



Full Length Article

Molecular analysis of additives and impurities accumulated on copper electrodeposited layer by time-of-flight secondary ion mass spectrometry

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ARTICLE INFO

Keywords:

Copper electrodeposition
TOF-SIMS
Molecular analysis
Atomic force microscopy (AFM)
Additives
Hierarchical cluster analysis (HCA)

ABSTRACT

The molecular analysis of additives and impurities accumulated on the copper electrodeposited layer from electroplating bath containing Cl^- , polyethylene glycol (PEG), and bis-(sodium sulfopropyl)-disulfide (SPS) was evaluated by Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) under static conditions and atomic force microscopy (AFM). The hierarchical cluster analysis (HCA) was applied in order to classify the surface chemistry of copper electrodeposited layers to four different classes. The molecular structure of polymeric complexes of PEG-Cu(I)-Cl and Cu(II)- $\text{SO}_3(\text{CH}_2)_3\text{-SO}_3$ which existed on the copper surface were identified and confirmed. A coordinative dissolution of a complex layer of PEG-Cu(I)-Cl by MPS (sodium 3-mercaptopropylsulfonate) molecules incorporated into the copper deposit via a covalent bond was proven. The methodology of a proper identification of molecular species in mass spectrum without the use of reference was proposed. A semiquantitative analysis of CuCl and $\text{CuCl}_2^-/\text{CuCl}^-$ ions. A higher ratio $\text{CuCl}_2^-/\text{CuCl}^-$ corresponds to a higher molecular ratio of $\text{CuCl}_2/\text{CuCl}$ compounds. Suppressing the role of PEG and the accelerated role of Cl^- ions on a higher level of incorporation of thiolate molecules by Cu-S covalent bond in PEG/Cl/SPS system in comparison with SPS/Cl system was calculated. It was also discovered, for the first time, that phosphate ions accumulate in high concentrations on a copper surface without the presence of chloride adlayer. The presence of chloride adlayer in SPS/Cl system plays an antagonistic role towards phosphate and sulfate ions, effectively removing these ions from the copper surface. Our studies by TOF-SIMS under a static condition combined with atomic force microscopy measurements prove that PEG exerts a synergetic effect with chloride ions to reduce waviness of the copper electrodeposited surface in a micro scale without a significant role in reducing crystallite size in a nano scale, whereas the synergy effect of PEG-Cl-SPS reveals levelling abilities both in a micro scale (waviness) and a nano scale (roughness). It shows that TOF-SIMS under static conditions is a complementary technique for the investigation of a molecular and geometrical arrangement of adsorbed species on a copper electrodeposited layer.

1. Introduction

The copper electrodeposition process is an attractive technology deposition for application in nano [1–3] and microtechnology [4–6]. Some examples of application for design and develop devices for X-ray optics [7,8], plasmonic [9], catalysis [10] and chemical sensor [11] illustrate only a large scale of applications and an importance of the copper electrodeposition technique. Nano and microstructure control in the provided examples play a key role for the performance and stability of the manufactured devices. The fact that copper surface characteristics at a nano and micro scale can be controlled by adjusting a few independent parameters, such as the composition of an electroplating bath and current density, together with simplicity and low-cost of

operations, increase the attractiveness of the copper electrodeposition technique for a number of years. For the superfilling processes on a nano scale (Damascene), a typical electroplating bath contains sulfuric acid and additives: PEG-Cl-SPS-LEV [1–2,5,12–16] at different concentrations of additives and current density. The optimization of additives concentrations is of crucial importance to the control of growth of crystallite in a nano scale (roughness) and a micro scale (waviness) [1–2,4,12,14,17]. Copper electrodeposited surface morphology and crystallite structure are determined by atomic force microscopy (AFM), [12,18–22], scanning electron microscopy [1,2,17,20,23,24] X-ray diffraction (XRD) [21,25], electron backscatter diffraction [26]. Investigations of the mechanism of copper growth and incorporation of additives into the deposit by *in situ* studies by means of scanning

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Received 15 May 2018; Received in revised form 25 August 2018; Accepted 27 August 2018

Available online 28 August 2018

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transmission microscopy combined with electrochemical-scanning tunnelling microscopy (EC-STM) [27–30] and combined sum frequency generation (SFG) spectroscopy with scanning tunnelling microscopy (STM) [31] were carried out. Molecular and elemental characterisation of compositions and its byproducts in an electroplating bath were provided by mass spectroscopy [32–34], liquid chromatography mass spectrometry (LC-MS) [35], high performance liquid chromatography (HPLC) [36] and atom absorption spectroscopy (AAS) [15]. The chemical reactions postulated under electrochemical conditions were conducted under non electrochemical conditions and investigated by X-ray diffraction (XRD) [37], nuclear magnetic resonance (NMR) [38,39], ultraviolet – visible spectroscopy (UV-VIS) [15], inductively coupled plasma – mass spectrometry (ICP-MS) [30]. On the other hand, a molecular identification of additives accumulated into the copper electrodeposited layer were studied by spectroscopic techniques: transmission Fourier transform infrared (FTIR) [40], surface-enhanced raman spectroscopy (SERS) [40–42], electrospray ionization mass spectrometry (ESI-MS) [40], X-ray photoelectron spectroscopy (XPS) [43], combined laser ablation/ionization with secondary ion mass spectrometry (LIMS/SIMS) [44], time-of-flight secondary ion mass spectrometry (TOF-SIMS) [8,26,45,75–77], as well as glow discharge optical emission spectroscopy (GD-OES) [45]. *Ex situ* studies on additives and base components adsorbed on copper foils by means of electron paramagnetic resonance (EPR) were also carried out [46]. As complementary studies to experimental techniques, very often density functional theory (DFT) calculations were applied [29–30,40–42]. As it was investigated by means of SERS (surface enhanced raman spectroscopy) by Feng [42], polyethylene glycol (PEG) is able to form PEG-Cu(I)-Cl complex that consists of complexed Cu(I) atom linking with two atoms O and one atom Cl. In another example, Schmitt et al. [41] investigated a mechanism of MPS (sodium 3-mercapto-1-propanesulfonate) acceleration of Cu electrodeposition in the presence of Cl^- by *in situ* shell-isolated nanoparticle-enhanced raman spectroscopy. One of the greatest benefits of this method is *in situ* measurements. On the other hand, a big drawback is the need to roughen the electrode to enhance signal intensity, which changes the adsorbing abilities of different additives from an electroplating bath, depending on crystallites orientations [21]. Another disadvantage is reduced signal intensity for copper in comparison with silver or gold substrate for techniques based on laser source [47]. As reported in sum frequency generation (SFG) spectroscopy with STM [31], surface roughening leads to an absorption of the infrared beam, reducing sensitivity of the method. In order to overcome the last problem, *in situ* shell-isolated nanoparticle-enhanced raman spectroscopy has recently been applied [41]. Even a combination of different techniques does not always lead to proper results. As an example, Schultz [40] proposed a formation of the CuCl-SPS (bis-(sodium sulfopropyl)-disulfide) complex by a coordination of a sulfonate group through CuCl, based on electrospray ionization mass spectrometry (ESI-MS) and by *in situ* surface enhanced Raman scattering (SERS) as well as density functional theory calculations. However, no recent studies [21,28–30,41] support the Schultz model of linking thiolate to copper through a sulfonate group. The difficulties in the interpretation of ESI-MS mass spectra are caused by a higher tendency to cluster by species belonging to different chemical moieties. Furthermore, species ionization is conducted after desorption from a solid substrate which limits investigations of geometrical arrangements of thiolate molecules on the substrate. Due to the above drawbacks, there is still a strong demand to investigate another very sensitive complementary technique so as to expand our knowledge about an interaction between additives on the electrode and electrode/electrolyte interface under realistic reactive conditions. That fact inspires us to apply *ex situ* TOF-SIMS under static regime, due to a very high detection limit, a good lateral resolution and a preserved molecular state of species on the measured sample. More details about TOF-SIMS measurement under static-condition can be found in excellent Fletcher's et al. review [48 and citations therein]. Up to now, there have been no

reported studies of molecular species on a copper electrodeposited layer by TOF-SIMS under static conditions. Previous TOF-SIMS studies focused on an elemental analysis of impurities incorporated into a copper deposit under dynamic conditions in order to evaluate the distribution of elements such as S, Cl, N, O, C in the function of the depth of a copper layer [8,26,44–45,49,70,75–77]. In paper [75], the authors demonstrate that higher incorporation of impurities in the form of Cl, S, and C increases with additive content, whilst in [77] it is demonstrated that impurities content is increasing as a function of time (at 9 h and 487 h) and concentration gradients of impurities towards the copper surface noticeably increased and is even more abrupt at 487 hrs after electrolysis. In the referenced papers [8,26,44–45,49,70,75–77] no molecular information determined by TOF-SIMS data was provided. The primary significance for a limited popularity of a molecular analysis by TOF-SIMS technique is matrix effects (SIMS matrix effect) which causes a big difficulty in predicting how organic and inorganic chemical species will influence one another [50–55].

As a result, the TOF-SIMS technique for a molecular species analysis is widely applied to simpler chemical moieties and systems such as assembly monolayers [56–57], a monolayer deposited by Langmuir-Blodgett technique [58–60] etc. Due to these reasons, in a situation of such a complicated surface chemistry system, which can be found on the copper electrodeposited layer, an appropriately designed experiment is highly relevant for a proper interpretation of the obtained results. In the first experiment, in order to determine the molecular structure and geometrical arrangement of incorporated molecular species into a 20 μm thick copper deposit, electrodeposited at 20 mAcm^{-2} from electroplating baths containing sulfuric acid, copper(II) sulfate and zero, one, two or three additives (Cl^- , PEG, SPS) were carried out. In the second experiment, on a thin copper layer deposited on a glass fibre by magnetron sputtering, a thiolate layer was dip-coated separately from aqueous solutions of MPS or SPS or MPS/Cl or SPS/Cl in order to evaluate the findings received in the first experiment. The main aim of our investigation was to identify molecular moieties present on the copper layer by the recognition of relevant ions corresponding to CuCl, CuCl_2 , SO_4^{2-} , SO_3^{2-} , SPS, MPS, PEG-Cu(I)-Cl, $\text{Cu(II)-SO}_3(\text{CH}_2)_3\text{-SO}_3$ and several others by TOF-SIMS under static regime. We also conducted studies on molecular arrangements of thiolate species on the copper electrodeposited layer. In combination with morphological studies by means of atomic force microscopy (AFM) in a nano scale, the roughness parameters were evaluated in connection with surface chemistry.

2. Experimental

Copper electrodeposition was conducted in a cylindrical glass vessel, containing 350 ml of electrolyte. A nitinol wire (0.2 mm diameter, 140 mm length, 0.8 cm^2 surface area, supplied by Fort Wayne Metals, USA), a copper O-ring copper with phosphor as an additive (45 mm outside diameter, 35 mm inside diameter, 1 mm thickness, supplied by Kurt J. Lesker, USA) were employed as cathode and anode electrodes, respectively. A quartz glass fibre (0.2 mm diameter) was supplied by Optical Fiber Technology Laboratory (Marie Curie-Sklodowska University, Lublin, Poland). A galvanostat AUTOLAB 302 N (Eco Chemie, The Netherlands) was used for controlling the current in the galvanostatic mode. The base electrolyte contained 0.56 M sulfuric acid (99.9% pure, POCH S. A., Poland) and 0.9 M copper(II) sulfate (99% pure, 61,245 Fluka, purchased from Sigma-Aldrich). Four additives were added: Cl^- (in the form of HCl, POCH S. A., Poland), PEG (mol. wt. 8000, Sigma-Aldrich), DTAC (Sigma-Aldrich), SPS (Raschig, Germany), MPS (Sigma-Aldrich). PEG, Cl and SPS concentrations amounted to $C_{\text{PEG}} = 5.18 \times 10^{-5}$ mol/l, $C_{\text{Cl}^-} = 7.62 \times 10^{-4}$ mol/l, $C_{\text{SPS}} = 3.55 \times 10^{-5}$ mol/l, $C_{\text{MPS}} = 3.55 \times 10^{-5}$ mol/l, respectively.

In the first experiment, 200- μm nitinol wire was withdrawn from the electrolyte solution, which was not stirred. The variable speed of the withdrawal allowed obtaining the conical shape with the thickness

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