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Properties of silica and silica-titania layers fabricated from silica sols containing fumed silica

Ivo Barton [a, *], Vlastimil Matejec [a], Jan Mrazek [a], Luminita Predoana [b], Maria Zaharescu [b]

[a] *Institute of Photonics and Electronics of the CAS, Chaberska 57, 182 51 Prague 8-Kobylisy, Czech Republic*
[b] *"Ilie Murgulescu" Institute of Physical Chemistry, Romanian Academy, 202 Splaiul Independentei st., 060021, Bucharest, Romania*

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ABSTRACT

Silica layers fabricated by the sol-gel method are usually amorphous and exhibit a relatively low refractive index (n~1.46 at about 0.6 μm), high optical transmittances at UV-VIS and near-IR ranges, as well as high thermal stability. Such layers can be used as high reflection or antireflection coatings, dielectric mirrors, bandpass filters, etc. However, crack-free layers with a maximum thickness of about 400 nm can be prepared in one coating cycle from sols of simple silicon alkoxides. This paper presents an approach for the preparation of crack-free silica layers that allows us to increase this maximum thickness. The approach is based on the dip-coating technique used for applying stable silica sols containing fumed silica. These sols were obtained from input silica sols based on tetraethyl orthosilicate (TEOS) with concentrations 1 and 2 mol/l, ethanol, HCl and water (RW 1.75). Fumed silica was dispersed in water/TritonX-100 solution and added into some of the input sols. Zeta potentials, average dimensions and diffusion coefficients of silica agglomerates in sols containing fumed silica are presented. Both types of sols were deposited onto silica slides and silicon wafers by the dip-coating technique using different withdrawing velocities 100,200 and 300 mm/min. Prepared silica gel layers were thermally treated at 450 or 900 °C. One of silica sols with fumed silica has also been used for the preparation of a silica-titania sol with a molar ratio Ti/Si = 3/7. Both these sols have been employed for the preparation of a Bragg mirror consisting of three pairs of high-index silica-titania and low index silica layers on a silica slide.

The appearance and thickness of prepared single silica and silica-titania layers have been characterized by optical microscopy and scanning electron microscopy. Optical properties of layers have been determined by spectral ellipsometry and UV-VIS-NIR transmission spectrometry. The measurements have shown that characteristics of layers fabricated from both types of the sols differ and that one can obtain stable transparent silica layers with thicknesses up to 650 nm and refractive indices in a range from 1.41 to 1.44 at 600 nm using TEOS sols containing fumed silica. It has been found that larger layer thicknesses can be achieved by using silica sols with fumed silica, by increasing the alkoxide concentration, by using increased withdrawing velocities, and by decreasing heat-treatment temperatures.

1. Introduction

Recently, sol-gel methods have been employed for the development of novel materials with controlled optical properties such as transmittance and reflectance [1,2]. Such methods enable us to obtain novel materials directly as bulk ones or as thin films by their application on substrates. For the preparation of novel materials, doping gel matrices with nanoparticles has been used because nanoparticles with sub-wavelength dimensions can suppress Rayleigh light scattering in these matrices and do not decrease their transparency [3,4]. Moreover, such nanocomposite materials can exhibit novel physical properties due to both bulk physical properties of nanoparticles used and due to their small dimensions responsible e.g. for quantum-size effects. Nanocomposite materials have been investigated for applications in antireflective coatings, optical waveguides, lasers, solar cells, devices based on non-linear optical phenomena, etc. [4].

Antireflective (AR) coatings on glass or transparent polymeric materials represent one of applications for which nanocomposite materials have been investigated [2,4–10]. Such coatings can be found on computer monitors, TV screens, car dashboards, in solar

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* Corresponding author.
E-mail address: barton@ufe.cz (I. Barton).

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cells, lasers, etc. They enable us to decrease the reflection of light from the coated surface practically to zero either at a particular wavelength or at certain wavelength ranges. For such purposes, single layers or multilayers have been prepared based on sols containing nanoparticles [4–10].

Two physical principles have been employed at the application of AR coatings from nanoparticle sols. First one relays on tailoring the coating refractive index by controlling the coating nanoporosity. In such coatings light undergoes the destructive interference resulting into minimum reflectance determined by the wavelength, angle and polarization of incident light rays [5,9]. In order to achieve the reflectance minimum, the coating optical thickness corresponding to a quarter-wave layer and the refractive index equals to the geometrical average of the substrate and incident medium refractive indices are designed. The second AR principle takes place at substrate coatings based nanostructure arrays [9,10]. In such an array, the refractive index smoothly changes from that of the incident medium (usually air) to the substrate refractive index and light tends to bend progressively from the coating/incident medium surface to the substrate.

AR coatings based on light interference have been fabricated from sols containing colloidal silica nanoparticles [3,5,6]. Such coatings enable us to achieve silica porosities of about 50% which corresponds to a refractive index value around 1.22. The coatings exhibit high laser damage thresholds and can be employed in optical systems for delivery of high laser powers. Sols of monodispersed silica nanoparticles for the application of such coatings have been prepared by the Stöber method from silica alkoxides hydrolyzed by ammonium hydroxide [5]. Coatings prepared from tetraethyl ortosilicate (TEOS) have made possible to achieve transmittances higher than 99%, however, they are hydrophilic and their porosity can decrease due to water condensation in pores. In order to tailor the coating hydrophobicity, hybrid inorganic-organic nanocomposites have been developed, prepared e.g. from TEOS and methyltriethoxysilane [4,6]. Single xerogel layers with a maximum thickness of 14 μm have been prepared from such hybrid nanocomposites [6].

Nanostructure arrays for AR coatings have been prepared by techniques such as oblique-angle deposition combined with standard film growth, chemical etching, etc. [10]. Single layers and multilayers composed of nanorod- or nanopillar-arrays have been fabricated from oxides such as silica or titania or from metals such as silver [9]. Aerogels have also been employed in AR coatings for the visible and near-IR spectral regions. Such coatings consist of one layer of silica nanoparticles, one layer of silica aerogel overcoated with a layer of superhydrophobic polytetrafluoroethylene [6].

Interference effects are used not only in AR coatings, but also in highly reflective mirrors, so called Bragg mirrors [11–22]. Such mirrors consist of repeated pairs of alternating layers with high and low refractive indices which usually have quarter-wave optical thicknesses. By using tailored refractive indices of these layers, optical waves multiple reflected from the layer interfaces can interfere constructively which results in a mirror with a high reflectivity. Bragg mirrors are usually fabricated by physical vapor deposition techniques which enable us to produce films with high optical quality. However, such techniques require complex preparation condition [11]. On the other hand, the sol-gel method offers a relatively simple way for the fabrication of Bragg mirrors. Oxides such as titania [11,12,14–19], tin oxide [20], dense barium strontium titanate [13], etc. have been used for preparing high-refractive index layers while silica [11,12,14–20], porous silica, porous barium strontium titanate [13], aluminosilicate can be employed for obtaining low-refractive index ones.

The sol-gel method has also been used for the preparation of one-dimensional photonic crystals (1DPC) consisting of two Bragg mirrors separated by a defect layer [16–20]. In such crystals light is confined into the defect layer due to the photonic band gap effect of the Bragg mirrors which causes that light intensity evanescently decays in the mirrors. Such photonic crystals have been used for controlling the luminescence of rare-earth ions, e.g. erbium or europium, immobilized in the defect layer composed usually of silica [18–20]. Only few papers deal with the fabrication of Bragg mirrors and 1DPCs by using sols containing nanoparticles. One of such papers has shown that stable sols of ZnO and Fe_2O_3 colloidal nanoparticles can be prepared in alcoholic solvents and used for the formation of photonic crystal multilayers [21]. Moreover, it has been found that Bragg mirrors based on titania contain anatase nanoparticles [15].

In addition to papers on nanocomposite-based photonics materials there are articles dealing with photonics materials prepared on the basis of fumed silica. It is well known that fumed silica consists of silica nanoparticles with an average diameter of about 10–40 nm which are fused together and form aggregates with average dimensions up to several micrometers. Such aggregates can form stable dispersions in polar solvents, e.g. in water, aliphatic alcohols, etc. [22,23]. Fumed silica has been investigated for the fabrication of composites and superhydrophobic materials [24,25]. It has also been employed for the preparation of bulk photonic materials [26,27] such as monolithic silica tubes and preforms of optical fibers. One of such preparation processes is based on acidic hydrolysis and polycondensation of tetraethyl orthosilicate (TEOS) in water with addition of fumed silica [26]. Final gel monoliths are supercritically dried. Another production process for silica monoliths relays on using stable dispersion of fumed silica in water that is gelled and produced gel monoliths are thermally dried and densified. Preforms of microstructure fibers have been produced by this process [27]. The process combining TEOS that is hydrolyzed and polycondensated in acidic water with fumed silica has also been employed for the fabrication of bulk silica glass doped with neodymium ions [28]. Planar silica waveguides have been fabricated by similar polymeric-colloidal approach and by using the spin-coating method [29].

This paper has been motivated by the performance of sol-gel approaches for the fabrication of optical coatings with controlled reflectivity such as Bragg mirrors. It is known that Bragg mirrors consist of alternating pairs of high-and low-index single layers each with controlled thickness and refractive index. However, the repeated application of such layers can induce cracks in these coatings, especially, if thicknesses of the single layers are close to the critical ones. Such effects can be expected during the preparation of Bragg mirrors designed for wavelengths longer than 1500 nm because in such mirrors increased optical thicknesses of high-and low-index layers are necessary. In order to avoid cracks in such multi-layered coatings, a rather complicated special heat-treatment procedure has been developed for fabricating Bragg mirrors based on titania and silica layers [30].

In this paper, we present a novel, on our view, a less complicated approach for preparing single silica-based layers that can avoid a special heat treatment and still is capable of preparing crack-free layers with enough high optical thicknesses. The novel approach employs silica sols containing TEOS and a low amount of fumed silica. In comparison with previously developed approaches relaying on fumed silica and water [25–29], our approach uses ethanol as solvent and hydrochloric acid as catalysts. It is shown that the approach allows us to prepare stable input alkoxide sols containing fumed silica. They are characterized by average particle-dimensions and by zeta potentials. The input sols are applied by dip-coating method using velocities of 100, 200, and 300 mm/min and gel layers heat-treated at 450° and 900 °C. Refractive-index values of prepared layers are presented. Moreover, a selected