Sensors and Actuators B 188 (2013) 482–487

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

Integrated-optical sensors based on chitosan waveguide films for relative humidity measurements

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ARTICLE INFO

Article history:
Received 15 February 2013
Received in revised form 29 May 2013
Accepted 13 July 2013
Available online 23 July 2013

Keywords:
Relative humidity
Biopolymer
Chitosan
Integrated-optical sensor

ABSTRACT

Here we report on fabrication and properties of integrated-optical sensors for relative humidity detection based on waveguide films of chitosan in neutral and salt forms. Obtained sensors have high sensitivity and short response time over a wide range of relative humidity.

1. Introduction

Development of low-cost high-sensitive sensors with a short response time, which are capable to work in a wide range of relative humidity (RH), is of great importance for numerous applications in chemical and food industry, agriculture, medicine, manufacturing, and environmental monitoring. The requirements for such systems have to satisfy the following practical requirements: high sensitivity in a wide range of relative humidity, rapid response time, no hysteresis in series of sharp increases and decreases of optical signal with relative humidity, low dependence on the temperature, and low cost [1,2]. This, in general, requires registration of the relative humidity in the range of 10–100%, at operating temperatures 0 to 40 °C and the response time of <10 s [2].

Many studies have been dealing with the development of optical sensors such as those described in [3–8]. Structurally, such sensor consists of a waveguide, at which the lights propagates, and deposited on it a special polymer layer acting as a sensing element. In the presence of water vapor polymer changes its physical characteristics that leads to a change in propagation conditions, and the waveguide forming the optical response. A number of studies consider as the hydrophilic polymer a natural polysaccharide chitosan, which contains hydroxyl and amino groups and, hence, provides a reversible adsorption of water molecules from the gas phase [9–11].

In this paper, the chitosan is used to form the waveguide as a sensing element of the relative humidity sensor, in contrast to most studies, where it is used as a sensitive layer formed at the surface of the waveguide [12–14]. We describe the results of studies of the optical, waveguide and the sensor characteristics of the films of different ionic forms of chitosan to measure the relative humidity level of the environment. The results are compared with the results of the characteristics of the known works, for the cases of the sensitive layer on the surface of the waveguide [12,15,7,16–20].

2. Materials and methods

Stock solutions containing 4% of chitosan (molecular mass 500 kDa, degree of deacetylation 80.5%) were prepared by dissolution of polymer in acetic or citric acids with concentrations 4% and 8%, respectively. Thin chitosan films were deposited on substrates by spin-coating (Laurell WS-400B-6NPP-LITE spin-coater) at rotation speeds, which were predetermined to give in all cases resulting film thickness about 1200 nm (Table 1). Films were fabricated on substrates with the refractive index lower than that of chitosan (sodium silicate glass $n = 1.523$, MgF_2 $n = 1.385$) to assure waveguide propagation of light in polymer film.

The films in salt forms obtained from chitosan solution in acetic (CH-Ac) and citric (CH-Cit) acids were deprotonated by immersion into 3% ammonia solution for 10 min followed by rinsing with distilled water. The resulting films in neutral form are further referred to as (CH-Ac-N) and (CH-Cit-N), respectively.

The thickness and the refractive index of chitosan films (in dry state on the surfaces of silicon wafers) were measured at $\lambda = 633$ nm

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0925-4005/$ – see front matter
http://dx.doi.org/10.1016/j.snb.2013.07.043

Table 1
Film characteristics.

Chitosan form	Rotation speed, rpm	Film thickness, nm
CH-Ac	1500	1200 ± 30
CH-Cit	8000	1250 ± 30
CH-Ac-N	1000	1300 ± 40
CH-Cit-N	2000	1250 ± 50

and an angle of incidence of 70° with a null-ellipsometer in a polarizer compensator-sample analyzer (Multiscope, Optrel Berlin) microfocus ellipsometer. Initially, the thickness of the native SiO_2 layer was calculated at refractive indices $n = 3.858 - ix0.018$ and $n = 1.4598$ for the Si wafer and the SiO_2 layer, respectively.

3. Experimental setup

Fig. 1 shows a scheme of the experimental setup. He–Ne laser ($\lambda = 633$ nm) with an average output power of 11 mW was used as a light source (1). Coherent LabMax power meter was used as a photodetector (5). The light was coupled into the waveguide (2) via a prism coupler ($n = 1.764121$). The measurements were performed for the $\mathbf{TE_0}$ mode.

Study of sensor characteristics was carried out in a special sealed chamber equipped with a hygrometer (3) (Testo 635, Germany), which allowed determination of the exact value of RH reached in the chamber. The RH level was preset by pumping the air through solutions of sulfuric acid with different concentrations (4) with flow rate about 0.25 L/min. Measurements were carried out at 21 °C. To study the dynamic characteristics of a hygrometer and a photodetector, they were synchronized with a computer.

The influence of RH on refractive index of chitosan was studied using the spectral ellipsometry technique at the wavelength $\lambda = 633$ nm, at which waveguide characteristics were further investigated (Fig. 2).

We have demonstrated [21] that along with increasing RH level the refractive index of the polymer film decreases due to the chitosan swelling and increase of water content in the film. However, the dependences of refractive index on RH are nonlinear and have threshold RH values, at which refractive index decreases sharply (Fig. 2, curves 1 and 2). For CH-Ac, this threshold is not so pronounced and observed at RH = 60%, while for CH-Cit the corresponding threshold is clearly observed at 75%. This difference in properties can be explained by the fact that citric acid, in contrast to acetic acid, is a non-volatile substance. Thus, highly hygroscopic citric acid remains in the spin-coated chitosan film and contributes to total hydrophilicity of the film.

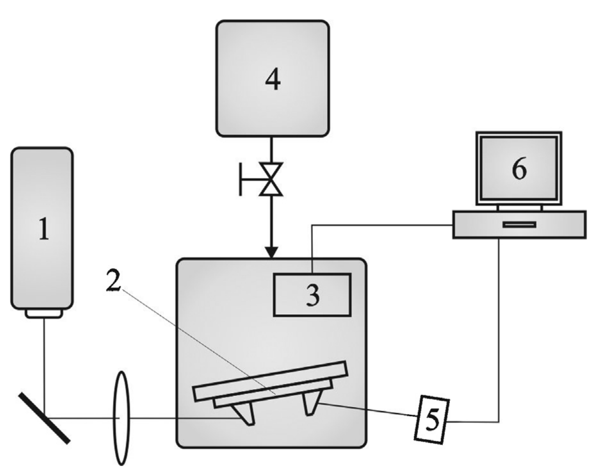

Fig. 1. Scheme of the experimental setup: 1 – light source, 2 – chitosan waveguide film on a substrate, 3 – hygrometer, 4 – aqueous solution of sulfuric acid, 5 – photodetector, and 6 – PC.

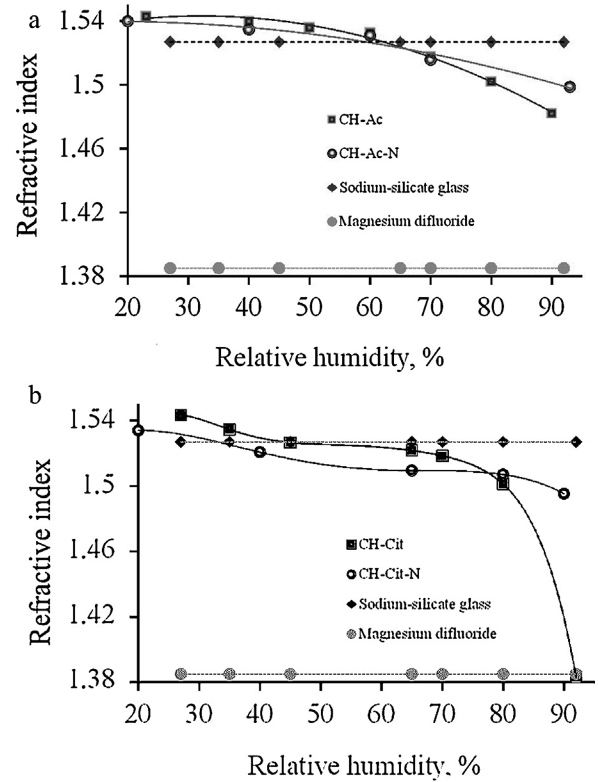

Fig. 2. Dependence of polymer film and substrate refractive indices on RH level: (a) acetic forms and (b) citric forms.

4. Optical response

Sensor characteristics of chitosan waveguide films were obtained at RH range from 15 to 95% (3% step) under conditions of increasing (water adsorption) and decreasing (water desorption) the RH level. The optical response was measured 15 min after RH change to assure equilibrium conditions. Changes in the light power (output power) transmitted through the waveguide were recorded for all chitosan-based films as a function of the RH level (Fig. 3). P_{out} is normalized power [12], defined as $P_{out} = 10 \times \log(P_1/P_2)$ where P_1 – output power at 15% RH and P_2 – output power at current RH.

For all chitosan films, except CH-Cit, the monotonic increase of the output power with increase of RH level was observed. Moreover, since chitosan is a porous material [9,10], the process of water adsorption leads to filling of air pores and thus reduces radiation scattering by inhomogeneities in refractive index. The effect leads to reduction of the value of the optical absorption of chitosan film by increasing the level of relative humidity (Fig. 4). The data shown in Fig 4 were obtained for 50 um thick acetate chitosan film formed by solution casting method.

Increasing the relative humidity leads to decreasing of film absorbance $\Delta A \approx 0.004$ (inset in Fig. 4). Thus, based on the equation of Lambert–Bouguer–Beer's the absorption coefficient of the film decreases by an amount $\alpha = 1.892$, which would reduce the attenuation losses in the waveguide at $\alpha = 8.1356$ dB/cm. In the described system, the optical response is formed by two rival processes: the translucence of the film by reducing the scattering of the light and a decrease in the refractive index of the film during the adsorption of water molecules. For both forms of chitosan films – acetate and neutral - the process of bleaching of the film is predominant, resulting in significant translucence of the film.