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Surface analysis monitoring of polyelectrolyte deposition on $Ba_{0.5}Sr_{0.5}TiO_3$ thin films

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Abstract

Thin films are currently gaining interest in many areas such as integrated optics, sensors, friction, reducing coatings, surface orientation layers, and general industrial applications. Recently, molecular self-assembling techniques have been applied for thin film deposition of electrically conducting polymers, conjugated polymers for light-emitting devices, nanoparticles, and noncentrosymmetric-ordered second order nonlinear optical (NOL) devices. Polyelectrolytes self-assemblies have been used to prepare thin films. The alternate immersion of a charged surface in polyannion and a polycation solution leads usually to the formation of films known as polyelectrolyte multilayers. These polyanion and polycation structures are not neutral. However, charge compensation appears on the surface. This constitutes the building driving force of the polyelectrolyte multilayer films.

The present approach consists of two parts: (a) the chemisorption of 11-mercaptoundecylamine (MUA) to construct a self-assembled monolayer with the consequent protonation of the amine, and (b) the deposition of opposite charged polyelectrolytes in a sandwich fashion. The approach has the advantage that ionic attraction between opposite charges is the driving force for the multilayer buildup. For our purposes, the multilayer of polyelectrolytes depends on the quality of the surface needed for the application. In many cases, this approach will be used in a way that the roughness factor defects will be diminished. The polyelectrolytes selected for the study were: polystyrene sulfonate sodium salt (PSS), poly vinylsulfate potassium salt (PVS), and polyallylamine hydrochloride (PAH), as shown in Fig. 1. The deposition of polyelectrolytes was carried out by a dipping procedure with the corresponding polyelectrolyte. Monitoring of the alternate deposition of polyelectrolyte bilayers was done by surface analysis techniques such as X-ray photoelectron spectroscopy (XPS), specular reflectance infrared (IR), and atomic force microscopy (AFM). The surface analysis results are presented through the adsorption steps of the polyelectrolytes layer by layer.

Keywords: BSTO; Polyelectrolytes; Self-assemblies; XPS; Polystyrene sulfonate sodium; Polyvinylsulfate potassium; Polyallylamine hydrochloride

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1. Introduction

Polyelectrolytes (PEL) are defined as materials for which the solution properties in solvents of high dielectric constants are governed by electrostatics interactions over distances larger than the typical molecular dimensions. Polymers with bound positive or negative charges are referred to as polyelectrolytes, macroions, or polyions. These polymers may be synthetic, natural or modified. The synthetic polyelectrolytes include polymers that can be made by several methods, the major one being chain growth polymerization. The distinctive behavior of polyelectrolytes in aqueous solutions is what separates this class of polymers from nonionic polymers. In aqueous solution, the polymer coils are greatly expanded by the presence of charged groups. If the solution is free of added electrolytes, the polymer coil expands as the polymer concentration decreases. This is known as the ‘‘polyelectrolyte effect’’. In the presence of added electrolytes, the polyelectrolytes behave like nonionic polymers and chain expansion is not observed.

Some authors described quantitatively the intrinsic viscosity of branched polyelectrolytes [1]. The interference between the polymer chain and the electrolyte character has generated considerable interest in the field and developed new applications. Several authors reported the possibility of PELs to form

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ordered structures in dilute systems [2–4]. The molecular behavior of water polyelectrolye systems has been studied systematically by Hatakeyama et al. using differential scanning calorimetry(DSC), nuclear magnetic resonance spectroscopy (NMR), and polarizing microscopy on highly concentrated solutions [5,6].

Ultrathin organic films are currently gaining more attention in scientific applied research such as: integrated optics, surface coating, biosensors, friction-inducing coating, and surface orientation layer [7]. Following the phenomena of self-organization by self-assembled monolayers, the polyelectrolytes multilayers are formed by the alternate immersion of a charged surface in a polyanion and a polycation solution [8]. The well-defined organization required by these systems is an important task for the preparation of films with properties in a unique geometrical arrangement [9]. Many articles have reported that the driving force of consecutive physisorption of anionic and cationic bipolar amphiphiles are the anionic attraction between opposite charges leading to a multilayer buildup [10,11].

Polyelectrolytes materials are widely used in industrial applications as dispersants in aqueous media, flocculating agents to coagulate slurries and industrial wastes [12], and for sizing in textile and paper manufacture. In addition, this is used as conditioning additive for drilling mud and soil. More recently, they have been applied in molecular self-assembling techniques for thin film deposition of electrically conducting polymers, conjugated polymers for light-emitting devices, nanoparticles and nonlinear optical (NOL) devices [13–15]. The alternate immersion of a charged surface in polyannion and a polycation solution usually leads to the formation of films known as polyelectrolyte multilayers. These polyanion and polycation structures are not neutral, but charge compensation appears on the surface; this constitutes the driving force of the polyelectrolyte multilayer film formation.

A new technique for constructing multilayer polymer films on solid surfaces, based on consecutively alternating adsorption of anionic and cationic polyelectrolyte, has been developed [9]. Decher et al. demonstrated the buildup of optically transparent multilayer films by anionic and cationic polyelectrolytes on solid surfaces, followed by UV–vis spectroscopy and small angle X-ray scattering (SAXS) [9,16,17]. Sukhorukov's research group constructed multilayer films of nucleic acids and polycations by consecutive adsorption of anionic and cationic polyelectrolytes [18]. Lavalle studied the growth of polyelectrolyte multilayer film using in situ AFM with the alternate polyelectrolytes (i.e., polystyrene sulfonate (PSS) and polyallylamine hydrochloride (PAH)) [19]. Other authors have measured the surface morphology and thickness of polyelectrolyte multilayers by liquid cell AFM [20–23]. In addition, Petric et al. measured the thickness of polyelectrolyte multilayers using spectroscopy ellipsometry, atomic force microscopy (AFM), and transmission electron microscopy to make a comparative study [24]. X-ray absorption spectroscopy and X-ray fluorescence spectrometry have been used for the study of polyelectrolyte multilayers, as well [25,26]. Dynamic contact angle method was used to measure ultrathin organic multilayer films using different polyelectrolyte systems [27]. Polyelectrolytes multilayers have been used for many purposes, and one of the most important has been as adhesion modifiers [28].

Recent research works have suggested the use of PEL multilayers as a modifier of physical properties in radio-frequency (Rf) technology. In these systems, the PEL is expected to promote a fine-tuning of these devices because of the buffer frequency ability of the substrate by over layers. In the present work, we propose a monitoring of PEL multilayers deposition on $Ba_{0.5}Sr_{0}.{}_{5}TiO_3$ (BSTO) by surface analysis techniques such as X-ray photoelectron spectroscopy (XPS), specular reflectance FT–IR, and AFM. In a future paper, the influence of these over layers on Rf properties will be addressed. To our knowledge, this is one of the first works that monitors the sequential deposition of the polyelectrolytes by AFM. Also, we could not find other any other report which uses surface analysis techniques to choose the appropriate quantity of polymer overlayers for phase shifter applications. The results of the experiment qualitatively revealed that some PEL bilayers are necessary to reduce pinholes for future Rf technology applications.

2. Experimental

2.1. Materials

The poly(vinylsulfonic acid) (PVS) (25% w/w in water), poly(styrenesulfonate) sodium salt (PSS) (20% w/w in water) and poly(allylamine) hydrochloride (PAH) were supplied by Aldrich; 11-mercaptoundecylamine (MUA) by Dojingo (see Fig. 1). The bariumstrontiumtitanate $Ba_{0.5}Sr_{0.5}TiO_3$ (BSTO 50:50) thin films on $LaAlCO_3$ substrate were obtained from Neocera (commercial samples). The water used in our experiments was previously distilled and pumped through a nanopure system (Barnstead) to give 18 MΩ cm water.

For surface modification, pieces of BSTO thin films were sonicated during 5 min in ethanol, then 5 min in acetone to remove any organic residue. The pieces were dried under nitrogen flux. Once the pieces were clean, they were introduced

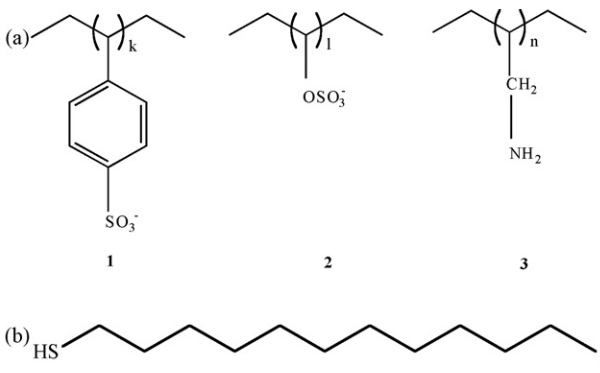

Fig. 1. (a) Molecular structures of polyelectrolytes and (b) the polyelectrolyte linker 11-mercaptoundecanamine (MUA) to attach to barium strontium titanate ($Ba_{0.5}Sr_{0.5}TiO_3$) (BSTO). (a) (1) poly(styrenesulfonate) sodium salt (PSS) (20% w/w in water), (2), poly(vinylsulfonic acid) (PVS), and (3) poly(allylamine) hydrochloride (PAH).