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Influence of molecular packing on the corrosion inhibition properties of self-assembled octadecyltrichlorosilane monolayers on silicon

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ABSTRACT

The corrosion inhibition properties of octadecyltrichlorosilane (OTS) self-assembled monolayers (SAMs) on silicon were investigated. Atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), contact angle (CA), and lateral force microscopy (LFM) were used to determine the OTS film formation time, packing density, and corrosion protection efficacy. The OTS films reached adsorption saturation after 15 s; however, the molecular density continued to increase up to 24 h. The films were exposed to the strong oxidant $KMnO_4$, and while 15-s film samples exhibited corrosion after a 1 min exposure, samples with films grown for 24 h were protected even after 24 h.

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1. Introduction

Self-assembled monolayers (SAMs) are of great interest for use in applications such as wetting [1,2], lubrication [2], chemical sensing [3], adhesion enhancement [4,5], corrosion resistant coatings [2,6], and electro-optic engineering [2]. Preparation of SAM films is simple and direct, and the resulting highly-ordered molecular films can be tailored to exhibit desirable chemical and physical properties [2]. For example, the lubrication properties of SAM films have been investigated for microelectromechanical systems (MEMS) and nanoelectromechanical systems (NEMS) to reduce nanoscale surface friction and increase device lifetimes [7,8]. Film packing density can be indirectly controlled by changing the SAM molecular chain lengths [9,10], anchoring group [10,11], underlying substrate [10], phase [10], or the chemical composition of the alkyl chains [12,13]. Molecular packing density of SAMs is a key factor in controlling the tribological properties of MEMS/NEMS device surfaces.

A self-assembled monolayer films is formed spontaneously by chemisorption and self-organization of an active surfactant onto a solid surface. The properties of the formed film are highly dependent on the surfactant chemistry and structure, as well as the substrate surface and preparation conditions. The common use of alkylsilanes, especially octadecyltrichlorosilane (OTS) on SiO_2, is indicative of the important role SAMs now play in silicon based device technology, specifically MEMS and NEMS [1].

The effectiveness of organosilane SAMs on various metals, *e.g.* aluminum, magnesium, steel, and their eco-friendly characteristics, have also been investigated [14]. The SAM films acted as an effective corrosion shield to inhibit degradation of the surface, and could be removed, if necessary, prior to further processing [15–17]. Fan et al. [18] studied the influence of molecular structure on the corrosive suppression properties of SAMs on brass, and suggested that the thiolate bond provided the strong anchorage that resulted in protective action. Further, numerous studies have reported that densely packed SAMs composed of silane derivate, sulfur-containing compounds, can be effective corrosion inhibitors for copper [18–22].

The carbon chain length of a given SAM molecule strongly effects the molecular organization and frictional properties of the surfactant film. For example, long alkyl chains exhibit close-packing and ultra-hydrophobic properties that may improve corrosion protection. Sharadha et al. [23] demonstrated that SAM films on silicon that were formed from silane chains with 12–18 carbon atoms exhibited the highest molecular ordering and the lowest friction coefficients. Thus, SAM precursor molecular structure and organization, or packing, have a significant influence on the corrosion and oxidation inhibition properties of the resulting films.

$KMnO_4$ is a strong oxidizing agent that may be used for systematic oxidation and corrosion studies. Favaro et al. [24], for example, tested the corrosion resistance of various polymers to $KMnO_4$, and reported on the surface modifications that occurred due to oxidation. In this work, we investigated the correlation between the molecular packing density of an OTS SAM film on silicon and its corrosion inhibition properties when exposed to $KMnO_4$. Atomic force microscopy (AFM), contact angle (CA), X-ray photoelectron

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spectroscopy (XPS), and lateral force microscopy (LFM) techniques were used to characterize the changes in surface topography, surface energy, and to study the nano-corrosion surface process. A correlation between SAM film packing density and corrosion resistance was observed and is discussed.

2. Experimental

2.1. Materials

Octadecyltrichlorosilane [CH_3 $(CH_2)_{17}SiCl_3$, OTS] (Gelest Inc., 95%) and toluene (TEDIA company, Inc., Anhydrosolv, 99.8%) were used without further purification to prepare OTS solutions. The reaction substrate was double-sided polished silicon (100) wafer (TSR Technology Inc.; P-type/boron dopant), with a resistivity of 1–10 Ω cm. The wafer was cut into $1.5 \times 1.5\ cm^2$ and $0.8 \times 0.9\ cm^2$ sections for AFM and XPS measurements, respectively. $KMnO_4$ was purchased from Sigma–Aldrich, ACS, ⩾99.0%, the cleaning solvents anhydride ethanol (GC, 99.5%) and acetone (ACS) from ECHO Chemical Co. Ltd., and the detergent solution was purchased from Merck (Germany). Millipore purified water (Milli-Q purification system, resistance is 18.2 MΩ cm) was used throughout.

2.2. Sample preparation

Silicon (100) substrates were first cleaned using a neutral cleaning agent followed by acetone, then rinsed rigorously with water and dried under a stream of nitrogen gas. All silicon substrates were plasma cleaned (Harrick Scientific Products, Inc., model PDC-32G) for 2 min using dry air as the reactive gas in order to increase the OH concentration at the surface [25,26]. The silicon wafer samples were then immersed (dip coating method) into the OTS solution (5 mM OTS dissolved in toluene) for various reaction times (1, 3, 5, 15 s and 24 h), then rinsed sequentially with toluene, ethanol and pure water to remove the unbound SAM, and finally dried under a stream of dry nitrogen.

For corrosion experiments, bare silicon and OTS-modified silicon wafer samples were immersed in a fully saturated $KMnO_4$ solution for durations up to 24 h. $KMnO_4$ solution was prepared by dissolving 10 g $KMnO_4$ powder in 20 mL water (50 g/100 cm^3 at 30 °C and 1 atm), which was more concentrated than saturated $KMnO_4$ solution (9.03 g/100 cm^3 at 29.8 °C and 1 atm) [27]. Following timed exposure, the samples were rinsed with water and dried under nitrogen gas before further characterization. All glassware was cleaned using silicon wafer cleaning procedures and then baked in an oven at 110 °C for 24 h to remove excess moisture (to reduce self-agglomeration of OTS).

2.3. Characterization

Topographical and lateral force images of all the OTS/Si samples were obtained using an AFM (MFP-3D™, Asylum Research, Santa Barbara, CA). AFM measurements were performed using an AC240-TS cantilever (Olympus) with a measured spring constant of $1.42 \pm 0.2\ N\ m^{-1}$, which was determined using the thermal method [28,29]. All images were acquired using a scan rate of 1 Hz, and an image resolution of 512 × 512 pixels. AC (tapping) mode was used for topographical imaging and contact mode was used for lateral force images and measurements.

The chemical composition of the OTS modified surfaces before and after oxidation with $KMnO_4$ was determined using a JEOL XPS (JPS-9010 MX) instrument at 2×10^{-9} torr chamber pressure with a Mg Kα (1253.6 eV) X-ray source.

Water contact angle measurements on bare silicon wafer and OTS modified silicon wafers were performed on a PGX model instrument (Belgium, Deerlijk) at room temperature. The water volume of each droplet was 1.5 μL and the reported data were obtained after averaging 10 measurements.

3. Results and discussion

3.1. Effect of OTS concentrations on molecular packing

We used a Langmuir–Blodgett trough (NIMA-312D) to characterize OTS concentration effects on molecular packing according to the method described in [7]. The LB surface pressure–area curves at OTS concentrations of 0.5, 1, 2, and 5 mM in toluene solvent are shown in Fig. 1. At lower concentrations (0.5 and 1 mM), no obvious collapse point was observed in isotherm pressure–area curves, indicating that a Langmuir monolayer did not form. However, significant collapse points in isotherm pressure–area curves at OTS concentrations of 2 and 5 mM were observed at 32 and 45 cm^2, with corresponding surface pressures of 41 and 47 mN/m, respectively. The large surface pressure at the collapse point indicates strong intermolecular interactions between OTS and the solvent. Thus, OTS molecular packing density and intermolecular interactions increased progressively with increasing OTS concentration [7].

3.2. Formation and characteristics of OTS films

Topographic AFM images and height measurements of a clean Si surface and a series of OTS/Si samples prepared at different film growth times (1, 3, 15 s and 24 h) are shown in Fig. 2. Cross-sectional line scans from each data set are shown below their corresponding image. The bare-silicon substrate (Fig. 2a) was included as a benchmark for comparison to the OTS/Si samples and was very flat with a measured root mean square (RMS) roughness of 57.9 pm over the entire $5 \times 5\ \mu m^2$ scan area. Fig. 2b was acquired after a 1-s immersion of the Si sample into the OTS solution. The bright areas (islands) represent the growing OTS monolayer film, and the dark regions between islands correspond to the silicon substrate. The height of OTS islands from the 1-s wafer sample was about 2.5 ± 0.5 nm (Fig. 2b), and the RMS roughness was 620.3 pm. These values are consistent with previous literature results [30,31]. Since the length of an OTS molecule is ~2.6 nm [31], our results suggest that the island consists of a standing

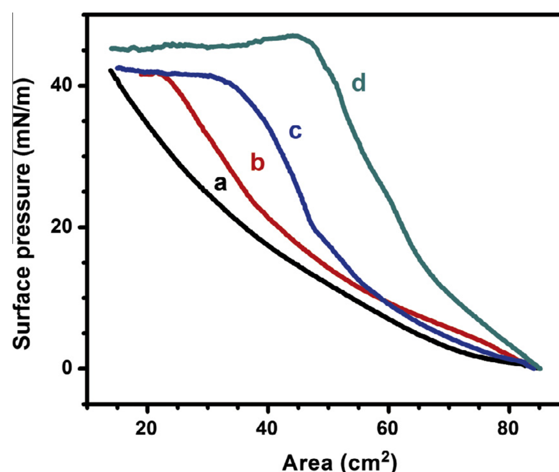

Fig. 1. Surface pressure vs. area isotherms of OTS films prepared with toluene at OTS concentrations of (a) 0.5, (b) 1, (c) 2, and (d) 5 mM.

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