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Investigation of humidity influence upon waveguide features of chitosan thin films

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Abstract

Optical properties of chitosan films of different ionic forms as well as their mutual correlation were investigated. By using spectral ellipsometry and mode spectroscopy methods it was discovered that these properties depend upon relative humidity of environment. It was shown that all specimens studied are characterized by the relative humidity thresholds at which their optical properties vary. The data obtained allow one to consider chitosan as a material with optical properties controlled by the humidity level change

Keywords: integrated optic; biopolymers; chitosan; waveguides

1. Introduction

During the recent years natural biopolymers draw a great attention of the scientists and other experts who specialize in the fields of waveguide optics and optical sensors development. Aminopolysaccharide chitosan is one of the most promising biopolymers fit for the purpose of development of optical waveguides and sensors [1, 2]. Its advantages are not limited to the simplicity of chitosan-based films fabrication; the refractive index of chitosan film can be easily altered by injection of metal ions into the film with their subsequent conglomeration to nanoparticles [3] or by injection of optically active

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inorganic nanocrystals which makes it possible to fabricate optical materials meant for different application areas.

Moreover, the interaction of chitosan as hydrophilic polymer basis with organic solvents, water vapor, mineral and organic acids leads to a change of hydration level and/or degree of polymer protonation which, in its turn, alters the optical features of the film. Thus, the investigation of the environmental conditions influenced on waveguide features of chitosan thin films is the goal of the paper.

2. Materials and methods

In our work we used chitosan made by «Bioprogress» (Moscow, Russia) (molecular weight 500 kDa, deacetylation degree 80.5%) which, in order to get a concentration required, was dissolved in the solvent of acetic (acetate) or citric (citrate) acids with molar ratio NH_2/-COOH (1:2).

For film coating preparation we used substrate of magnesium fluoride (n_s = 1.385) with 50*100 mm square. For getting a uniform film coating a «Laurell WS-400B-6NPP-LITE» spin-coater was used. Polymer solvent was distributed uniformly along the substrate rotating at 500-4000 rpm speed (the speed was changed according to a film thickness required). The thickness was controlled by atomic force microscopy method.

For investigation of humidity influenced on waveguide features of chitosan film a leakproof chamber with a prism-coupled waveguide placed inside was constructed. The chamber was installed upon a goniometric stage for precision adjustment and measurements of light input-output angles.

The humidity level inside the chamber was preset with the use of vapours of water solution of sulfuric acid of various concentration and was controlled by a hygrometer. As a light source, a laser diode operating at the wavelenght of 650 nm was used. A registration of light intensity was performed by a 0.3 Mpix resolution CDD camera with the pixel size of 9 μm.The propagation losses of the guide were measured by using the sliding-prism method described in [4].

3. Results and discussion

Refractive indices of chitosan films were measured by spectral ellipsometry method with use of «Ellips 1891 - SAG» device (Novosibirsk, Russia) within 400-1050 nm wavelength range with 1 nm scanning step.

In order to investigate the dependence of refractive index of two ionic forms (citrate and acetate) of chitosan on relative humidity with use of spectral ellipsometry three samples of each form were fabricated. The films thickness deviation didn't exceed 0.1%. The experimentally obtained dependencies of chitosan films and substrates refractive indices on the environment relative humidity are shown in Fig. 1.

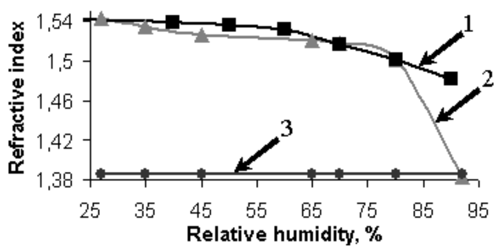

Fig. 1. The obtained dependencies of chitosan films and substrates refractive indices on the environment relative humidity: 1 – Chitosan acetate; 2 – Chitosan citrate; 3 – Magnesium fluoride (substrate).

As it follows from the obtained results all types of chitosan film display a decrease in refractive index when the humidity rises up. As it takes place one can witness humidity thresholds at which the refractive index decreases faster, especially in case of the chitosan citrate sample. These thresholds are equal to 60% and 75% for chitosan acetate and chitosan citrate correspondingly.

Investigation of optical losses in chitosan-based waveguides carried out by sliding prism method has shown that these losses depend considerably on ionic form of the chitosan. The losses measured for the TE_0 mode at 20% relative humidity reach 7.263 dB/cm and 0.825 dB/cm for the chitosan acetate and chitosan citrate correspondingly.

Fig. 2 shows dependencies of the TE_0-mode output power on the relative humidity for the cases of chitosan citrate and chitosan acetate.

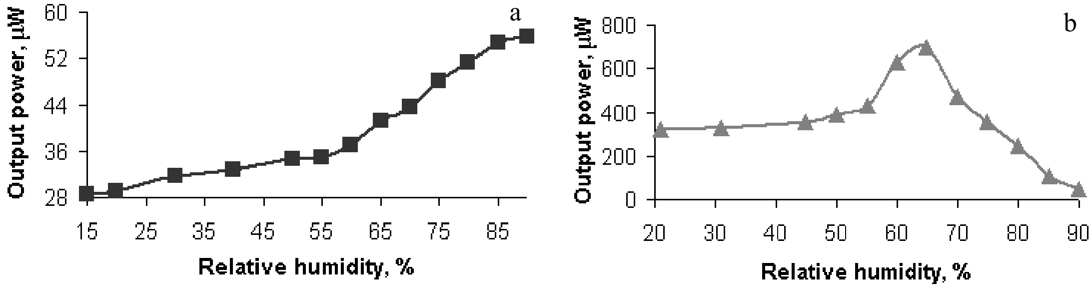

Fig. 2. Dependencies of TE_0-mode output light power on the relative humidity measured in the waveguides based upon: a) chitosan-acetate; b) chitosan-citrate.

Eventually observed thresholds of relative humidity at which it considerably affects optical properties of chitosan films are almost equal to those at which the rate of change of chitosan films refractive index accelerates (Fig. 1). In case of chitosan acetate this threshold equals to 60%-75%, for the case of chitosan citrate it equals to 55%-75%. It seems that these values of the relative humidity are the lower limits at which hydrophilic properties of the chitosan commence to emerge substantially. The further increase of relative humidity causes change of chitosan films structure and, as a result, a change of their optical properties.

Such behavior of the samples under study is explained by alteration of waveguide propagation conditions. Analysis of dependence of modal spectrum profile of the radiation at the output of the chitosan waveguide on change of the environment relative humidity has shown that an increase of the relative humidity causes a broadening of the waveguide modal spectrum along the both axis with preservation of the central maximum. Fig. 3 demonstrates dependence of the chitosan acetate based waveguide modal spectrum on the environment relative humidity.

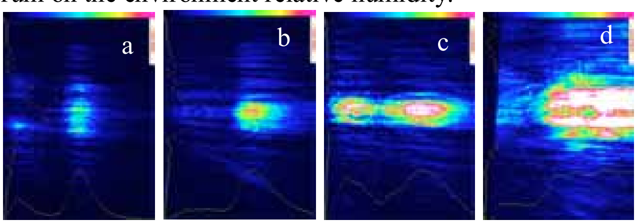

Fig. 3. Changes of mode spectrum of chitosan-based waveguide witnessed at different levels of humidity: a) 18%, b)54%, c)70%, d)90%

The angle of excitation of waveguide TE0-mode remains constant during the increas of relative humidity in our experiments. Since the clamping area of input and output prisms was isolated from the humidity, so the optical properties of the films in this area didn't change.

Thus, the obtained dependence of modal spectrum profile of the light passed through chitosan waveguide on change of the environment relative humidity is caused by the next two reasons: the change of refractive index and film's thickness in the area of waveguide-environment contact. This takes place either for the chitosan acetate and the chitosan citrate. The same alteration of properties of chitosan coatings upon the solid surface due to a swelling process was investigated previously by «in situ» ellipsometry method and is described in [5].

Optical properties of waveguides based upon chitosan acetate and chitosan citrate differ dramatically, especially in case of exceeding the typical threshold of relative humidity. It should be emphasized that, as it was previously observed, the nature of counter anion affects the chitosan physic-chemical properties [6] including film-producing ones [7]. Differences in structures of the films fabricated from chitosan solutions in different ionic forms are verified by the results of wide angle X-ray diffraction experiments which have shown that crystallization degree of chitosan-acetate films is significantly greater than that of chitosan-citrate films [8].

4. Conclusions

The carried out investigations revealed that the environment relative humidity affects optical properties of ionic forms of chitosan as well as chitosan-based film waveguides considerably, and it is expressed by an alteration of waveguide propagation conditions. The effect consists in decrease of refractive index of the material and change of output power of TE_0-mode propagating along the waveguide. The obtained results allow one to consider ionic forms of chitosan a prospective material with optical properties that can be modified by change of the environment relative humidity.

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