Precision Thickness Measurement of Ultra-Thin Films via XPS

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Abstract. XPS (X-ray Photoelectron Spectroscopy) or ESCA (Electron Spectroscopy for Chemical Analysis) can accurately measure the thickness of ultra-thin films thinner than 2 nm and its precision is ±0.1nm. XPS remedy the deflection of TEM that is difficult to determine the thickness for films thinner than 1 nm, but XPS is not accurate for films thicker than 10 nm. This paper aims at reviewing the application of XPS in determining thickness of ultra-thin films.

Introduction

Ultra-thin films such as SiO₂ films are very important for novel nanoelectronic devices and circuit [1]. Precise thickness determination is thus critical in these applications. There are a number of analytical techniques capable of measuring thickness of thin films including XPS (X-ray Photoelectron Spectroscopy), AES (Auger Electron spectroscopy), SIMS (Secondary Ion Mass Spectrometry), RBS (Rutherford Backscattering) and TEM (Transmission Electron Microscopy) [2]. However, no single technique is able to perform a precision measurement in the entire range from 0 to 20 nm. XPS and AES can offer precise thickness measurements for ultra-thin (<2 nm) films. SIMS has been used for characterizing relatively thick films (>10 nm). TEM is capable of accurate measurement of films thicker than 1 nm. As film thickness is scaled down to several atomic layers, XPS offers precision determination for thickness thinner than 2 nm. The present paper attempts to review this aspect of XPS application.

1. Thickness of SiO₂ film

It is well known that XPS as a tool to check thin film thickness is due to the finite mean free path length, which is function of kinetic energy of the photoelectron. For example, XPS can offer precise thickness measurements for ultra thin SiO₂ film. The thickness \( d_m \) of SiO₂ film formed on Si substrate was determined using the following equation [3, 4]:

\[
d_m = \lambda_m \sin \theta \ln \left( \frac{I_m}{I_{m0}} + 1 \right). \tag{1}
\]

where \( \lambda_m \) is the attenuation length of the Si 2p photoelectrons in SiO₂, \( \theta \) is a photoelectron take-off angle, i.e., the angle between the sample surface plane and the incident beam, \( \beta = I_m/I_{m0} \) (where \( I_m \) and \( I_{m0} \) are the Si 2p intensities of “infinitely thick” (greater than 30nm) SiO₂ and Si, respectively) and \( I_m/I_{m0} \) is the ratio of intensities from the unknown film. Unfortunately, there is considerable disagreement in the XPS literature in the two sample-dependent constants: \( \lambda_m \) and \( \beta \). Reported \( \lambda_m \) values vary from 2.4-3.8nm, while \( \beta \) varies from 0.6-1.01 [4, 5, 6, 7, 8]. It has been suggested that much of the discrepancy in the reported \( \lambda_m \) values stems from the use of poorly calibrated ellipsometry 'standards' that tend to overestimate the thickness of ultra thin SiO₂ films [1, 4, 9, 10, 11]. For this reason, it was decided to use an attenuation length of 2.7±0.2nm, averaged from four different TEM/XPS publications [4, 5, 6]. The value of \( \beta \) was determined by analyzing two different standard
samples: a 5% HF etched Si (100) surface and a thick thermal SiO₂ film that is thicker than 30nm. Both standards were lightly sputtered with 3 keV Ar⁺ to remove absorbed organic species and the native oxide and fluoride (on the HF etched Si sample). Normally, the β value is about between 0.75 and 0.85 [6, 12].

For ultra-thin SiO₂ films, XPS gives very precise thickness according to Eq.1. For example, Fig.1 shows the ability of XPS to measure very small difference in ultra-thin oxides of SiO₂ [12]. Although TEM can offer the precise thickness measurement, analysis on films thinner than 1nm is extremely difficult [2]. Furthermore TEM sample preparation is also an arduous endeavor. In order to check the precision of thickness measurement by XPS, the same sample of SiO₂ film was measured by both XPS and TEM. According to Fig.2 [6] and Eq.1, the calculated thickness of SiO₂ film is 6.4nm which is amazingly the same as the TEM result (Fig.3) [6]. XPS is so sensitive to small changes in oxide thickness for ultra-thin films (<2nm, the precision is ± 0.1nm). However, the inherent limitation is its insensitivity to change in oxide thickness of thicker films (>10nm) because the Si relative intensity decays exponentially with the increase of oxide thickness ($I_o \propto e^{-2x/10nm}$). This can be seen from Fig.4 [12].

![Fig.1 Si 2p spectra of ultra-thin SiO₂ oxides showing difference of as small as 0.1nm [12]](image1)

![Fig.2 XPS Si 2p spectrum of a 6.4 nm SiO₂ film on Si (bulk) (100) [6]](image2)

![Fig.3 TEM micrograph showing the thickness of SiO₂ film on Si(100) [6]](image3)
2. Thickness of lubricant layer on magnetic disk

Control of lubricant film thickness is a serious problem in magnetic disk mass production process. XPS is an important tool to measure the thickness of lubricant layer on a magnetic disk. For example, the thickness of a perfluoropolyether lubricant layer on the resin coated surface of a magnetic disk was measured by XPS according to C1s signal from the perfluoropolyether lubricant layer and the resin substrate [13, 14]. However, C1s Signals can not be used to measure the lubricant thickness of thin layer magnetic disks because C1s has a multiple signal form such as contamination. M. Hoshino and Y. Kimachi [15] measured the thickness of lubricant layer on magnetic recording disks by using a model with a lubricant layer on a silicon dioxide substrate and the XPS O1s signal ratio of lubricant and silicon dioxide according to this equation (the take-off angle is 90°):

\[ d = 16 \ln \left( 7.2 \left( \frac{I_1}{I_2} \right) + 1 \right) \]  

(2)

Where \( d \) is the thickness of lubricant layer, \( \frac{I_1}{I_2} \) is the ratio of the intensities of O1s photoelectrons coming from lubricant layer (perfluoropolyether) and from silicon dioxide. It is obvious that the thickness of lubricant layer can be calculated from the ratio of \( \frac{I_1}{I_2} \) that can be obtained from the XPS spectra as demonstrated in Fig.5 (x axis is Bending energy) for different concentration polyether.

Fig.5 XPS O1s signal of different concentration perfluoropolyether, O1s from SiO2 (534.6eV), O1s from perfluoropolyether (537.2eV) [15]
Summary

XPS gives precise determination of thickness of ultra-thin films such as SiO₂ film and the precision is ± 0.1nm for films thinner than 2nm, which remedy the limitation of TEM for films thinner than 1 nm. However, XPS thickness measurement is not accurate for thicker films (thicker than 10nm) because of the exponential decaying of the Si relative intensity with the increasing of oxide thickness. Furthermore, the thickness of ultra-thin lubricant layer on magnetic disk can be determined by using the XPS O1s signal ratio of lubricant layer and silicon dioxide.

References