

Vapor-phase self-assembled monolayers of aminosilane on plasma-activated silicon substrates

S. Fiorilli^{a,b}, P. Rivolo^c, E. Descrovi^c, C. Ricciardi^{b,c}, L. Pasquardini^{b,d}, L. Lunelli^d, L. Vanzetti^d,
C. Pederzoli^d, B. Onida^{a,e}, E. Garrone^{a,e,*}

^a Dipartimento di Scienza dei Materiali ed Ingegneria Chimica, Politecnico di Torino, Corso Duca degli Abruzzi 24, I-10129 Torino, Italy

^b LaTEMAR, Centre of Excellence funded by MIUR (Italian Ministry for Education, University and Research), Italy

^c Dipartimento di Fisica, Politecnico di Torino, Corso Duca degli Abruzzi 24, I-10129 Torino, Italy

^d Fondazione Bruno Kessler-IRST, Center for Scientific and Technological Research, Sommarive Str. 18, 38050 Povo (Trento), Italy

^e INSTM, Unità di Ricerca Torino Politecnico, Italy

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Abstract

Aminosilane self-assembled monolayers on silicon substrates have been prepared via a gas-phase procedure based on the consecutive reactions of the aminosilane precursor and water vapor. X-ray photoelectron spectroscopy, atomic force microscopy, and contact angle measurements have been used to characterize the aminosilane layers. For comparison, substrates modified with aminosilane through a liquid-phase procedure have been prepared and characterized by means of the same techniques. The vapor-based procedure was found to yield more uniform layers characterized by fewer and smaller aggregates as compared with liquid-treated substrates. Grazing angle reflection Fourier transform infrared measurements were carried out on the vapor-treated substrates before and after water exposure to investigate the hydrolysis of the alkoxy groups and further reaction to form siloxane bonds. The surface density of amino groups, as estimated through a colorimetric method, is very similar for vapor- and liquid-treated substrates, suggesting a similar reactivity and accessibility of the functional groups on the surface.

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1. Introduction

Organosilane self-assembled monolayers (SAMs) have been widely used to tailor the surface properties (both physical and chemical) of glass, quartz, oxidized Si wafers, and silica particles [1–4]. Silane-modified substrates have found important applications in the fields of adhesion [5] and metal corrosion protection [6], as supports for inorganic catalysts, and for modification of electrodes [1–4]. Silanized surfaces may also act as building foundations for self-assembly of different types of molecules including ionic polymers [7–9], chromophores [10–12], fullerenes [13], and even inorganic colloidal particles [14]. This functionalization approach has been extensively

applied also for the immobilization of molecules of biological interest, such as enzymes, immunosensors, and DNA microarrays [15–18], to develop biosensing systems widely used in the fields of medical care and drug manufacturing.

Self-assembly of organosilane molecules, with general formula $(X)_3\text{Si}-Y$, where X is an alkoxy ($-\text{O}-\text{CH}_3$ or $\text{O}-\text{CH}_2-\text{CH}_3$) or halogen ($-\text{Cl}$) ligand, occurs via the reaction of the X groups with hydroxyl ($-\text{OH}$) groups at substrate surfaces, to produce the $\text{Si}-\text{O}-\text{Si}$ linkage accompanied by ROH or HCl as by-product. The formation of organosilane monolayers in the liquid phase has been widely studied [3], although the dependence on temperature, solvents, and silane concentration is still not completely clear. Most commonly, the silanization reaction is carried out in hydrocarbon solvents such as toluene, bicyclohexyl, hexadecane, etc. [3,19]. The major problem associated with the liquid-phase procedure arises from the ability of the precursor to copolymerize in the presence of traces of water,

* Corresponding author. Fax: +39 011 5644699.

E-mail address: edoardo.garrone@polito.it (E. Garrone).

so obtaining clumpy and disordered layers on substrate surfaces [20].

Control over polymerization is very difficult, even under a strict control of reagent purity and working in a controlled atmosphere. The low reproducibility and the high cost associated with liquid-based procedures represent significant limitations to the use of organosilane precursor. Lack of control over film quality is particularly a drawback when organosilane coatings are employed to tailor the surfaces of micron-sized devices, such as silicon-based microelectromechanical systems (MEMS). Indeed, silanization has been proposed as antistiction treatment of micromachine surfaces, where adhesion is one major factor limiting the widespread use and reliability of these systems [21–23]: when properly prepared, these monolayers improve greatly the adhesion properties of microstructures. Because of the formation of large and nonremovable aggregates, which may interfere with operation of the device, a liquid-based process is not a satisfactory method to apply silane coatings.

Another emerging application of MEMS is the development of microcantilevers-based biosensors, which can transduce a biochemical signal into a mechanical motion with extremely high sensitivity [24,25]. Detection of biological targets requires the immobilization of probe species on microcantilever surfaces, properly modified with reactive groups. Because both homogeneity and reactivity of functional layers strongly affect specificity and sensitivity of biosensors, a strict control on the functionalization process is essential also in this case.

To overcome the limitations of liquid-phase processes, deposition from vapor phase has been proposed because the lower molecular density in the vapor phase should decrease the extent of self-polymerization of the silane precursor. Gas-phase silanization has been attempted in vacuum [26] by distillation of the silane precursor: this approach, however, is rather time consuming and requires sophisticated equipment. Heating of the environment to enhance silane evaporation [27] also promotes polymerization of the precursor before reaction with substrate surfaces and consequently yields nonreproducible monolayers. Compared to these procedures, the silanization method proposed by Sugimura et al. [28] is more viable: the silicon substrates are sealed in a dry N₂ atmosphere under atmospheric pressure conditions and exposed to the vapor of silane at a moderate temperature. Reproducible and smooth aminosilane layers on silicon oxide surfaces have been prepared through chemical vapor deposition by Song et al. [29], exposing the substrates to the vapors of a solution of silane in toluene at 100 °C.

In this study, a gas-phase procedure was used for deposition on silicon surfaces. In particular, a vacuum system equipped with a plasma source was employed for the deposition of a 3-aminopropyltriethoxysilane SAM on a silicon surface: the surface activation step, using the air plasma treatment prior to the monolayer deposition, is essential to clean any organic contamination and to ensure hydroxylation of the surface. This surface conditioning allows omission of the oxidation step on silicon wafer, before silylation reaction, thus representing a great savings in time and cost.

Aminosilane layers formed through a liquid-phase procedure on silicon substrates were also characterized for compar-

son. The choice of the aminosilane molecule as precursor is due to the wide use of this species to modify substrates in view of surface-bound biomolecules for biosystems development.

The quality of silane layers deposited via solution-based and vapor-based processes, was checked by means of atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), contact angle analysis, and reflection–absorption infrared spectroscopy (RAIRS). Quantitative determination of accessible and reactive amine groups was carried out on aminated substrates prepared by both wet and dry procedures.

2. Experimental

2.1. Materials

One hundred oriented p-type (40–100 Ω/cm) polished silicon wafers were provided by MEMC Electronic Materials Novara-Italy. 3-Aminopropyltriethoxysilane (APTES; anhydrous; 99%; Aldrich) and toluene (anhydrous; 99.8%; Aldrich) were used without any further purification. The sulfosuccinimidyl-4-[2-(4,4-dimethoxytrityl)]butyrate (sSDTB) reagent was from Apollo Scientific Ltd. (UK). Dimethylformamide (DMF) and perchloric acid 60% v/v were from Fluka (Switzerland). Sodium carbonate and bicarbonate powders for the related buffer solution were from Sigma.

2.2. Vapor-phase functionalization system

The apparatus consists of a glassware cylindrical horizontal vacuum chamber connected to a rotary pump (base pressure ~10⁻¹ Torr) and a delivery system composed of glass reservoirs (containing the reactants) connected by metering valves to a stainless steel line that admits reactant vapors into the reaction chamber. Both the delivery frame and the reservoirs are heated to avoid condensation of the reactants and contamination from residual vapor. A primary vacuum gauge and a type-K thermocouple positioned at the delivery line are used to monitor the process parameters. Semicylindrical parallel plate electrodes, external to the reaction chamber, allow the formation of an *in situ* radiofrequency (RF) plasma by the use of a radiofrequency (13.56-MHz) generator.

2.3. SAM preparation

2.3.1. Solution-phase procedure

A silicon oxide film on silicon wafer was grown by thermal oxidation at 1100 °C in an O₂ atmosphere for 3 h. Before oxidation, wafers were cleaned in buffered oxide etch and *piranha* solution (70% H₂SO₄:30% H₂O₂).

Before exposure to organosilanes, the SiO₂/Si substrates were cut into 1 × 1-cm² pieces, soaked in *piranha* solution for 15 min to remove organic contaminants, rinsed with doubly distilled water, and dried in a stream of nitrogen. Freshly cleaned substrates were then incubated with 1% (v/v) solution of APTES in toluene at 60 °C for 10 min. Silane-coated substrates were rinsed several times with toluene and then dried in a stream of nitrogen: these substrates are referred hereafter as SiO₂/Si_APTES-*wet*.

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