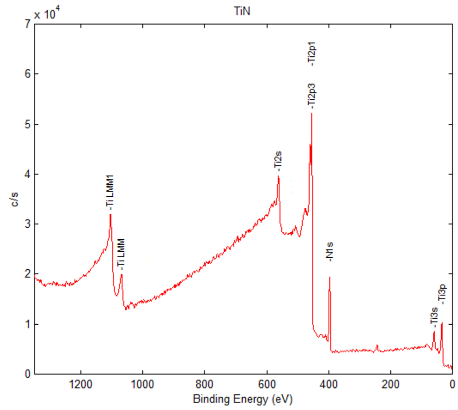

Figure 6. Survey spectrum of TiN by XPS

Firstly, a survey spectrum is acquired to determine the elements existed on the TiN coating (figure 6). For quantification, it is required to integrate the area under the elemental peak. Direct quantification of Ti:N ratio using Ti2p3 and N1s peaks could obtain stoichiometric Ti to N ratio (figure 7).

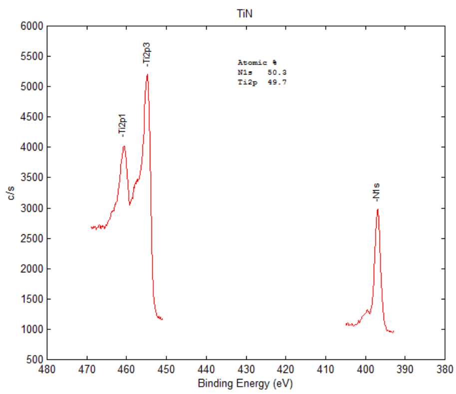

Figure 7. Ti2p3 and N1s spectrum in TiN coating by XPS

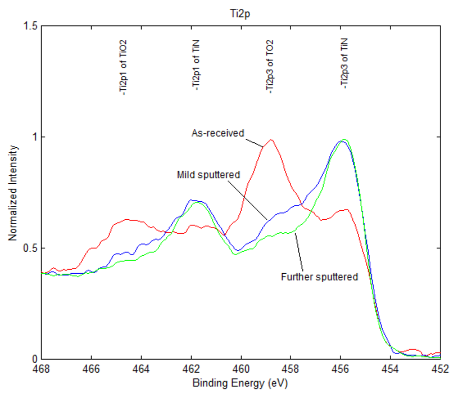

Figure 8. Ti2p3 peaks with different sputter treatments

One of the advantages of XPS over AES is chemical analysis. The binding energy of the element detected could tell the chemical state information. On the as-received surface of TiN coating, the TiO_2 signal (at ~459eV) is dominant over the TiN signal (at ~456eV). Use of inert gas ion gun could help to sputter the sample surface in order to remove surface oxide and contaminant, making the quantification of Ti and N possible with minimum chemical interference. The XPS spectra show that the TiO_2 peak gradually decreases whereas the TiN peak becomes the dominant peak after sputter cleaning by in-situ Ar ion gun (figure 8).