Vacuum 113 (2015) 5–10

Contents lists available at ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum

A model for quantification of GDOES depth profiles

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ARTICLE INFO

Article history:
Received 1 October 2014
Received in revised form
13 November 2014
Accepted 14 November 2014
Available online 21 November 2014

Keywords:
GDOES depth profiling
MRI model
CRAS model
Roughness
Crater effect
Preferential sputtering

ABSTRACT

The MRI (Mixing-Roughness-Information depth) model and the CRAS (Crater-Simulation) model are combined for the quantification of GDOES (glow discharge optical emission spectroscopy) depth profile by taking into account the effects of crater, roughness and preferential sputtering in depth profiling. This combined model is successfully applied for the quantification of the measured GDOES depth profiles of N in a nitride coating and of Ni in a Ni-coated copper substrate.

1. Introduction

Glow discharge optical emission spectroscopy (GDOES) is a powerful and promising technique for depth profiling analysis, owing to the combinations of fast sputtering rate, high depth resolution, excellent sensitivity and multi-element capability and low cost [1–3]. Compared with AES, XPS and SIMS depth profiling techniques, the rapid measurement of GDOES depth profiling is unique and its sputter rate could be as fast as the order of 1 μm/min [4]. This technique allows depth profiling analysis for thin/thick films from few nanometers to several tens of microns and for various application fields from organic molecular to alloy films, galvanized or painted steels, hard coating etc. [5–7]. The ultimate depth resolution of ~1 nm could be achieved due to much low energy sputtering (<100 eV). The main distortional effects upon GDOES depth profiling come from the atomic mixing, the surface/interface roughness, the preferential sputtering, the non-linearity response between measured intensity and surface concentration, and the crater effect due to non-homogenous sputtering flux, re-deposition, and surface diffusion. In the Mixing-Roughness-Information depth (MRI) model, the effects of the atomic mixing and the surface/interface roughness and the preferential sputtering have already been taken into account. While, the crater effect has been considered in the Crater-Simulation (CRAS) model.

In this paper, it will be demonstrated that, by the combination of the MRI and the CRAS models, the measured GDOES depth profile could be quantitatively evaluated.

2. Theory

2.1. The MRI model

The MRI model and its extension developed by Hofmann and his coworkers have been widely used for the quantification of AES, XPS, and SIMS depth profiles [8–14]. According to the MRI model, the measured profile $I(z)/I^0$ can be expressed as the convolution of the original concentration distribution $X(z)$ with the depth resolution function (DRF) $g(z)$ as.

$$\frac{I(z)}{I^0} = \int_{-\infty}^{+\infty} X(z')g(z-z')\mathrm{d}z' \tag{1}$$

In the conventional MRI model [8–11], the DRF is constructed by three partial characteristic DRFs describing the three main distortional effects in any depth profiling process: atomic mixing (g_w), surface/interface roughness (g_σ) and information depth (g_λ), as follows.

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http://dx.doi.org/10.1016/j.vacuum.2014.11.015
0042-207X/

$$\begin{cases} g_w(z) = \dfrac{1}{w}\exp\left(-\dfrac{z+w}{w}\right) & z > -w \\ g_\sigma(z) = \dfrac{1}{\sqrt{2\pi}\sigma}\exp\left(-\dfrac{z^2}{2\sigma^2}\right) \\ g_\lambda(z) = \dfrac{1}{\lambda}\exp\left(\dfrac{z}{\lambda}\right) & z \le 0 \end{cases} \tag{2}$$

Recently, an analytical DRF for the MRI has been derived [9]. For the GDOES depth profiling, the depth information λ can be ignored and this analytical DRF for a given rectangle layer with interface positions z_1 and z_2 is expressed as:

$$\begin{aligned}\left(I(z)/I^0\right)_{\mathrm{d-MRI-GDOES}} = & \frac{1}{2}\cdot\left[\mathrm{erf}\left(\frac{z+w-z_1}{\sqrt{2}\sigma}\right)-\mathrm{erf}\left(\frac{z+w-z_2}{\sqrt{2}\sigma}\right)\right] \\ & +\frac{1}{2}\cdot\exp\left(-\frac{z+w}{w}+\frac{\sigma^2}{2w^2}\right)\times\left\{\exp\left(\frac{z_2}{w}\right)\right. \\ & \cdot\left[1+\mathrm{erf}\left(\frac{z+w-z_2}{\sqrt{2}\sigma}-\frac{\sigma}{\sqrt{2}w}\right)\right]-\exp\left(\frac{z_1}{w}\right) \\ & \left.\cdot\left[1+\mathrm{erf}\left(\frac{z+w-z_1}{\sqrt{2}\sigma}-\frac{\sigma}{\sqrt{2}w}\right)\right]\right\}\end{aligned} \tag{3}$$

For low energy sputtering, the atomic mixing parameter w can be ignored and Eq. (3) is simplified as

$$\left(I(z)/I^0\right)_{\mathrm{d-MRI-}\sigma} = \frac{1}{2}\cdot\left[\mathrm{erf}\left(\frac{z-z_1}{\sqrt{2}\sigma}\right)-\mathrm{erf}\left(\frac{z-z_2}{\sqrt{2}\sigma}\right)\right] \tag{4}$$

With respect to the preferential sputtering effect, in the extended MRI model [15], the total sputter rate of a multi (N)-elements matrix q_M is assumed to be linearly composition dependent and given as

$$q_M(z) = \sum_i^N q_i X_i(z) \tag{5}$$

where q_i is the sputter rate of pure element i, and X_i is its concentration in the matrix with $\sum_1^N X_i = 1$.

Then, the sputtering time t is given by

$$t(z) = \int_0^z \frac{dz'}{q_M(z')} \tag{6}$$

The preferential sputtering effect breaks not only the non-linearity of sputter rate (see Eq. (6)), but also affects the sputtered-induced concentration change due to the interplay between the preferential sputtering effect and the cascade mixing [16–18]. To consider this non-linear effect, the atomic mixing process is described by a differential equation as [19]:

$$\frac{dX_i}{dz} = \frac{X_i^0(z+w)-f_i(z)X_i}{w} \tag{7}$$

where $f_i(X_1 \ldots X_N) = q_i/q_M$, X_i and q_i are the concentration and sputter rate of element i ($i = 1 \ldots N$), respectively.

The surface concentration-sputtered depth profile $X(z)$ after mixing process obtained from Eq. (7) is then convoluted with the function of g_σ for roughing effect to get the simulated depth profile $I(z)$ by Eq. (1). After changing the depth scale z to the sputtering time scale t by Eq. (6), the simulated depth profile $I(t)$ is ready for the comparison with the measured depth profile, i.e. the intensity versus the sputtering time profile.

2.2. The crater effect modeling

The crater effect that is the main distortion factor in GDOES depth profiling was firstly evaluated by Z. Weiss [20], and then by S. Oswald and V. Hoffmann in the CRAS model [21,22]. Compared to the other methods, for example, the complex modeling network (Monte Carlo, fluid and collisional-radiative models) by Bogaerts at al. [23], the above method is simple and flexible to be applied and extended based on the phenomenological description for the sputtered crater.

During glow discharge sputtering process, a crater forms gradually a circular region with diameter $r^{\max}$ of 1–8 mm. Any lateral position in the crater is indicated by a radius r^{real} or a dimensionless radius r given by $r = r^{\mathrm{real}}/r^{\max}$. The measured intensity can be regarded as all the signal contributions from the crater surface and is given by

$$I(t) = K \iint_{\mathrm{crater}} I^{\mathrm{local}}(x,y)\,dx\,dy \tag{8}$$

where I^{local} represents the measured intensity at position (x,y) within the crater in orthogonal coordinate and K represents the normalized factor. Considering the radial symmetry, Eq. (8) is simplified in polar coordinate as:

$$I(t) = K\int_0^1 r\cdot I^{\mathrm{local}}(r)\,dr \tag{9}$$

It is demonstrated that the measured GDOES intensity is proportional to the sputtering rate q and the surface concentration X by Refs. [24,25]:

$$I(X,t) = S_i(X)\cdot q\cdot X \tag{10}$$

where S_i represents the sensitive factor of element i, which includes the correction factor for self-absorption and the emission yield (setting as unity for simplicity), q is the matrix sputtering rate.

Due to the different weights in signal from the different positions of the crater with respect to the detected axial direction, the transfer function $W(r)$ [26] is given as

$$W(r) = \frac{1}{1+r} \tag{11}$$

By substituting Eqs. (10) and (11) into Eq. (9), it is obtained

$$I(t) = K\cdot\int_0^1 r\cdot W(r)\cdot q(r,X)\cdot X(t,r)\,dr \tag{12}$$

where the normalized factor K is given as the reciprocal of the intensity I^0 for pure element ($X = 1$), then $K = 1/\int_0^1 r\cdot W(r)\cdot q(r)_{X=1}dr$.

In the CRAS model, the radius r and the sputtering flux intensity $J(r)$ has a phenomenological relationship as [22]:

$$J(r) = J_C\left[1 + a\cdot r^b\right] \tag{13}$$

where $a = (J_E - J_C)/J_C$ with J_C ($=J(r = 0)$) and J_E ($=J(r = 1)$), which represent the flux intensities at the center ($r = 0$) and the edge ($r = 1$), respectively.

Introducing the crater parameter $p = J_E/J_C$, and the mean value of flux intensity $\bar{J}$, Eq. (13) can be rewritten as