Spectrochimica Acta Part B 135 (2017) 34–41

Contents lists available at ScienceDirect

Spectrochimica Acta Part B

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

Evaluation of different strategies for quantitative depth profile analysis of Cu/NiCu layers and multilayers via pulsed glow discharge – Time of flight mass spectrometry

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ARTICLE INFO

Article history:
Received 12 May 2017
29 June 2017
Accepted 30 June 2017
Available online 01 July 2017

Keywords:
Glow discharge
Time of flight mass spectrometry
Elemental depth profile analysis
Quantitative depth profile analysis
Electrodeposited multilayers

ABSTRACT

There is still a lack of approaches for quantitative depth-profiling when dealing with glow discharges (GD) coupled to mass spectrometric detection. The purpose of this work is to develop quantification procedures using pulsed GD (PGD) - time of flight mass spectrometry. In particular, research was focused towards the depth profile analysis of Cu/NiCu nanolayers and multilayers electrodeposited on Si wafers. PGDs are characterized by three different regions due to the temporal application of power: prepeak, plateau and afterglow. This last region is the most sensitive and so it is convenient for quantitative analysis of minor components; however, major elements are often saturated, even at 30 W of applied radiofrequency power for these particular samples. For such cases, we have investigated two strategies based on a multimatrix calibration procedure: (i) using the afterglow region for all the sample components except for the major element (Cu) that was analyzed in the plateau, and (ii) using the afterglow region for all the elements measuring the ArCu signal instead of Cu. Seven homogeneous certified reference materials containing Si, Cr, Fe, Co, Ni and Cu have been used for quantification. Quantitative depth profiles obtained with these two strategies for samples containing 3 or 6 multilayers (of a few tens of nanometers each layer) were in agreement with the expected values, both in terms of thickness and composition of the layers.

1. Introduction

Glow discharge (GD) - optical emission spectrometry (OES) can be considered at present a mature technique for depth profile analysis of a wide variety of materials [1], not only for qualitative but also for quantitative purposes. A tutorial review collecting the different calibration methods with GD-OES was published not long ago [2].

Although still less well established for depth profile analysis, different quantification methodologies have been proposed with GD coupled to mass spectrometry (MS) [1]. The use of ion beam ratios (IBRs) is a common strategy, however it is only suitable for semiquantitative analysis and does not provide depth information [3]. When aiming at more accurate results, certified reference materials (CRMs) are required to construct calibration curves and the mass content of an element can be calculated via relative sensitivity factors (RSFs) [4]. “Standard RSFs” [5] or synthetic standards [6,7] can be employed when the lack of CRMs is an issue. These strategies are only suitable for bulk analysis or for quantitative depth profiling of low concentrations of dopants or impurities in a given material. In particular, several articles have been published by Di Sabatino et al. [8–11] for depth profiling of trace contents in silicon.

In case of depth profile analysis of layered materials, the use of absolute sensitivity factors has been proposed by Jakubowski and Stuewer [12] with a quadrupole mass analyzer. Their approach required weighing the sample before and after analysis for each layer to determine the mass sputtered from the sample. However, in the conventional multi-matrix depth profile calibration methodology employed in GD-OES (equivalent to the absolute sensitivity factors) this is not needed because all elements present at each given sputtering time are simultaneously measured and, therefore, concentration and depth can be directly obtained [13].

The coupling of a pulsed GD (PGD) to time of flight MS (TOFMS) offers special advantages in comparison with other GD-MS instruments as all elements are simultaneously measured with TOFMS analyzers; therefore, a similar approach to the common multi-matrix depth profile quantification method employed in GD-OES can be used. To the best of our knowledge, just three examples using multi-matrix calibration have been reported so far for PGD-TOFMS quantitative depth profile analysis: thin film solar cells based on amorphous silicon [14], coated glasses [15] and the determination of B and As ultralow energy implants in silicon [16], in all cases using an instrument prototype. More recently, Valledor

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http://dx.doi.org/10.1016/j.sab.2017.06.016
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Table 1
Description of samples used in this work. All of them contain a 20 nm Cu layer as starting and cover layers. Also, after the internal Cu layer there is a 5 nm Cr layer deposited to help adhesion of the following layers. In between each CuNi layer there is a pure Cu layer of the same thickness as the CuNi layers. In the notation, each layer is separated from the subsequent one by //.

Sample	Ni(Cu) concentration (at.%) Depth of each layer (nm)	Total theoretical depth[*] (nm)
1-a	(100)//60(40)//100//substrate 20//320//20	370
3-LMH	(100)//40(60)//100//75(25)//(100)//90(10) //(100) //substrate 20//80//80//80//80//20	440
3-HLM	(100)//90(10)//100//40(60)//(100)//75(25) //(100) //substrate 20//80//80//80//80//20	440
3-LHM	(100)//40(60)//100//90(10)//(100)//75(25) //(100) //substrate 20//80//80//80//80//20	440
6-LMHLMH	Two samples containing 6-CuNi layers have twice repeated the sequence of the 3 CuNi layers samples.	734
6-HLMHLM		823

[*] According to electrodeposition parameters.

et al. [17] used the variation of the thickness of different Al layers (1–50 nm) to construct a calibration curve representing signal vs Al layer thickness. Y-axis was obtained by considering the product of the Al intensity (measured at the maximum of the depth profile) and the full width at half maximum of the Gaussian fitting obtained for the Al profile. Unfortunately, only samples well characterized can be analyzed in this strategy and, for instance, if any element is present as a consequence of contamination or because of the deposition process, estimation of elemental concentrations would be compromised.

In the present work, two strategies based on absolute sensitivity factors and multi-matrix calibration have been assayed for depth profile analysis of a series of Cu//NiCu nanometric multilayers prepared by electrodeposition. Such aim was pursued with the new commercial PGD-TOFMS instrument from Horiba Scientific (PP-TOFMS Plasma Profiling Spectrometer). PGDs are characterized by three different regions due to the temporal application of power: prepeak, plateau and afterglow. This last region is the most sensitive one and so it is very convenient for quantitative analysis of minor components; however, major components are often saturated, which was the case for Cu in the samples investigated in this work. Therefore, we propose the measurement of elemental signals in the afterglow for all analytes except for Cu which will be investigated either using (i) the Cu signal measured in the plateau region, or (ii) the signal from the ArCu dimer measured in the afterglow time domain.

2. Experimental

2.1. Samples description

The electrochemical cell contained about 40 mL solution in which the horizontally placed recessed cathode lied at the bottom of the cell. An acetate-stabilized citrate bath was used with the following composition: 0.3 M nickel sulfate (from $NiSO_4 \cdot 7H_2O$), 0.05 M nickel acetate (from $Ni(CH_3COO)_2 \cdot 4H_2O$), 0.025 M copper sulfate (from $CuSO_4 \cdot 5H_2O$), 0.25 M sodium citrate (from $Na_3C_6H_5O_7 \cdot 2H_2O$) and 0.03 M sodium chloride [18]. The pH was 5.16 and required no adjustment. Citrate-type Ni-Cu baths have been proved to plate homogeneous Ni-Cu alloys [19], the composition of the deposit can be easily tuned by the current density in the alloy formation regime [20], and the fairly high pH provided a sufficient stability of the solution [21]. The occurrence of Co and Fe in the deposit is caused by the slight impurity of the Ni compounds that is enlarged due to very high deposition preference of Co and Fe beside Ni. The accumulation of the impurities was expected to take place the more, the lower the Ni deposition rate.

A Ni wire was used as a counter electrode and a saturated calomel electrode (SCE) served as potential reference. The deposition was performed with an Ivium CompactStat electrochemical workstation. The Cu layers were deposited at −775 mV vs. SCE, and the deposition current density for the CuNi layers of various compositions ranged from −1.5 to −13.5 mA cm^{-2}. The deposition was started in each case with a Cu layer in order to achieve a steady-state for the Cu deposition and hence, to avoid a significant composition transient at the beginning of the deposition of the subsequent CuNi layer.

Table 1 collects a summary of the different samples, with their corresponding compositions and thicknesses, used in this work. Both the layer thicknesses in the multilayer samples and the total thickness for single-layer deposits were calculated by using the following equation derived from Faraday's law:

$$\frac{It\eta}{zF}\frac{M}{\rho}=Ad$$

where I is the current applied, t is time, η is current efficiency (hence $It\eta$ yields the charge passed for metal deposition), z is the number of electrons involved in the electrochemical reactions ($z = 2$ for both Cu^{2+} and Ni^{2+} reduction), F is the Faraday constant ($F = 95{,}786 C/mol$), M is the molar weight, ρ is the density, A is the sample surface area and d is the layer thickness. The current efficiency is about 95% for Ni deposition as measured in independent experiments and 100% for Cu deposition. The molar weight and the density of the alloys were calculated from the weighted average of the relevant parameters of the alloying elements; however, since the difference in both the density and the molar weight is relatively small, this calculation mode does not lead to a substantial error. The most uncertain factor in the sample preparation is the active surface area, which is sensitive to the compression of the gasket that holds the cathode and may vary some 12% from one sample to another. Although this may influence the total surface area and hence the layer thicknesses themselves, it does not modify the thickness ratio of the layers since the active cathode surface area does not change during the deposition.

All samples were prepared by using Si//Cr(5 nm)//Cu(20 nm) substrates (cathode). The initial layers were evaporated on the Si wafer without removing the native oxide layer. The Cr layer provided the sufficient adhesion and the Cu layer ensured a sufficient electrical conductivity. Three different groups of samples were available for this work. Sample 1-a contains a single CuNi layer (in between the 20 nm Cu layers). The second group corresponds to the samples formed by three different CuNi layers (80 nm each), each of them with a different CuNi concentration, denoted as H (90% Ni), M (75% Ni) and L (40% Ni). Each CuNi layer is separated from the following one by a pure Cu layer with a thickness of 80 nm. The third group is formed by samples containing six CuNi layers. In case of the second and third group, the most external

Table 2
Materials employed to construct calibration curves used to achieve quantitative analysis.

Reference material	Si (wt%)	Cr (wt%)	Fe (wt%)	Co (wt%)	Ni (wt%)	Cu (wt%)
33X GM7 (MBH Analytical Ltd.)	0.09	0.02	0.08	–	0.44	85.5
BSH1B (Brammer Standard Company Inc.)	0.049	–	1	–	71.4	0.01
BSH8 (Brammer Standard Company Inc.)	0.2	29.43	14.61	2.58	41.8	1.66
WASP1 (MBH Analytical Ltd.)	0.59	16.64	2.16	12.8	56.26	0.08
G26H2 (MBH Analytical Ltd.)	7.6	0.07	0.8	–	0.37	3.5
N50.01 (MBH Analytical Ltd.)	0.03	–	5.2	–	50.92	23.3
Cu-ETP (Aurubis AG)	–	–	–	–	–	99.9