Characterizing Chemically Reactive Thin Layers: Surface Reaction of [2-[4-(Chlorosulfonyl)phenyl]ethyl]trichlorosilane with Ammonia

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Thin layers of organosilanes on oxidic surfaces are of great interest for various applications including the control of surface properties and immobilization of catalysts and biomolecules and in nanotechnology. In the present work, the reaction of thin layers on silicon oxide consisting of [2-[4-(chlorosulfonyl)phenyl]ethyl]-trichlorosilane (CSTS) with ammonia is studied by means of contact angle (CA) measurements, ζ-potential measurements, X-ray photoelectron spectroscopy (XPS), and Fourier-transform infrared spectroscopy (FT-IR). CA measurements are used for a fast monitoring of film quality and as a first probe for the reaction of the CSTS sample with ammonia. The results from XPS measurements show that the chlorine peak of the CSTS molecule disappears completely after the reaction with ammonia and instead a well-resolved nitrogen peak appears. FT-IR spectroscopy in conjunction with theoretical calculations is used to gain a more in-depth understanding of the chemical reaction. The shift of the asymmetric S═O vibrational mode during the surface reaction is in line with the theoretical predictions and serves as a proof for the surface reaction to happen. By FT-IR, an additional side reaction of sulfonic acid groups, which are present in the commercial CSTS, to the ammonium sulfonate salt is observed.

Introduction

Thin layers and self-assembled monolayers (SAMs) of organosilanes on silicon oxide surfaces (e.g., on silicon wafers or glass substrates) are of great interest for numerous applications and play an increasingly important role in nano- and biotechnology.[1−5] A huge variety of organo-modified chloro- or alkoxysilanes are described, and a lot of them are commercially available. The range of attached organic functional groups spans from apolar to polar groups and from anionic to cationic groups and includes, for example, also fluorescent dyes and electroactive moieties. This allows the use of silane-based SAMs for engineering surface properties over a wide range and makes them suitable for the immobilization of catalysts, (bio)-molecules, nanoparticles, or analytes on the surface. They can be applied as adhesion promotors between organic and inorganic compounds for control of the wettability, surface polarity, and chemical reactivity.

Moreover, such materials have been used in electronic applications[6,7] and as interfacial layers of organic devices such as ambipolar organic transistors[8] or monolayer field effect transistors,[9] which can also be chemoresponsive.[10] In organic thin film transistors (OTFTs) they have also been used to gain control of the threshold voltage.[11−13]

One interesting example of a functionalization of the silicon oxide surfaces is the introduction of sulfonyl chloride and sulfonic acid groups by depositing the corresponding silane-based molecules. In this context, thin layers of [2-[4-(chlorosulfonyl)phenyl]ethyl]trichlorosilane (CSTS) have been applied as interfacial layers in organic thin film transistors, strongly impacting the final device performance.[12] Silanes bearing chlorosulfonyl functionalities deposited by Langmuir−Blodgett techniques on silicon layers were also used as initiation sites for the preparation of graft polymers by atom transfer radical polymerization. Defined acrylates, glycopolymers,[14] and ferrocenyl-functionalized polymers[15] were prepared from such surfaces. In combination with microphase separation phenomena[16] or electron beam irradiation,[17] patterned growth of polymers was achieved. The sulfonic acid chloride groups were alternatively introduced by sulfonation of immobilized benzyl chloride moieties and subsequently used as initiation sites for ATRP.[18] The same functionalization technique can be used for the preparation of nanoparticles coated by a polymer shell, as was shown for iron particles coated by poly(butyl acrylate) with applications in magnetorheological fluids.[19] In a similar way, magnetite particles were coated with poly(methyl methacrylate).[20]

Functionalized surfaces bearing sulfonic acid groups were used to change the adhesive and friction forces between a SiN tip and a silicon wafer surface.[21] Sulfonic acid- and mixed sulfonic acid/lysine-functionalized silica surfaces were discussed for binding of plasminogen, resulting in fibrinolytic surfaces.[22] Altankov et al. investigated the influence of the surface polarity and surface charge of functionalized layers including sulfonic acid derivatives on the interaction with living cells.[23] The electrostatic interaction between the sulfonate group and cationic metal complexes was used for immobilization of iron and manganese porphyrins for the catalytic oxidation of hydrocarbons.[24−26] Arenesulfonic acid functions introduced into the pore

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