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Review

Wet chemical surface functionalization of oxide-free silicon

Peter Thissen, Oliver Seitz, Yves J. Chabal*

Department of Materials Science and Engineering, University of Texas at Dallas, 800 West Campbell Road, Richardson, TX 75080, USA

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ABSTRACT

Silicon is by far the most important semiconductor material in the microelectronic industry mostly due to the high quality of the Si/SiO₂ interface. Consequently, applications requiring chemical functionalization of Si substrates have focused on molecular grafting of SiO₂ surfaces. Unfortunately, there are practical problems affecting homogeneity and stability of many organic layers grafted on SiO₂, such as silanes and phosphonates, related to polymerization and hydrolysis of Si–O–Si and Si–O–P bonds. These issues have stimulated efforts in grafting functional molecules on oxide-free Si surfaces, mostly with wet chemical processes. This review focuses therefore directly on wet chemical surface functionalization of oxide-free Si surfaces, starting from H-terminated Si surfaces. The main preparation methods of oxide-free H-terminated Si and their stability are first summarized. Functionalization is then classified into indirect substitution of H-termination by functional organic molecules, such as hydrosilylation, and direct substitution by other atoms (e.g. halogens) or small functional groups (e.g. OH, NH₂) that can be used for further reaction. An emphasis is placed on a recently discovered method to produce a nanopattern of functional groups on otherwise oxide-free, H-terminated and atomically flat Si(111) surfaces. Such model surfaces are particularly interesting because they make it possible to derive fundamental knowledge of surface chemical reactions.

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Abbreviations: Si, silicon; SiO₂, silicon oxide; SAM, self-assembled monolayer; XPS, X-ray photoelectron spectroscopy; FT-IR, Fourier transform infrared; AFM, atomic force microscopy; NN, nearest neighbor; NNN, next nearest neighbor; RT, room temperature; TFT, thin film transistor; ALD, atomic layer deposition; MPA, methylphosphonic acid; ODP, octadecylphosphonic acid; DFT, density functional theory; KMC, kinetic Monte Carlo; ML, monolayer; H, hydrogen; T-BAG, tethering by aggregation and growth; OH, hydroxyl; UHV, ultra-high vacuum; MOFs, metal organic frameworks; SURMOFs, surface metal organic frameworks; LBL, layer-by-layer; PL, photoluminescence; F, fluorine; Cl, chlorine; Br, bromine; I, iodine; N, nitrogen.

* Corresponding author.

E-mail address: chabal@utdallas.edu (Y.J. Chabal).

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1. Introduction

Silicon has been dominating the microelectronic industry in part because it is plentiful and relatively cheap and can be produced with high purity, but mostly because of the chemical and electrical stability of the interface with its oxide [1,2]. In fact, the low concentration of electrical defect states at the Si/SiO₂ interface has been a strong driver to use Si for future devices such as electrical biosensors and photovoltaic components [1,2].

Much work has therefore been devoted to modifying SiO₂ surfaces by grafting molecules via OH groups that typically terminate SiO₂ surfaces after wet chemical cleaning [3,4]. There are however two rather fundamental issues associated with modification of SiO₂ surfaces. The first is the very high activation energy for the reaction a number of species with surface OH groups, most notoriously for grafting phosphonic acid molecules [5]. The second is the poor chemical stability of the Si–O–Si bond at the interface between the organic layer and SiO₂, due to facile hydrolysis under neutral or basic pH conditions [5].

Two main methods have been used to functionalize SiO₂. Silanization [6,7] has been the first method to graft organics to SiO₂, but this method often suffers from the low surface OH group content of the Si surface oxide [3,4]. Indeed, comprehensive Si surface coverage by silanization derives from amorphous siloxane polymerization, and the degree of siloxane cross-condensation depends critically on the water content of the deposition solvent [7]. Attaining structural order in such films is also problematic [5].

Alternatively, phosphonate molecules have been grafted on SiO₂ using a method called tethering by aggregation and growth or T-BAG [5]. During the T-BAG process, a phosphonic acid is initially weakly physisorbed from a solution onto the oxide substrate forming a reasonably well-ordered layer thanks to the interaction of the phosphonate headgroups of adjacent molecules, then chemically attached by a heating step, during which Si–O–P bonds are formed. The sample is then typically rinsed to remove any remaining physisorbed multilayers present on the surface on top of the chemisorbed SAM. T-BAG is a simple and reliable method to grow SAMs with phosphonate bonding on oxide surfaces. The phys-

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