A Method for the Measurement of Thickness of Inorganic Solid Films by Medium Energy Electron Excited X-ray Fluorescence

Hailong Zhou¹, Feng Yu¹ and Zhenguo Ji²*

¹Zhejiang Sunflux Electron Co. Ltd, Binghai New City, Shaoxing 312366, China
²College of Materials & Environmental Engineering, Hangzhou Dianzi University, Hangzhou 310018, China
Email: jizg@hdu.edu.cn

Abstract. In this paper, a new non-destructive method of measuring the thickness of nanometer thin films by medium energy electron excited X-ray fluorescence was introduced. Due to strong decay of the intensity of incident electron beam with energy of the order of 1 keV in solid materials, the penetration depth is very small, only in the order of 1 nm. Therefore, the escape depth of the X-ray fluorescence excited by the electron beam is also limited by the penetration depth of the incident electron beam, i.e., the X-ray fluorescence detected is emitted only from the top most layers. By simply compare the intensity of an XRF peak from the substrate with/without the deposition of thin film, the thickness of the films can be easily calculated. The method described in this paper is simple in participle, non-destructive, and applicable for films of any elements. As an example, a set of Al films deposited on Si substrate was demonstrated, the results show that this method is feasible, and the detection limit can be as low as 1 nm or less.

Keywords. Electron beam, X-ray fluorescence, film thickness.

1. Introduction

Thin films have been widely used in electronic, onto-electronic, and optical devices. Among many parameters, film thickness is one of the key parameters which affect the performance of devices. Non-destructive measurement of the film thickness is favourable due to the high cost of film fabrication, e.g., for films deposited on 12-and 16-inch silicon wafers.

There several methods of non-destructive measurement of film thickness, such as optical interference [1, 2], X-ray fluorescence(XRF) [3], ellipsometry [4], X-ray photoelectron spectroscopy (XPS)/Auger electron spectroscopy (AES) [5-7], in situ Quartz oscillation monitor [8-9], small angle X-ray reflection (SAXRR) and high resolution X-ray diffraction (HRXRD) rocking curve [1, 10-11], and TEM and SEM cross-section, etc, [10, 12]. All of the above methods have shortages. Optical interference method only applicable for film thickness greater than 10 nm or so, and the films should be transparent. X-ray fluorescence method can also measure films with thickness greater than 10 nm or so, and the films must contain composition elements with atomic number greater than certain number, such as 13, i.e., aluminium, but not suitable for films consist of light elements, such as Li, Be, B, C, N, O, S, etc. Ellipsometry can measure thickness as thin as 1nm and even thinner, but is not applicable opaque films, such as metal or alloy films. XPS and AES can detect monolayer thickness, or 0.1 nm, but its detection depth is limited to the order of 1 nm since the small escape length of the
emitted electrons. For thicker films, ion sputtering is needed, but this is destructive, and is not meets the need of non-destructive of most device fabrication process. Quartz oscillation monitor is high sensitive for thickness, but it is an in situ method, and only used to monitor the films during deposition, and is not applicable for ex situ applications. SAXRR and HRXRD can measure nano-meter film thickness, but it needs atomic smooth surface, and is not good at 2D thickness imaging since the larger spot-size of the X-ray. SEM cross-section and TEM are both destructive method and should be avoid in routine work.

Above all, no one method is as perfect for all purpose. In this paper, we propose a universal method for inorganic thin films, i.e., electron excited X-ray fluorescence (EEXRF), which may overcome most shortages of common thickness measurement method. The principle of the EEXRF is exactly the same as EDS in SEM.

2. Theory and Experimental

As electron beam incident onto solid surface, X-ray fluorescence emits which contains the composition information of the solid surface, such as Energy Dispersive Spectroscopy (EDS) in a common SEM. While in that cases, high energy electron beam (~5-20 keV) are normally used to excite the surface, both the penetration depth of the electron and the escape depth of the emitted X-ray fluorescence are too large for film thickness analysis, even though for the analysis of nano-meter thick films. But, if the incident electron energy is reduced to 1 keV or so, then the interaction between incident electrons and the atoms in the solid will much stronger, thus reduce the penetration depth of the incident electron, the case is similar to photoelectrons/Auger electrons in XPS/AES. Thus, by simply changing the electron beam energy, the analysis depth can be easily controlled.

As shown in figure 1, an electron beam with intensity is incident on the surface of the film deposited on the surface. The emitted X-ray fluorescence peak intensity of a certain element of the substrate can be written as:

\[ I = I_0 e^{-\mu_d \cos \alpha} e^{-\mu_x \cos \beta} \]  

where \( I \) and \( I_0 \) are intensities of X-ray fluorescence emitted from certain element of the substrate with and without film deposited, respectively, \( d \) is the thickness of the film, \( \mu_e \) is decay factor of the incident electron beam in the film, \( \mu_x \) is the decay factor of the X-ray fluorescence in the film, \( \alpha \) is the incident angle of the electron beam, \( \beta \) is the emission angle of the X-ray fluorescence.

In most cases, the penetration length of X-ray is much larger than that of electrons with energy of the order of 1 keV, therefore, \( \mu_x \) is much smaller than \( \mu_e \), and if the incident angle \( \alpha = 0 \), then equation (1) can be simplified as:

\[ I = I_0 e^{-\mu_e d} \]  

In practice, \( \mu_e \) can be determined by measuring a standard sample with known thickness, therefore, the film thickness is reduced as:

\[ d = \frac{1}{\mu_e} \ln \frac{I_0}{I} \]  

Figure 1. Schematic diagram of the thickness measuring method proposed.
Finally, thickness measurement was carried out on a SEM microscope with incident electron energy of 2 keV, beam current of 50 nA, and the incident angle $\alpha = 0$.

### 3. Results and Discussions

A set of Al films on Si substrate was prepared by e-beam evaporation, the thickness of the films are 5 nm, 10 nm, 15 nm, and 20 nm respectively, as measured by in situ quartz oscillation monitor during deposition. Figure 2 shows the EDS spectra of Al and Si from the samples. The peak at 1.485 keV is from Al films, and the peak at 1.739 keV was at Si substrate. It is clear that as the Al film thickness increases, the Al peak intensity increase, while the Si peak intensity decreases.

![Figure 2. EDS spectrum of samples with various Al film thickness.](image)

Figure 3 shows the relationship between Si peak intensity and Al film thickness, exponential decay trend is clear as predicted by equation (3). Exponential data fitting using equation (2) gives $\mu_e = 0.154$ nm$^{-1}$ for incident electron energy of 2 keV. Having the result of $\mu_e$, we can measure unknown thickness samples with equation (3) easily.

![Figure 3. The relationship between Si peak intensity and Al film thickness.](image)

Figure 4 shows the relationship of the Al thickness as measured by in situ quartz oscillation monitor and the data calculated by equation (3). Good linear relation is observed.

It is seen from the above example, that medium energy electron excited X-ray fluorescence can be used to measure the thickness of solid films. For electron energy of 2 keV, 5 nm deposited Al film will
reduce the substrate Si signal to about half of the original value without the Al film. That means it is a sensitive method for the measurement of nano-meter films.

![Graph](image)

**Figure 4.** Relationship between the thickness determined by in situ quartz crystal oscillator during deposition and the thickness determined by this method.

4. Conclusion

This method has many advantages, such as suitable for films consisting of any elements including Li, B, C, N, O, F, etc., which are interested by many researchers, since all elements in the film will strongly interact with medium energy electron beam, and the X-ray fluorescence is from the substrate but not the film itself. The only limitation is that at least one element in the substrate can emits X-ray fluorescence which can be detected by the X-ray detector, no matter what elements is in the film. In addition, the penetration depth of the electron beam can be changed easily to facilitated films with various thickness, so that the detection limit can be easily extended to 100 nm, 1000 nm, and even thicker, simply by increasing the working voltage of the electron gun. Furthermore, it is easy for line scan and 2D imaging of the film thickness, and can get high resolution line and 2D thickness distribution in minutes. One last benefit is that the measurement can be operated on any SEM microscope with EDS function, without any extra expense on hardware for users.

References

[1] Ji Z G, Feng D D, Xi J H, Mao Q N, Yuan Y, Hao F and Chen M M 2008 *Materials Science and Engineering* **26** (3) 325-7 (in Chinese)
[2] Kitagawa K 2014 *Optics Letters* **39** (14) 4172-5
[3] Lopes F, Amorin L, Martins L, Urbano A, Appoloni C and Cesareo R 2016 *Journal of Spectroscopy* 9509043
[4] Gonçalves D and Eugene EA, 2002 *Quimic Nova* **25** (5) 794-800
[5] Zhang L, Lloyd K and Fennimore A 2019 *Journal of Electron Spectroscopy and Related Phenomena* **231** 88-93
[6] Lian S Y, Lin B, Yan X L, Wang J Y and Xu C K 2019 *Vacuum* **160** 109-13
[7] Goyal A, Brajesh S, Yadav B S, Raman R, and Kapool A 2018 *AIP Advances* **8** 025021
[8] Ramadan B, Piyakis K, and Kos J F 1979 *Review of Scientific Instruments* **50** 867
[9] Gribova L K, Savchenko V E, and Sorokin A V 2005 *Measurement Techniques* **48** (2) 146-8
[10] Ménesguen Y, Boyer B, Rotella H, Lubeck J, Weser J, Beckho B, Grötzsch D, Kanngießer B, Novikova A, Nolot E and Lépy M C 2017 *X-Ray Spectrom.* **46** 303-8
[11] Liang M M, Weng G E, Zhang J Y, Cai X M, Lv X Q, Ying L Y and Zhang B P 2014 *Chinese Phys. B* **23** 054211
[12] Li F, He H, Tian Q, Xiao C D, Li J H and Zhu W H 2016 *IEEE Transactions on Components, Packaging and Manufacturing Technology* **6** (6) 954-8