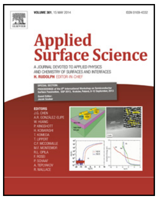
Applied Surface Science 301 (2014) 378–382

Contents lists available at ScienceDirect

Applied Surface Science

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



Adsorption properties of thermally sputtered calcein film

I. Kruglenko[a], J. Burlachenko[a,*], S. Kravchenko[a], A. Savchenko[b], M. Slabkovska[c], Yu. Shirshov[d]

[a] V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine, Nauki Av. 41, 03190 Kyiv, Ukraine
[b] Microbiology and Tumor Biology Centrum, Karolinska Institutet, Nobelsväg 16, 17177 Stockholm, Sweden
[c] V.M. Glushkov Institute of Cybernetics of NAS of Ukraine, Kyiv, Ukraine
[d] New Zealand Science Centre "Science Alive", 392, Moorhouse Ave, PO Box 40020, Christchurch, New Zealand

ARTICLE INFO

Article history:
Received 13 September 2013
Received in revised form 21 January 2014
Accepted 16 February 2014
Available online 24 February 2014

Keywords:
Adsorption
Swelling
Calcein
Surface
Quartz crystal microbalance
Humidity

ABSTRACT

High humidity environments are often found in such areas as biotechnology, food chemistry, plant physiology etc. The controlling of parameters of such ambiences is vitally important. Thermally deposited calcein films have extremely high adsorptivity at exposure to water vapor of high concentration. This feature makes calcein a promising material for humidity sensing applications. The aim of this work is to explain high sensitivity and selectivity of calcein film to high humidity. Quartz crystal microbalance sensor, AFM and ellipsometry were used for calcein film characterization and adsorption properties investigation. The proposed model takes into account both the molecular properties of calcein (the presence of several functional groups capable of forming hydrogen bonds, and their arrangement) and the features of structure of thermally deposited calcein film (film restructuring due to the switching of bonds "calcein–calcein" to "calcein–water" in the course of water adsorption).

1. Introduction

Controlling of humidity is necessary in many areas [1,2]. In particular there are some processes occurring in highly humid ambience. Among them there are biotechnology processes, like enzyme and protein storage [3], food microbiology [4] and food chemistry [5], botany and plant physiology [6,7], agriculture [8]. Therefore the development of humidity sensors and sensing materials able to detect water vapor of high concentration, particularly in the presence of other components in the air mixture, is of great practical importance. Understanding of the nature of adsorption properties of such materials will make their choosing, modification and practical applications more reasonable.

An organic dye calcein is widely applied in biology and medicine, in particular, when making nanosensors to detect metal ions, amino-acids, for checking vital activity of cells, etc. [9–13]. There are only few literature references on use of calcein films for preparation of sensor coatings [14–17]. At the same time, the calcein films have rather interesting adsorption and other physico-chemical properties, one of which is reversible swelling caused by humidity. The investigation of those properties is of big practical importance.

The calcein films, both thermally deposited and obtained from solution, demonstrate very high response to water vapor of high concentration [16,17].

Now there exists no complete physico-chemical model that could fully explain or forecast the features of interactions between organic films and volatile molecules. Thus, for polymer films on the quartz crystal microbalance (QCM) surface, sorption is realized owing to polar or hydrogen bonds and is well described within the linear sorption energy relationship (LSER) that showed itself to advantage in gas chromatography [18]. This approach suggests mainly specificity of volatile molecules adsorption by polymer films with different character of the main chain and side ligands [19].

Another specificity mechanism was proposed in [20] for porphyrins-based sensors. Here the determining factor is coordination of sorbate molecule by central metal atom in a porphyrin molecule which is not taken into account in the LSER concept. This model is also well confirmed by experimental results [21]. In particular, the authors of [21] stressed that two mechanisms should be taken into account: (i) that of Van der Waals adsorption acting between nanocavity surface and volatile molecule (it ensures adsorption isotherm linearity) and (ii) specific sorption that is typical of some character of interaction determined by central atom coordination.

However, the existing approaches are not enough for explaining the adsorption properties of calcein films, in particular, extremely

---

[*] Corresponding author. Tel.: +380445255626.
E-mail address: deltayulek@mail.ru (J. Burlachenko).

http://dx.doi.org/10.1016/j.apsusc.2014.02.086
0169-4332/

high response and selectivity to water vapor of high concentration. In this work, we propose a model based on analysis of spatial arrangement of peripheral calcein substituents, bearing in mind probability of hydrogen bonds formation and allowance for the features of calcein molecules arrangement in a thermally deposited film. The reversible swelling of the film caused by humidity is demonstrated. High sensitivity and selectivity to water vapor of high concentration, good reproducibility, reversibility and long-term stability of calcein-based sensor response make this material very promising for future practical applications.

2. Experimental

2.1. Calcein film preparation

The calcein films (thickness of 30 nm) were prepared using thermal deposition from a Knudsen cell in a vacuum at room temperature. The deposition rate was 0.1 nm/min. Coatings were deposited in a single cycle onto two substrates: (i) silver electrodes of QCM, and (ii) silicon (ellipsometry, atomic force microscopy (AFM)). Film thickness was monitored in the course of deposition with a quartz thickness meter.

2.2. Quartz crystal microbalance

Both the frequency measurement procedure for a quartz crystal with a molecular film on its surface and experimental setup are described in detail in [22]. The QCM-sensor action is measurement of variation of the resonant oscillation frequency of a piezoelectric crystal caused by change of its mass due to analyte molecules adsorption onto the sensitive layer surface. Our measurements with the QCM technique were made as follows. The sensors were placed in a measurement flow-type cell and held in argon flow until stabilization of the quartz resonators frequency (deviation of ±2 Hz). Then analyte vapor in argon passed through the cell with a constant rate of about 60 ml/min. Analyte concentration was set by diluting saturated vapor with a dry argon flow. The cell temperature in the whole measuring volume was kept constant (at a level of 22 °C). We measured a frequency shift of sensor oscillations that was proportional to sensor mass change due to adsorption of molecules of the analyte under investigation.

2.3. Ellipsometry

The ellipsometric parameters Δ and Ψ were measured at light reflection from the silicon–calcein film sample with an ellipsometer LEF-3M (at a wavelength $\lambda = 632.8$ nm of a He–Ne laser) according to the polarizer-compensator sample analyzer (PCSA) scheme, with averaging over two zones [23]. The compensator angle was -45°, while the angle of incidence was 70°.

A silicon plate with calcein film was placed in a Petri dish that was on the ellipsometer table. The initial parameters Δ and Ψ were measured in the room atmosphere (air humidity was ~60%). Then a small piece of cotton wool impregnated with water was put near the sample, and the Petri dish was covered. After keeping in saturated vapor for 20 min, we took the cover off and measured again the parameters Δ and Ψ in 10, 20 and 30 min. Then the thickness of the film was calculated from the parameters Δ and Ψ using the single-layer model.

2.4. AFM characterization

AFM patterns of thermally deposited calcein films on silicon substrates were obtained using scanning probe microscopy (AFM microscope NanoScope IIIa Dimension 3000).

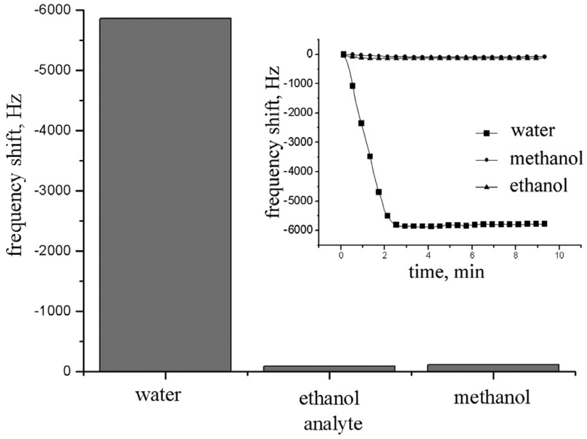


Fig. 1. Amplitude of QCM-sensor response to saturated vapors of water, ethanol and methanol (inset—kinetics of frequency shift at adsorption of water vapor).

3. Results and discussion

3.1. Adsorption capacity of the calcein film

Quartz crystal microbalance technique was used for the evaluation of adsorption capacity of the calcein film.

Fig. 1 presents amplitudes of QCM-sensor responses to saturated vapors of water (29,400 ppm), ethanol (78,000 ppm) and methanol (166,000 ppm) (frequency shift variation with time is given in the inset). The reduction of oscillation frequency was 5860 Hz, 88 Hz and 116 Hz for response to water, ethanol and methanol vapor, respectively. As a rule, the typical responses of QCM-sensors (coated with thin films of organic materials) to such analytes as alcohols and water are tens and hundreds of hertz. So the response to water vapor presented in Fig. 1 should be treated as extremely high. Moreover, the response to water vapor is 50–60 times higher than those to alcohols. Therefore, sensor selectivity to water at high vapor concentration can be considered as high.

In our previous work it was demonstrated that surface plasmon resonance sensor gives high response on the saturated water vapor as well (35 angle minutes) [16].

Extremely high adsorptivity of thermally deposited calcein films to water vapor can be explained from analysis of the structural features of both water and calcein molecules. Contrary to methanol and ethanol molecules, a water molecule has two hydrogen atoms capable of forming hydrogen bond. Just this feature is decisive at formation of water clusters in the course of water adsorption onto a surface. Besides, both the degree of hydrogen bonds formation and their strength depend on dipole moment of polar molecule that forms new bonds. The highest dipole moment is that of water molecule (1.84 D); those of methanol and ethanol molecules are 1.7 D and 1.6 D, respectively.

A flat calcein molecule involves several functional groups (–OH; =O; –COOH) capable of forming hydrogen bond. The arrangement of these centers is geminate. The above features of calcein molecule structure ensure a skeleton for water clusters formation, i.e. condensation. Their size depends on concentration of water vapor in an air mixture.

With QMB data it is possible to calculate the number of adsorbed water molecules, as well as its interrelation with the number of calcein molecules. The adsorbed mass may be calculated from the Sauerbrey equation:

$$\Delta F = -\frac{2f_0^2}{A\sqrt{p_q \mu_q}}\Delta m \quad (1)$$