Electrochemically Induced Sol–Gel Deposition of Zirconia Thin Films

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Abstract: A novel electrochemical method for deposition of ZrO₂ thin films is described. The films, 50–600 nm thick, were obtained by applying moderate positive or negative potentials (+2.5 V to −1.5 V versus SHE) on conducting surfaces immersed in a 2-propanol solution of zirconium tetra-n-propoxide [Zr(OPr)₄] in the presence of minute quantities of water (water/monomer molar ratios in the range of 10⁻⁵ to 10⁻³), which was the limiting reagent. Oxidative electrochemical formation of solvated H⁺ and reductive formation of OH⁻ catalyze the hydrolysis and condensation of the metal alkoxide precursor. The magnitude of the applied potential and its duration provide a convenient way of controlling the film thickness. The films consist of an amorphous phase, as revealed by XRD measurements. The effects of different parameters, such as the applied potential and its duration, the amount of added water and the current–time characteristics, were studied. A mechanism for the electrodeposition of the zirconia films which is in accordance with our findings is proposed.

Keywords: electrochemistry • sol–gel processes • thin films • zirconia

Introduction

Thin-film deposition of metal oxides and hydroxides by electrochemical methods is a rapidly developing field.[1–16] In a review on this area, Cryston and Lee[2] suggested that electrochemical methods offer simple and inexpensive alternatives to currently used techniques. These methods of deposition can be categorized into three main groups: electrophoretic deposition,[17–24] deposition on electrochemical formation of less soluble metallic species and deposition by electrochemically altering the pH of the solution near the electrode surface.[1,3,4,6,7,10,11,13–16] Recently, we employed the last-named approach[25] in a novel electrochemical sol–gel process in which thin films of methylated silica are deposited on conducting surfaces by application of moderate potentials (in the range of −0.5 V to −1.5 V versus Ag/AgCl). We suggested that the variation of the pH near a conductive surface in the presence of the (hydrolyzed) alkoxysilane effected its polymerization. While electrochemical induction of pH changes is known in the context of the formation of insoluble oxides and hydroxides and their subsequent precipitation,[1,3,4,6,7,10,11,13–16] its use for locally effecting the polymerization of sol–gel monomers and increasing their rate of polymerization is, to the best of our knowledge, unknown. Here we extend our methodology[25] to the important family of zirconia coatings, and report on the electrochemically induced formation of these films and convenient thickness control in the range of several hundreds of nanometers.

As ZrO₂ films have already been prepared electrochemically,[4,13–15,26] we highlight the special features of the electrochemical sol–gel approach reported here. First, whereas precipitation of ZrO₂ has been effected by electrogeneration of a base at negative potentials, the electrochemical sol–gel method makes it possible to use both positive potentials (leading to acid-catalyzed polymerization) and negative potentials (leading to base-catalyzed polymerization). Second, the precursor is [Zr(OPr)₄] instead of the commonly used Zr salts.[3,13–15] Third, water is used as a limiting reagent in an alcoholic medium (in contrast to the standard use of water as both solvent and reagent[4,13–15]). Fourth, a polycondensation process rather than precipitation[4,7,10,13–15] leads to film formation. Fifth, the films are exceptionally smooth,[27] down to a roughness of 0.7 nm for a 5×5 μm area. The convenient control of film thickness by changing the applied potential or the time for which it is applied is a key feature of this method.

Results and Discussion

Zirconia-based thin films were electrodeposited from a solution of zirconium tetra-n-propoxide [Zr(OPr)₄] in 0.1 M LiClO₄ in 2-propanol, to which small and controlled amounts of water were added (solution A). Deposition was...