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Optical properties of zinc oxide ultrathin hybrid films on silicon wafer prepared by layer-by-layer method

Dániel Sebők [a], Krisztina Szendrei [a], Tamás Szabó [a], Imre Dékány [a,b,*]

[a] Department of Colloid Chemistry University of Szeged, H-6720 Szeged, Aradi vértanúk tere 1, Hungary
[b] Supramolecular and Nanostructured Materials Research Group of the Hungarian Academy of Sciences, H-6720 Szeged, Aradi vértanúk tere 1, Hungary

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Abstract

ZnO nanoparticles were prepared and self-assembled hybrid nanolayers were generated on the surface of silicon wafers using the layer silicate hectorite and PSS (sodium polystyrene-sulfonate) polyelectrolyte. The thickness, light absorption and interference properties of the hybrid films were studied. The influence of layer silicates and polymers on the self-organizing properties of ZnO nanoparticles was examined. Utilization of the nanofilms as optical sensors was investigated: they can adsorb ethanol vapor and their reflection and light interference properties are thereby significantly altered.

Keywords: Deposition process; Multilayers; Optical coatings; Reflection spectroscopy; Sensors; Zinc oxide

1. Introduction

Hybrid structures can be prepared from inorganic nanostructured materials such as zinc oxide. The partner of zinc oxide in the composite can be many kinds of inorganic materials. Meneau et al. incorporated zinc oxide nanoparticles into Y-zeolite. After adsorption and hydrolysis of the zinc precursor, they calcined the samples and confirmed the presence of zinc oxide particles with diameters of 1–2 nm [1]. Cannas et al. synthesized ZnO/SiO_2 nanocomposites by impregnation of mesoporous silica [2]. Ali et al. generated self-assembling composite structures containing zinc oxide nanoclusters by using diblock copolymers [3]; Yoshida et al. combined self-assembly with electrodeposition to prepare composite nanofilms [4]. The preparation and characterization of ultrathin films are discussed in a large number of publications [5–10]. Nanostructured hybrid layers can be obtained from materials of layered structure, e.g. layer silicates such as laponite or montmorillonite and polyelectrolytes by the so-called layer-by-layer (LBL) self-assembly method [8]. LBL is a very widely used method for the preparation of thin layers, e.g. protein/polyelectrolyte nanocomposite films [11,12], Langmuir-Blodgett films [13–16], membranes [17], photonic crystals and photocatalytically active nanofilms [18], graphite oxide films [19] and thin layers built of carbon nanotubes [14]. Sequential deposition of layers was also monitored by SPR (surface plasmon resonance spectroscopy), the ordered structure of the layers was detected and their thickness determined [20]. The advantage of these films is that they are highly stable and their ordering can also be demonstrated by XRD measurements. The LBL technique can also be applied for the preparation of hybrid films consisting of a cationic polyelectrolyte and semiconductor nanoparticles (CdS, PbS, TiO_2) [6,7,18–20]. Self-assembly is due to electrostatic attraction between the particles, i.e. the positive surface charge of the polyelectrolyte and the negative surface charge of the colloidal particles or polyelectrolytes with different functional groups and charges [20–29]. The essence of

* Corresponding author. Department of Colloid Chemistry University of Szeged, H-6720 Szeged, Aradi vértanúk tere 1, Hungary. Tel.: +36 62 544210; fax: +36 62 544042.
E-mail address: i.dekany@chem.u-szeged.hu (I. Dékány).

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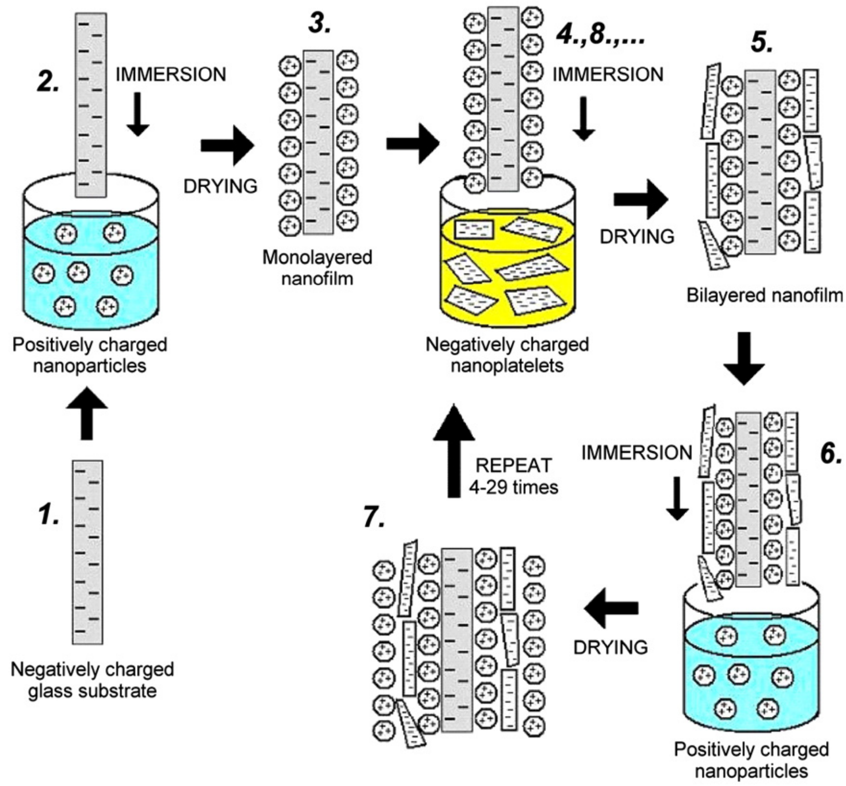

Fig. 1. Schematics of the layer-by-layer deposition protocol.

the method is bringing into contact components with opposite surface charges; thus, the electrostatic interaction between them induces a fuctionalization process leading to the development of the structure characteristic of nanoparticle-layer silicate or nanoparticle-polymer hybrids.

We prepared zinc oxide nanoparticles by homogeneous nucleation. In this procedure ZnO nanoparticles are produced in liquid phase by photolysis. The concentration and size of the particles formed can be controlled by the concentrations of the zinc precursor and the stabilizer. It is important to note that the lamellae of layer silicates and polyelectrolytes prevent the aggregation of nanoparticles, thereby stabilizing the ultrathin films.

In an earlier publication [8] we have reported on the appearance of interference colors when white light reflected from ZnO/hectorite multilayered nanofilms. In the present work, this observation is studied further to obtain a more quantitative insight into the optical properties of ZnO/clay thin coatings. In addition, ZnO/polyelectrolyte films will be also considered.

2. Materials and methods

2.1. Synthesis of ZnO nanoparticles

For the method using photolysis, 6 g of zinc acetate dihydrate (Fluka, purum), was dissolved in 300 ml of ultrapure water (18 MΩcm resistivity, obtained from a Milli-Q membrane filtration system; Millipore Corp.) and to this solution 10 ml of 30% hydrogen peroxide was added. The solution was irradiated with a 75 W Xe lamp for 4 h under continuous stirring; at half-time 10 ml of hydrogen peroxide was added to the system, which facilitated the completion of oxidation. Part of the acetate ions present in the solution are degraded by oxidation and intensive UV-irradiation and ZnO is formed. The procedure results in the formation of stable, milky zinc oxide nanosol [8] with a concentration of 8.5 g/L.

The particle size distribution of the ZnO sol was determined by Malvern Nanosizer dynamic light scattering device. The resulting mean hydrodynamic particle diameter was 66 nm. The ZnO nanosol prepared has a positive surface charge and streaming potential (+55 mV) in aqueous dispersion, as verified by our measurements in a Mütek PCD-02 streaming potential detector. The pH of the sol prepared varied between 5.1 and 5.2, which is of importance because in the nanodispersion of acidic medium a positive surface charge develops, resulting in the formation of surface groups of the $Zn{-}OH_2^+$ type.

2.2. Preparation of ultrathin films

The following starting materials were used: zinc oxide nanosol, ultrapure water, synthetic hectorite (Optigel, Süd-Chemie GmbH), polystyrene sulfonate sodium salt (PSS) (Aldrich, M=70,000). The samples were deposited on Si wafers (Crystal GmbH, Germany) using the LBL method. Multilayer composite nanofilms were prepared on the solid surface by exploiting the self-assembling ability of nanoparticles and layer silicates or polyelectrolytes. The silicon plates