Available online at www.sciencedirect.com
ScienceDirect
Thin Solid Films 515 (2007) 4624–4628
www.elsevier.com/locate/tsf

Preparation and characterization of ultra-thin sol–gel films

Leora Shapiro [a], Sharon Marx [b], Daniel Mandler [a,*]

[a] Department of Inorganic and Analytical Chemistry, The Hebrew University, Jerusalem, 91904, Israel
[b] Department of Physical Chemistry, Israel Institute for Biological Research, Ness Ziona, 74100, Israel

Received 6 June 2006; received in revised form 1 November 2006; accepted 25 November 2006
Available online 24 January 2007

Abstract

The formation and characterization of nanometer thick sol–gel films are reported. The films were prepared by spin-coating of a diluted solution of a silane precursor on a number of different substrates. The effect of dilution, rotation speed and nature of substrate on the thickness and homogeneity of the films was examined. Characterization of the films was carried out by profilometry, reflectance spectroscopy, atomic force microscopy, adhesion test and electrochemistry. We find that the dilution factor has a pronounced effect on the film thickness. Moreover, the time of dilution, namely, whether dilution was carried out before or after a period of hydrolysis, has a noticeable effect on the thickness as well as on the permeability of embedded species.

Keywords: Sol–gel; Silane; Ultra-thin films; Electrochemistry

1. Introduction

The preparation of oxide thin films on different solid supports has been studied in past years, as part of the propensity to miniaturize the dimensions of various systems to the meso-scale [1–3]. Such films will be beneficial in different industries and fields of research such as sensing, corrosion inhibition, tribology and catalysis [4–6]. As more opportunities become available for implementation of ultra-thin films, there is a growing need to develop reproducible methods for producing nanometric-thick films as well as to analyze the physical and chemical qualities of these coatings. The nanometric dimension can be advantageous due to better control of chemical and physical processes across the films.

The sol–gel process is a convenient and inexpensive technique for the production of oxide films of a variety of metals [7–9]. Even though this process has been well known for decades, interest in novel methods for application of this technology has increased significantly in the last twenty years [10–14]. The most common techniques for preparing sol–gel films involve primarily spin-coating [15–19], dip-coating [20–25], spraying [26,27] and electrodeposition [28]. In these methods, solutions containing metal alkoxides, pre-hydrolyzed monomers, or colloidal metal hydroxides are used as precursors that undergo further condensation to form a glassy substance at room temperature after a drying process. However, there is a crucial problem regarding this research, considering that the formation of sol–gels on a solid support creates in many cases uneven, films with defects [29,30]. Many of these defects, e.g., cracks, are due to strong capillary forces that exert on the matrix in the course of the drying process. Moreover, most of the techniques mentioned above usually yield films with a thickness of submicron to a few microns, which do not suit many applications, where coatings of a few nanometers are required. In general, the analysis of thin sol–gel films is not trivial as they exhibit inhomogeneities. Evidently, advancing the ability to form homogeneous and smooth sol–gel films in the nanometer thickness is not only of academic interest but also of real demand in many areas where sol–gel films could be applied and beneficial.

In our research, we have developed a procedure for preparing silica sol–gel films with thickness of nanometer scale, which is based on spin-coating of diluted sol–gel solutions on different substrates. The main goal of this report is to inspect the dependence of the thickness of the films on the concentration of the silica monomers, and to examine the roughness and

---

* Corresponding author. Tel.: +972 2 6585831; fax: +972 2 6585319.
E-mail address: mandler@vms.huji.ac.il (D. Mandler).

0040-6090/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2006.11.117

homogeneity qualities of the films. Moreover, we studied the effect of different substrates on the quality of the deposited films by means of atomic force microscopy and profilometry. Finally, electrochemistry was used for studying the diffusion of electroactive species across the films.

2. Experimental details

2.1. Instrumentation

Electrochemical experiments were performed using a μ-Autolab potentiostat (EcoChemie, Utrecht, Netherlands). Sol–gel films were deposited using a P-6000 spin-coater (Integrated Technologies Inc., MA). The thickness of the deposited films was measured with either a profilometer (P-15, KLA-Tencor Co.) or F-20 reflectance spectroscopy instrument (Filmetrics). Atomic force microscope (AFM) images were acquired with NanoScopeII (Digital Instruments, CA), operated in the contact mode using a cantilever with a spring constant of 0.58 N m^{-1}. Digital images were taken using an Olympus BX60 optical microscope.

2.2. Chemicals

Indium tin oxide (ITO) was purchased from Delta technologies Ltd. (Stillwater MN, resistance 20–25 Ω). n-Si(111) wafers were generously given by Wacker Siltronic (AG, Germany). Hydrofluoric acid (electronic grade) was purchased from Baker. Thin gold films (2000 Å) were deposited on glass on which a thin layer (ca. 5 nm) of chromium was first deposited. High purity deionized water (EasyPure UV, Barnstead) was used for preparing all solutions. Tetramethyl orthosilicate (TMOS, 99+% purity) as well as all other chemicals were purchased from Aldrich.

2.3. Procedures

2.3.1. Surface pretreatment

The different substrates included ITO slides (7 × 15 mm), silicon wafers either with a native oxide layer, or H-terminated (after dipping in hydrofluoric acid for one minute) and thin gold films (2000 Å) deposited on glass. All of the gold films were cleaned with acetone and ethanol, and then flame annealed. Further treatment of the gold substrates involved either dipping in nitric acid (22%), 2-mercaptoethanol (10 mM in ethanol) or left unhandled.

2.3.2. Sol preparation

Precursor solution was prepared using TMOS, methanol, deionized water and HCl. The TMOS and methanol mixture was first prepared, and then HCl (diluted to 0.1 M with water) was added. A clear solution was obtained with the molar ratio of 5.1:1:13.6 (methanol:TMOS:HCl) after sonication for 5–15 min. At that point, the solution was diluted 2, 10 and 50 fold either before or after one day of hydrolysis at room temperature. 25 μL of the solutions were then pipetted onto the different substrates and spin-coated at 2000, 4000 or 6000 rpm for 1 min.

2.3.3. Drying details and physical characterization

After spin-coating, the sol–gel films were dried at room temperature for one day preceding characterization. The thickness of the deposited films was determined by either scanning across a notch in the film (made with a wooden stick after drying) with a profilometer, or using an F-20 reflectance spectroscopy instrument. The adhesion of the films was examined using a D 3359–02 standard of the American Society for Testing and Materials Standards, test method B [31]. Cyclic voltammetry (CV) was carried out on ITO in a conventional three-electrode cell, using a Ag/AgCl (KCl sat') electrode as the reference electrode. All potentials are quoted vs. this reference electrode. The counter electrode used was a Pt wire. After drying the sol–gel films on the ITO slides, they were examined using 1 mM $Ru(NH_3)_6Cl_3$, $K_3Fe(CN)_6$ and catechol as redox probes in 0.1 M K_2SO_4 solutions. More electrochemical measurements were performed in 0.1 M K_2SO_4 solution with sol–gel, in which ferrocenemonocarboxylic acid (FMA) was embedded in the course of film preparation.

3. Results and discussion

Developing the capability of coating conducting and semiconducting substrates with ultra-thin sol–gel films (of the order of tens of nanometers) is of specific importance in designing electrochemically-sensing devices [32]. Such films will allow fast diffusion of the analytes across the sol–gel matrix [33–37], and at the same time will be sufficiently thick to accommodate selective sites for specific recognition. Since spin-coating is the most common method for preparing thin films on flat surfaces, we have focused on this coating approach. Sol–gel films are deposited from a partially hydrolyzed solution consisting of oligomers or even small colloids of the precursor, such as TMOS. Thus, we anticipated that the film thickness could be controlled by varying the concentration of the oligomers or colloids.

Fig. 1 shows the dependence of the film thickness on the spin-coating rate and the dilution of the precursor solution on a

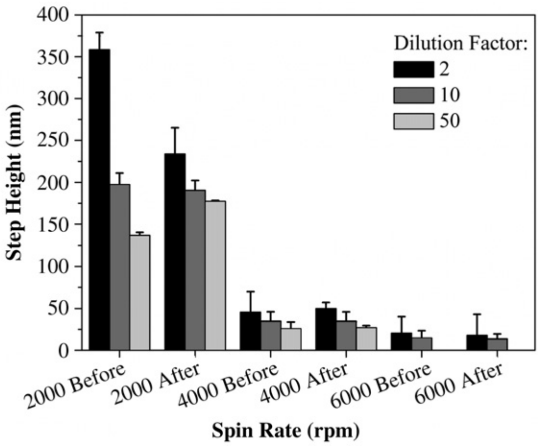

Fig. 1. Dependence of the film thickness of TMOS on the spin-coating rate and dilution factor. Films were cast on native n-Si(111). Thickness measured by both profilometry and reflectance spectroscopy.