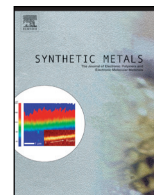
Synthetic Metals 223 (2017) 199–204

Contents lists available at ScienceDirect

Synthetic Metals

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



Effect of order and disorder on degradation processes of copper phthalocyanine nanolayers

Lucyna Grządziel[a,*], Maciej Krzywiecki[a,b], Georgi Genchev[b], Andreas Erbe[b,c]

[a] Institute of Physics – Center for Science and Education, Silesian University of Technology, S. Konarskiego Str. 22B, 44-100 Gliwice, Poland
[b] Max-Planck-Institut für Eisenforschung GmbH, Max-Planck-Str. 1, 40237 Düsseldorf, Germany
[c] Department of Materials Science and Engineering, NTNU, Norwegian University of Science and Technology, 7491 Trondheim, Norway

ARTICLE INFO

Article history:
Received 26 July 2016
Received in revised form 10 October 2016
Accepted 22 November 2016
Available online 28 November 2016

Keywords:
Nanoelectronics
Organic thin film
Phthalocyanine
Degradation processes
Morphology
Raman spectroscopy

ABSTRACT

The impact was examined of surface ordering of 50 nm-thick copper phthalocyanine (CuPc) layers on the layer's susceptibility to ambience-induced degradation processes. The surface morphology of CuPc layers obtained by physical vapor deposition with different deposition rates, 0.01 nm/s (r_1) and 0.02 nm/s (r_2), was diagnosed applying atomic force and scanning electron microscopes. The images exhibited compact, ordered surface topography with crystallites of homogeneous geometry for a layer with r_1 while randomly distributed bigger crystallites on a rougher and more expanded surface for a layer with r_2. X-ray diffraction revealed the α-form of phthalocyanine, mostly with an orientation of the a axis perpendicular to the substrate plane. Mean grain size in bulk was slightly larger for CuPc with r_2. Energy dispersive X-ray spectroscopy demonstrated an increase of C/Cu and N/Cu elemental ratios compared to the expected composition for both layers but significantly more pronounced for layer with r_2. Morphological features and traces of CuPc-air interaction were mirrored also in the Raman spectra. Samples with r_2 exhibited an increased peak width, and their peaks were shifted compared to samples with r_1, which was attributed to surface disorder. The Raman spectra exhibited the appearance of additional peaks of oxidation products indicating C—O—C, C=O and N—O bonds, with intensities coinciding to an increased carbon and nitrogen content. More intensive peaks were recorded for layers obtained with higher deposition rate, proving their stronger susceptibility to environment-induced degradation processes.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Promising candidates for several electronic applications emerge from the group of organic semiconductors, the metallophthalocyanines (MePc) – heterocyclic conjugated molecules with high thermal and chemical stability [1]. In the form of thin films, MePc's have been already tested in third generation solar cells, gas sensors and advanced opto-electronics technologies [2–7].

However, operating in a "real world" environment, the organic-based devices are inevitably subjected to the influence of the ambient conditions [8]. Particularly, exposure to surrounding air leads to the adsorption of species on the surface of organic layer. Adsorption may be accompanied by charge transfer and subsequently provoke changes of surface chemical structure, electronic and vibrational properties [9]. All air-originated changes of layer properties degraded the device efficiency, lifetime and consequently have an impact on the effective use of devices [10].

Yet, the aging of phthalocyanines and the other organic thin films was mainly investigated by means of the electrical measurements [11–13], Kelvin probe [12], and photoemission methods like e.g. photoemission yield spectroscopy [14], ultraviolet and X-Ray photoelectron spectroscopies (XPS) [15]. In these studies, the main emphasis was placed on specification of the variation of electronic and chemical properties after interaction with air over different time scales [16]. For instance, the propensity of organic layers for a strong interaction with the atmosphere depends on their morphological features, which in turn are determined during film preparation by specific conditions [17].

In this work, the products of air-induced chemical degradation of 50 nm-thick copper phthalocyanine (CuPc) films on Si(111) was investigated by energy dispersive X-ray (EDX) and Raman spectroscopy, in relation to the surface topographical ordering. The variation of surface morphology was obtained during the deposition process by changing the deposition rate. Samples' morphologies were characterized by atomic force and scanning

* Corresponding author.
E-mail address: Lucyna.Grzadziel@polsl.pl (L. Grządziel).

http://dx.doi.org/10.1016/j.synthmet.2016.11.024
0379-6779/© 2016 Elsevier B.V. All rights reserved.

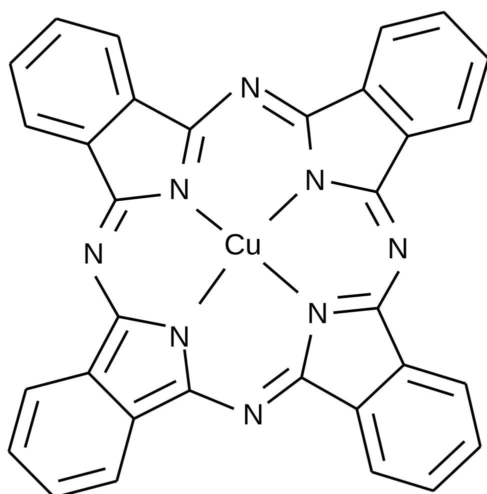


Fig. 1. Scheme of CuPc molecule.

electron microscopies (AFM and SEM, respectively). The phase and mean crystallite size were checked by X-ray diffraction (XRD). The analysis of Raman peak shape and positioning revealed impact of samples' morphological order/disorder. Up to now, Raman spectroscopy as fast, non-destructive and cost-effective diagnostic method [18], has been applied for MePcs mainly as the tool for distinguishing of their molecular orientation and polymorphic phase [19–22]. At present, the detailed analysis of Raman peaks suggested ability of this technique to fingerprint phthalocyanine surface homogeneity and its inclination for degradation processes.

2. Experimental details

2.1. Sample preparation

CuPc (Copper (II) Phthalocyanine, see Fig. 1 for molecule scheme; molecular formula: $C_{32}H_{16}N_8Cu$) layers with thickness of 50 nm were thermally evaporated from sublimed powder (Sigma-Aldrich, >97% purity, β-form) in high vacuum by physical vapor deposition on p-type Si(111) native substrates (BOSCH GmbH) kept at room temperature. The powder was degassed and purified in vacuum conditions at 220 °C prior deposition in order to extract residual contaminations. Substrates were pre-cleaned with acetone in an ultrasonic bath, rinsed with deionized water and dried with nitrogen. The CuPc films were deposited at the pressure of 10^{-6} Pa with different deposition rates *r* equal to 0.01 nm/s and 0.02 nm/s. The respective samples will be denoted also as r_1 and r_2 hereafter. The thicknesses of the layers were controlled by a quartz crystal microbalance (Inficon XTC3M) and verified with AFM measurements on the layer edges. The obtained film thickness assured that no substrate/overlayer interfacial effects would affect the studies. After deposition, the CuPc films were subjected to ambient air exposure for a 1-year period at room temperature in a dry box with stable humidity of 40%.

2.2. Characterization

The surface morphology of obtained CuPc thin films was investigated by AFM and SEM.

The AFM measurements were performed using a PSIA XE-70 microscope in non-contact mode (NC-AFM) applying BS Tap300Al cantilevers with resonance frequency of 300 kHz and spring constant of 40 nm^{-1}. Acquired images were processed using image processing software WSxM 5.0® [23] in order to revise sample inclination and distortions caused by the z-scanning stage. All quantitative morphological parameters were specified with the application of WSxM built-in algorithms. As a measure of surface roughness, the root mean square (RMS) of roughness was quantified, where the root mean deviation from a plane was analyzed. Surface area estimation was performed by triangulating the surface (as stated in the algorithm description) and summing up their area to obtain the total area. Further details can be found elsewhere [24].

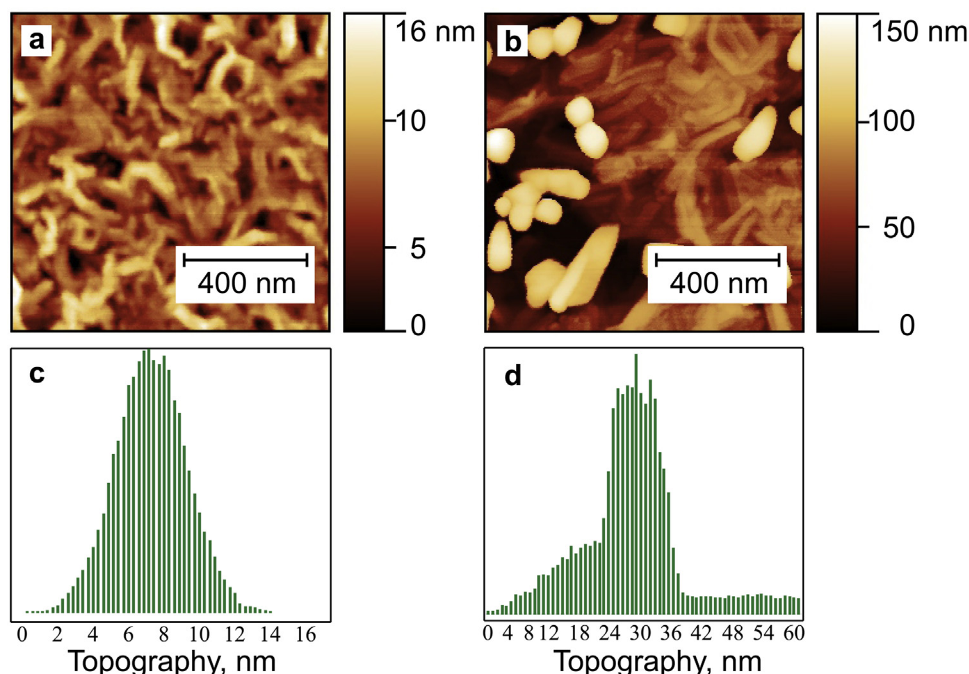


Fig. 2. NC-AFM images of surface topography of 50 nm-CuPc layers obtained with deposition rates r_1 (a) and r_2 (b). Corresponding roughness analysis histograms (c) and (d), respectively.

Download English Version:

https://daneshyari.com/en/article/5435669

Download Persian Version:

https://daneshyari.com/article/5435669

Daneshyari.com