



Shadow-casted ultrathin surface coatings of titanium and titanium/silicon oxide sol particles via ultrasound-assisted deposition



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ABSTRACT

Ultrasound-assisted deposition (USAD) of sol nanoparticles enables the formation of uniform and inherently stable thin films. However, the technique still suffers in coating hard substrates and the use of fast-reacting sol–gel precursors still remains challenging. Here, we report on the deposition of ultrathin titanium and titanium/silicon hybrid oxide coatings using hydroxylated silicon wafers as a model hard substrate. We use acetic acid as the catalyst which also suppresses the reactivity of titanium tetraisopropoxide while increasing the reactivity of tetraethyl orthosilicate through chemical modifications. Taking the advantage of this peculiar behavior, we successfully prepared titanium and titanium/silicon hybrid oxide coatings by USAD. Varying the amount of acetic acid in the reaction media, we managed to modulate thickness and surface roughness of the coatings in nanoscale. Field-emission scanning electron microscopy and atomic force microscopy studies showed the formation of conformal coatings having nanoroughness. Quantitative chemical state maps obtained by x-ray photoelectron spectroscopy (XPS) suggested the formation of ultrathin (<10 nm) coatings and thickness measurements by rotating analyzer ellipsometry supported this observation. For the first time, XPS chemical maps revealed the transport effect of ultrasonic waves since coatings were directly cast on rectangular substrates as circular shadows of the horn with clear thickness gradient from the center to the edges. In addition to the progress made in coating hard substrates, employing fast-reacting precursors and achieving hybrid coatings; this report provides the first visual evidence on previously suggested “acceleration and smashing” mechanism as the main driving force of USAD.

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1. Introduction

Metal oxide surface coatings find use in several applications such as corrosion protection, catalysis, and solar cells. One practical route for the preparation of metal oxide surfaces is the sol–gel coating technique. In sol–gel coating process, reactive sol particles (sols) applied on the surfaces undergo gelation and yield metal oxide networks [1,2]. Various methods such as dip-, spin-, spray-, and brush-coating are in wide use for the preparation of sol-based coatings. Each of these methods has certain advantages, but poor interfacial adhesion, cracking, and peeling are their common shortcomings [3,4]. Ultrasound-assisted deposition (USAD) of sols is promising to overcome listed problems. Since the coating

process already takes place under a chemically harsh and physically agitated environment, USAD of sols realizes inherently stable metal oxide coatings.

When high-intensity ultrasound is applied to a liquid medium, ultrasonic energy converts to mechanical and thermal energy through the cavitation process. Ultrasonic cavitation process initiates with density oscillations in the liquid medium due to the oscillating pressure of acoustic waves [5–7]. Dissolved gas molecules and the vapor of the liquid medium itself trigger the nucleation of bubbles (cavities) in multiple locations and nucleated bubbles grow with the oscillating field until reaching an unstable size [7,8]. Unstable bubbles implisively collapse resulting in local and transient hot spots of high temperature (>5000 K) and pressure (>100 bar) [8–10]. In addition, collapsing events taking place near the solid surfaces trigger the formation of high-velocity liquid microjets (>300 m/s) that can accelerate dispersed particles [11–13]. Hot spot and microjet formation processes are considered to act as the fundamental driving forces of USAD.

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Previous studies showed USAD of various inorganic micro/nanoparticles including metal oxides on a wide range substrates such as silica spheres [14], titania particles [15], poly(methyl methacrylate) chips/spheres [16], bare [17,18] and Parylene-modified [19] glass slides, stainless steel plates [20], cellulosic papers [21–23], cotton fabrics [24], polymeric tubings [25], and polyester fibers [26]. Those studies collectively established USAD technique as a promising way of surface modification. Nevertheless, the coating processes mainly relied on the physical embedding of nonreactive particles rather than the formation of chemical bonds between the particles and the substrates. In accordance, the resulting coatings were often patched lacking conformity and stability. The use of *in situ* synthesized and surfactant-stabilized titanium oxide sols in USAD by Perkas et al. made a progress in addressing these problems [27]. However, the substrates were glass slides modified with Parylene, a soft polymer with high chemical inertness [28,29]. Thus, despite the use of reactive sol particles, no chemical bonds expectedly formed between the substrates and the coatings.

It is challenging to obtain conformal and homogeneous coatings on hard substrates (e.g. metals and silicon) employing USAD process. But, sol–gel chemistry enables the preparation of such coatings on activated hard substrates through interfacial chemical bondings. In our previous studies [30,31], we have demonstrated the preparation of homogeneous and well-adhered silicon oxide sol(–gel) coatings on metal substrates using USAD. Formation of chemical bonds between the hydroxylated surface and the silicon oxide sols through condensation reactions allowed us to grow dense, conformal and homogeneous coatings of 80–250 nm thickness. We achieved to deposit strongly bound multiple layers of silicon oxide nanosols with sizes increasing from the substrate interface towards the solution interface as the particles keep growing during USAD.

In this study, we confront a more challenging case; *i.e.* USAD of a more reactive precursor, titanium tetraisopropoxide (TTIP), on a model hard substrate, silicon wafer. To correlate the particle sizes with the deposition process, we studied the growth kinetics of sols using laser light scattering (LLS). Acetone/ethanol mixture of 80/20 v/v% was chosen as the solvent since this ratio delays gelation in this system as shown in our previous study [32]. In order to produce titanium/silicon oxide sol coatings effectively, we used acetic acid (HAc) as the catalyst which also suppresses the reactivity of titanium tetraisopropoxide while increasing the reactivity of tetraethyl orthosilicate [33–35]. USAD of titanium and titanium/silicon oxide sols was performed on hydroxylated silicon wafers by varying the amount the HAc in reaction media. Resulting nanocoatings were analyzed by field-emission scanning electron microscopy (FESEM), atomic force microscopy (AFM), x-ray photoelectron spectroscopy (XPS) and rotating analyzer ellipsometry (RAE). The present study extends our previous efforts on the USAD of silicon oxide films to the preparation of ultrathin titanium and titanium/silicon hybrid oxide coatings. Importantly, showing visual evidence of particle “acceleration and smashing”, our results also provide a fundamental insight regarding the mechanism of USAD.

2. Experimental

2.1. Chemicals

Titanium tetraisopropoxide (TTIP, >97%) and tetraethyl orthosilicate (TEOS, ~98%) were obtained from Alfa Aesar. Acetone was procured from VWR International (BDH Prolabo). Absolute ethanol, acetic acid (HAc), sulfuric acid, and hydrogen peroxide

(30%) were purchased from Merck Chemicals. All chemicals were used as received without further purification and were handled carefully to prevent water vapor contamination. The origin of silicon wafers was University Wafers. Deionized type I (~18.2 MΩ cm) H₂O was produced using Milli-Q filtration system (Millipore Co.) and was used in all reactions and cleaning steps.

2.2. Sol–gel synthesis and growth monitoring

In our previous study [30], we have observed that one of the crucial parameters in USAD process is the selection of solvent medium. We have found that acetone is a better medium for USAD of silicon oxide nanosols compared to water or ethanol. However, titanium oxide precursor we use, titanium tetraisopropoxide (TTIP), precipitates out fast when mixed with acetone. Recently, we overcame this obstacle by introducing 20% ethanol in acetone as the cosolvent which delays the gelation significantly [32]. Thus, here in this study, we employed 80/20 v/v% mixture of acetone/ethanol as the solvent media and paid attention to the mixing order of reactants. We prepared two mixtures as Mix-A: acetone (20 mL) + H₂O (750 μL) and Mix-B: ethanol (5 mL) + HAc (100–400 μL) + precursor(s) (TTIP: 75 μL or TTIP: 75 μL plus TEOS: 760 μL) (refer to Table 1 for amounts). Precautions were taken with the timing of the additions to obtain reproducible results. Just after the addition of HAc on ethanol, we added TTIP and waited for ~60 s before mixing already prepared Mix-A and Mix-B. In hybrid sol production, we added TEOS on Mix-A ~30 s after introducing TTIP.

Before focusing on the effect of HAc on USAD, we analyzed sol growth behavior of each formulation using laser light scattering (LLS) until reaching the gelation point. All LLS measurements were performed at 25 °C on a Zetasizer Nano-S (Malvern Instruments Ltd.) by regular sampling. Further details of the measurement routine can be found elsewhere [32]. We analyzed scattering data in both dynamic and static modes. Dynamic light scattering (DLS) analysis based on the intensity fluctuations of the scattered light signal provided solvodynamic diameter (SDD) values of the particles. Static light scattering (SLS) analysis provided derived count rate (DCR) values, *i.e.* a measure of the concentration of particles [36–38]. The DCR values, which represent the actual amount of scattered light, were obtained thanks to the attenuation of scattered light signal down to the linear response regime of the detector using a combination of built-in neutral density filters. Using SDD and DCR values, within the Rayleigh approximation [39,40], we evaluated the relative particle (number) density of different formulations as DCR/SDD⁶ [32].

2.3. Substrate preparation

Silicon wafers were cut into ca. 25 × 25 mm² pieces and were treated in a home-made cleaner equipped with an ultraviolet lamp (254 nm, 9 W) and ozone generator (3 g/h) for ~5 min. Ultraviolet-ozone cleaning was followed by ultrasonic cleaning in acetone and water each for 15 min using an ultrasonic bath (VWR International Ltd.). Treated wafers were rapidly exposed to freshly prepared piranha solution (*i.e.* 70 v% sulfuric acid + 30 v% hydrogen peroxide) in its own temperature. (CAUTION: Piranha solution is extremely energetic and potentially explosive. It must be handled very cautiously and should be neutralized by applying appropriate procedures right after use.) After piranha treatment, substrates were rinsed with an excessive amount of H₂O and dried under nitrogen gas flow thoroughly. Substrates were always treated just before the deposition experiments to ensure surface cleaning and activation.

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