Applied Surface Science 331 (2015) 140–149

Contents lists available at ScienceDirect

Applied Surface Science

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

Quantitative reconstruction of the GDOES sputter depth profile of a monomolecular layer structure of thiourea on copper

Y. Liu[a], W. Jian[a], J.Y. Wang[a,*], S. Hofmann[b], K. Shimizu[c]

[a] Department of Physics, Shantou University, 243 Daxue Road, Shantou, 515063 Guangdong, China
[b] Max Planck Institute for Intelligent Systems (formerly MPI for Metals Research), Heisenbergstrasse 3, D-70569 Stuttgart, Germany
[c] University Chemical Laboratory, Keio University, 4-1-1 Hiyoshi, Yokohama 223-8521, Japan

ARTICLE INFO

Article history:
Received 3 November 2014
Received in revised form 9 January 2015
Accepted 10 January 2015
Available online 17 January 2015

Keywords:
MRI model
GDOES
Depth profile
Depth resolution function
Thiourea monolayer

ABSTRACT

High-resolution depth profiles of a thiourea (CH_4N_2S) molecular monolayer on a copper substrate obtained by radio frequency glow discharge optical emission spectroscopy (rf-GDOES) are quantified by the Mixing-Roughness-Information depth (MRI) model. Based on the molecular structure of the self-assembled thiourea layer, the measured intensity-sputtering time profiles of N, S, C and Cu are fitted to the MRI model results with an appropriate depth resolution function. The sputtering rate is determined accordingly, using two different approaches based on constant sputtering rate and on composition dependent sputtering rate. While the first approach requires an additional background for a fairly acceptable solution, the approach using a newly developed multielement dependent sputtering rate results in a complete and consistent reconstruction of all the measured elemental depth profiles. It is demonstrated that for depth profiling of the first few monolayers with rf-GDOES, the depth resolution Δz can be as low as 0.5 nm, which is of the order of the theoretical limit.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

The technique of glow discharge optical emission spectroscopy (GDOES) is generally used for depth profiling analysis of relatively thick films because of its extremely high sputtering rates (>1 μm/min) [1]. However, it shown that GDOES, and particularly radio frequency GDOES (rf-GDOES), also has advantages for depth profiling of rather thin layers of the order of 10 nm thickness down to the atomic monolayer regime [2–7], where usually AES or SIMS depth profiling are applied [5,8]. The main advantages of GDOES for thin surface layer profiling are [1–4]: (a) low Ar ion sputtering energies (<50 eV); (b) all elements detectable (including hydrogen); (c) low matrix effects, (d) no requirement for ultra-high vacuum. Additional advantages of rf-GDOES are its applicability for both conducting and non-conducting samples by providing in-situ charge compensation, and an easier ignition and immediately stable working of the discharge [1–3]. A general disadvantage of GDOES with respect to depth resolution and profile shape is the formation of a sputtering induced crater and therefore unavoidable crater rim effects which distorts the profile. Since usually crater edge dependent degradation of the depth resolution increases linearly with sputtered depth [3,8], this effect is insignificant at low depth (<10 nm). Because GDOES does not operate in ultrahigh vacuum, another disadvantage is contamination from atmospheric particles, in particular of hydrocarbons, which directly influences the analysis of carbon and hydrogen.

Quantification of GDOES depth profiles is most often done by application of elemental sensitivity factors obtained from bulk or thick film standard samples and estimated or measured average sputtering rates to the measured intensity-sputtering time profile to obtain a concentration–depth profile [1,9]. This method is adequate for bulk samples or for relatively thick layers (i.e. for depth resolution small against the layer thickness or the inverse maximal slope of an intensity gradient [8,10]). For thin layers (i.e. depth resolution equal or larger than the layer thickness or the inverse maximal slope), the concentration between neighboring layers is superimposed during the sputtering process, and the usual method results in an apparent instantaneous concentration which does not represent the true, original layer composition. To obtain the latter, an appropriate model description of the action of sputtering and analysis method is necessary, which is generally described by an appropriate model such as the MRI model [8,10]. With this model, a deconvolution of the measured profile with the help of a convolution integral, i.e. a true quantification of a depth profile, is possible. This has been demonstrated for many measured SIMS, AES and XPS depth profiles (see e.g. [8,10–12] and references therein). A

---

* Corresponding author. Tel.: +86 754 82902225; fax: +86 754 82902225.
E-mail address: wangjy@stu.edu.cn (J.Y. Wang).

http://dx.doi.org/10.1016/j.apsusc.2015.01.065
0169-4332/© 2015 Elsevier B.V. All rights reserved.

similar method based on the convolution integral was employed by Präßler et al. [13] to extract the influence of crater formation in GDOES on the shape of a multilayer profile. However, the full MRI model is for the first time applied here to a profile measured by GDOES.

It is a great challenge to apply profile reconstruction for extremely high depth resolution GDOES profiles in the sub-nanometer regime in order to obtain more detailed information about the key parameters in depth profiling. In this paper, it is demonstrated that the high-resolution rf-GDOES depth profiles of a monolayer of a thiourea molecule adsorbed on a copper substrate published 10 years ago [3] can be fairly well reconstructed by applying the Mixing–Roughness–Information depth (MRI) model on the basis of the molecular structure of thiourea.

2. Rf-GDOES depth profiling results of a thiourea monolayer on copper

We refer to the first example of an rf-GDOES depth profile of a layer with sub-nanometer thickness which was already presented in ref. [3]. This selected example is a self-assembled monolayer of thiourea adsorbed on a mirror-polished copper substrate. Details of the thiourea monolayer preparation and the rf-GDOES depth profiling measurement have been described in ref. [4]. Here, a brief summary is given:

Copper sheets of 99.99% purity were mechanically polished using a suspension of fine alumina particles of size ~0.05 μm. The mechanically polished specimens were then rinsed in 10% H_3PO_4 solution at 293 K to remove residual oxide, rinsed thoroughly in distilled water, and immersed immediately, without drying in air, in 0.01 M thiourea solution for 1 min at 293 K. After immersion in the thiourea solution, the specimens were rinsed thoroughly in distilled water, dried in a cool air stream, and analyzed immediately in a Jobin–Yvon RF 5000 GDOES instrument at an applied power of 40 W and argon pressure of 610 Pa.

The rf-GDOES depth profile of the thiourea-treated specimen is presented in Fig. 1a. It has been established that the thiourea molecule adsorbs to the copper surface through its sulfur end, with the C–S bond oriented perpendicular to the metal surface [14,15] as shown schematically in the inset of Fig. 1a. It is immediately evident that the nitrogen peak is separated from the copper substrate by the sulfur peak, as expected from the orientation of the adsorbed thiourea molecules. Further, the hydrogen peak is located prior to the nitrogen peak. However, the hydrogen profile is rather noisy and, therefore, a single-point signal peak in such a noisy profile is not conclusive enough to show that it is a real feature associated with the adsorbed thiourea molecules. A further point of interest is that the carbon peak appears to be located between the nitrogen and sulfur peaks. Thus, overall, the positions of the peaks are located in the following order from the surface: hydrogen, nitrogen, carbon, sulfur and copper. This agrees with what is expected from the orientation of the adsorbed thiourea molecules shown in the inset of Fig. 1a and in Fig. 2.

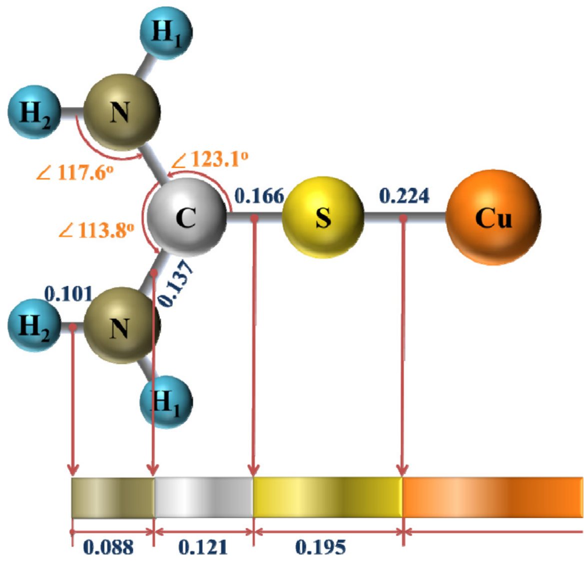

Fig. 2. Thiourea molecular structure schematic and its projected, transformed layer structure as input for MRI simulation, see details in the text. Besides the angles, all numbers given are lengths in the unit nm.

Adapted after [19,20].

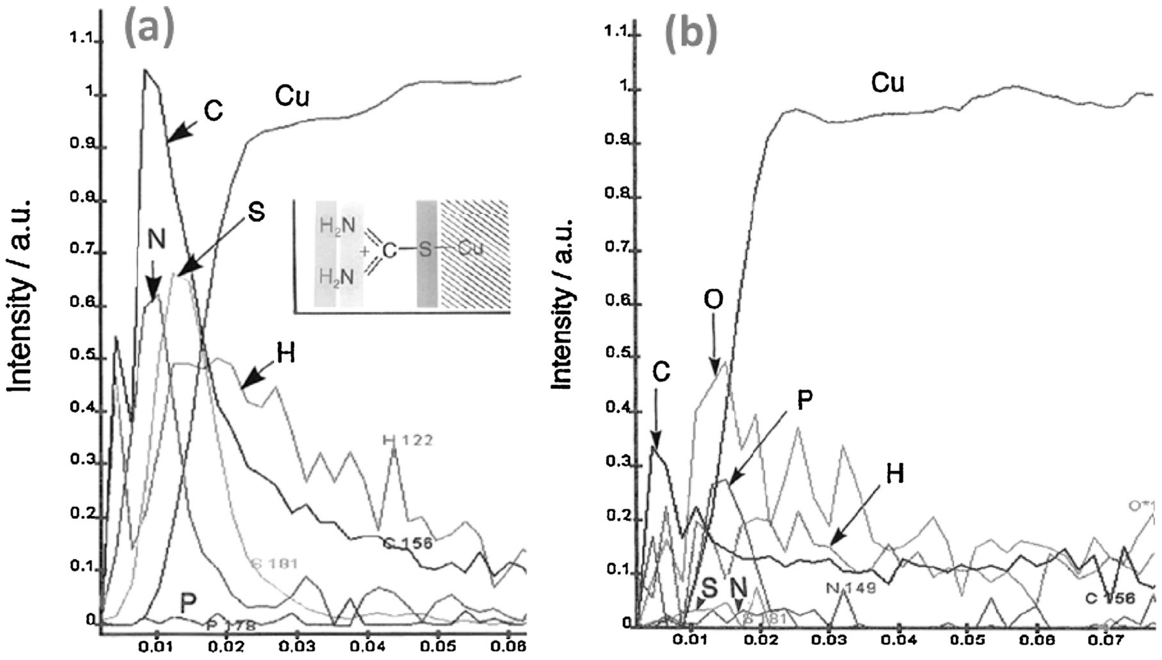

Fig. 1. Rf-GDOES depth profiles of (a) the thiourea molecule monolayer on the mirror-polished copper substrate and (b) the mirror-polished copper substrate.

Download English Version:

https://daneshyari.com/en/article/5359056

Download Persian Version:

https://daneshyari.com/article/5359056

Daneshyari.com