Applied Surface Science 356 (2015) 191–202

Contents lists available at ScienceDirect

Applied Surface Science

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

The polymeric nanofilm of triazinedithiolsilane fabricated by self-assembled technique on copper surface. Part 2: Characterization of composition and morphology

Yabin Wang[a,b], Zhong Liu[b], Yudong Huang[a,*], Yutai Qi[a,*]

[a] School of Chemical Engineering and Technology, Harbin Institute of Technology, Harbin, 150001, P. R. China
[b] Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, Xining, Qinghai, 810008, P. R. China

ARTICLE INFO

Article history:
Received 28 June 2015
Received in revised form 11 August 2015
Accepted 12 August 2015
Available online 14 August 2015

Keywords:
Copper
Triazinedithiolsilane
X-ray photoelectron spectroscopy
Scanning electron microscope
Interface

ABSTRACT

In the first part, a novel design route for metal protection against corrosion was proposed, and a class of triazinedithiolsilane compounds was conceived as protector for copper. The protective capability of the polymeric nanofilm, fabricated by self-assembling one representative (abbreviated as TESPA) of triazinedithiolsilane compounds onto copper surface, has been investigated and evaluated by electrochemical tests. The results show that the polymeric nanofilm significantly inhibits copper corrosion. This study, on the one hand, concentrates on the chemical composition of the TESPA polymeric nanofilm by means of X-ray photoelectron spectroscopy (XPS). The XPS results reveal that the chemical bonds between copper and TESPA monomers, three dimensional disulfide units and siloxane networks are responsible for the satisfactory protection of TESPA polymeric nanofilm against copper corrosion. On the other hand, scanning electron microscope (SEM) and energy-dispersive spectroscopy (EDS) are utilized to reveal the morphology and the uniformity of the TESPA polymeric nanofilm. The SEM-EDS results demonstrate that the copper surfaces are uniformly covered with TESPA self-assembled monolayer and the polymeric nanofilm. The TESPA-covered copper surfaces turn out to be smoother than that of the bare copper surface.

1. Introduction

In the first part, we have proposed a novel design route to synthesize new kinds of inhibitors that can be applied to resist corrosion for different metals [1]. By assembling protective triazinedithiol (TDT) and silane groups, triazinedithiolsilane compounds capable of protecting copper have been successfully prefabricated. 6-(3-triethoxysilylpropyl)amino-1,3,5-triazine-2,4-dithiol monosodium salt (TESPA-TDT, abbreviated as TESPA) is just one of such triazinedithiolsilane compounds. The polymeric nanofilm prepared by heating the self-assembled monolayer (SAM) of TESPA, protects copper from corroding with satisfactory inhibition efficiency. However, the texture of the polymeric nanofilm is highly empirical. The accurate information about the structure, elemental constituent, and the morphology of TESPA polymeric nanofilm has not been shed light on.

It is the objective of this study to understand the chemical reactions between TESPA monomer and copper substrate, and unravel the component changes during the process of preparing the polymeric nanofilm by X-ray photoelectron spectroscopy (XPS) and energy-dispersive spectroscopy (EDS). Furthermore, the morphologies of TESPA SAM and the polymeric nanofilm on copper surfaces were also evaluated by scanning electron microscope (SEM).

2. Experimental

2.1. Preparing the polymeric nanofilm of TESPA

The TESPA self-assembly solution consists of 5 mM TESPA monomer dissolved in ethanol/distilled water (95/5, v/v) mixed solvent, with pH of 5 by adding acetic acid examined by pH meter. The solution was stirred adequately and hydrolyzed for different time at 35 °C. Millipore-Q water (18.2 MΩ cm) was used in all solutions. Unless noted otherwise, all reagents used were of analytical grade. The pure copper plates, cut into the dimensions of 20 mm by 20 mm and 1 mm thick for electrochemical examinations, were abraded

---

* Corresponding authors. Tel.: +86 451 86414806; fax: +86 451 86221048.
E-mail addresses: ydhuang.hit1@yahoo.com.cn (Y. Huang), inqdsd@yahoo.com.cn (Y. Qi).

http://dx.doi.org/10.1016/j.apsusc.2015.08.099

with emery paper of 800 grit and 1000 grit, and followed by fine polishing with alumina paste of 0.35 mm, 0.2 mm, 0.1 mm particle size to achieve a mirror finish. The samples then degreased with acetone and alcohol in an ultrasonic bath for 15 min, and finally rinsed with copious Millipore-Q water. After cleaning, the copper specimens were immediately immersed into TESPA solution for 15 min and dried by cold air from a hair dryer, aged at 100 °C for 15 min in an air oven. Herein, a bare copper and another one heated at 100 °C for 15 min were used as references. To illustrate the protective abilities of TESPA on copper surface, a TESPA treated sample and a TESPA treated one with heating at 100 °C for 15 min were investigated, respectively. The abbreviations of the four samples are denoted as follows: Cu-Bare, Cu-Heat, Cu-TESPA, and Cu-TESPA-Heat. The purpose of Cu-Heat was to monitor the inhibitory action of copper oxide film produced both in Cu-Heat and Cu-TESPA-Heat situations when copper is thermally cured.

2.2. X-ray photoelectron spectroscopy (XPS)

XPS experiments were carried out on an ESCALAB 250Xi (Thermo Fisher Scientific) with Al Ka radiation ($h\upsilon = 1486.6$ eV; analysed area = 600 μm^2). Unless specified otherwise, the X-ray anode was run at 250 W and the high voltage was kept at 15.0 kV with a detection angle of 45°. The base pressure of the analyzer chamber was around 5×10^{-8} Pa. A survey scan (0–1300 eV) was taken for all the samples in order to detect the present elements. Individual elemental scans of all the elements were then recorded with a comparative high resolution. The binding energy scale was calibrated from the hydrocarbon contamination using the C1s peak at 284.8 eV. It should be noted that all the binding energies from the references were re-calibrated using the C1s peak with the binding energy of 284.8 eV, to clearly understand the changes of the chemical states for the analysis of the peaks in our paper. For example, Cazorla-Amoro et al. [2] set the C1s peak position at 284.6 eV as the referential one using the Al Ka radiation; therefore, 0.2 eV (284.8 eV–284.6 eV) was just added to all the peaks in that paper. This processing rationalizes the analysis.

The software of XPS Peak 4.1 was adopted to de-convolve the C1s, O1s, Cu2p, N1s, S2p, and Si2p peaks using the Shirley-type background [3]. The parameters bound up with each peak in the software were binding energy centre, full width at half maximum (FWHM), peak area, and the Gaussian-to-Lorentzian ratio. We kept a combination of 80% Gaussian-20% Lorentzian line shape [4,5], and maintained the FWHM of the various components in a given spectrum as close as possible [6]. The quality of the curve fit was monitored by the determination of χ^2; the “best fit” was achieved to consist with chemical meaning of each element during the process of performing the curve fitting.

The fractional concentration of a particular element X (X%) was calculated with formula 1 by applying atomic sensitivity factors (ASF) [7]:

$$X\% = \frac{(I_x/S_x)}{\sum(I_n/S_n)} \times 100\% \qquad (1)$$

Where I_n and S_n are the integrated peak areas and the sensitivity factors, respectively. The subscripts, x and n, stand for the element studied.

2.3. Scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS)

SEM-EDS study was performed at JSM-5610LV/INCA (JEOL Ltd., Japan), using a high-resolution environmental scanning electron microscope equipped with an energy-dispersive X-ray spectrometer (EDAX, Japan). Energy dispersive spectroscopy of the each surface was carried out in random areas for five times to identify the existed elements and their contents, which can further confirm the uniform coverage of the nanofilms.

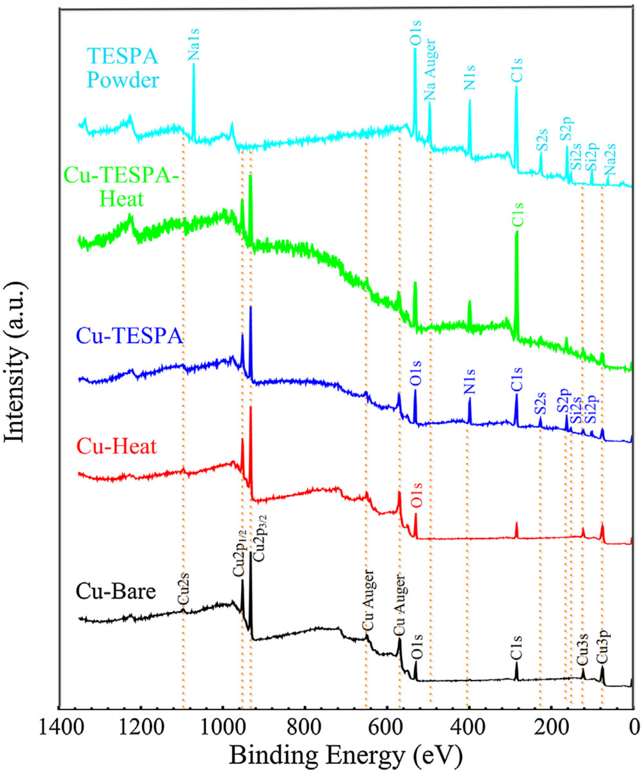

Fig. 1. Representative XPS survey spectra from TESPA powder, as well as the surfaces of the bare copper, the heated copper, the copper treated with TESPA, and the copper treated with TESPA plus following heating.

3. Results and discussion

3.1. Representative XPS survey spectra of TESPA powder and the investigated surfaces

Fig. 1 compares representative XPS survey spectra of the referential surfaces (TESPA powder, the bare copper and the heated bare copper), and the TESPA-treated copper substrates without/with the subsequent heating. Table 1 shows the present chemical elements in each surface and the corresponding atomic concentrations. Because C1s and O1s coexist in all the five surfaces, thus other elements are mainly analyzed and deciphered to reveal the chemical reactions between TESPA monomers and the copper surface.

It is intelligible that most samples exposed to the atmosphere will have a detectable quantity of adventitious carbon contamination commonly with a layer thickness of 1–2 nm. C1s spectrum of contamination typically has three components: C—C, C—O—C and O—C=O [8], which accordingly gives rise to oxygen contamination of C—O—C and O—C=O [9]. Therefore, bare copper surface, which has been thoroughly cleaned and theoretically excludes carbon and oxygen elements, exhibits C1s and O1s spectra as expected. As the bare copper is heated at 100 °C for 15 min, cuprous oxide and copper oxide produce leading to the increase of oxygen content. Na1s can be detectable only in TESPA powder, but disappears for TESPA-treated copper surfaces, when TESPA is hydrolyzed to modify the copper substrate. The fundamental reason is that TESPA as a monosodium salt is strong base-weak acid, and the —SNa groups transform into -SH groups under acetic ethanol/distilled water mixed solvent with a pH of 5, where triethoxysilyl groups in TESPA are easy to hydrolyze simultaneously. The generated Na^+