ω-Substituted Long Chain Alkylphosphonic Acids - Their Synthesis and Deposition on Metal Oxides and Subsequent Functional Group Conversion of the Deposited Compounds

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Summary: The crystal structure and the surface of alumina layers on silicon wafers were investigated by means of GIWAXS, WAXS, and AFM. Self-assembled monolayers of ω-substituted long-chain alkylphosphonic acids were deposited on alumina and the layer thickness and homogeneity were determined by ellipsometry revealing a dependency of thickness and homogeneity on the nature of the substituent. During the adsorption process surface etching by the phosphonic acid was observed causing an increase in surface roughness.
Furthermore, ex post functional group conversions were carried out yielding surface bound azides and rhodanides.
Keywords: alkylphosphonic acid; alumina; atomic force microscopy; self-assembled monolayer; surfaces

Introduction

This article is part of our research on scope and limitation of our concept of ex post chemical SAM (self-assembly monolayer) modification. First, a homogeneous SAM is generated on a surface using readily available anchor groups, which bear reactive functional groups. With this highly functionalized SAM modified surface on hand further chemical modifications can be carried out. Generally reactions with high conversion and high selectivity are applied. But, even if conversion is low, e. g. as in case of introduction of bulky substituents, this concept is advantageous over SAM formation of highly substituted anchor groups because bulky substituents always cause great distances between neighbored molecules due to spatial reasons. Thus, there will be empty space between the anchor moieties, which might be filled up by any

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sort of compounds, so to speak there will be plenty of space for permanent surface contamination. Co-adsorption of two different anchor molecules may lead to phase separation instead of formation of a homogeneous mixed layer. In contrast, our concept of ex post SAM modification forms a homogeneous SAM first which will be modified afterwards yielding a dense mixed layer.

The work described here aims at the development of surface modifiers for metal oxides. Such compounds will render the chemical properties of oxydic surfaces of metallic materials. These compounds can be used for corrosion inhibitors [1], anchor groups for dyes, polymers, bio-polymers, e. g. antibodies, enzymes, poly-sugars, and the like, peptide mimetics, additional applications are electronic devices and molecular recognition etc., simply by adopting the functional head-groups to the users needs. Phosphonic acids are versatile compounds for these purposes. They adsorb well on metal oxides like titanium oxide [2], iron oxide, and aluminum oxide [1] forming self-assembly layers on the surfaces of metal oxides.
Furthermore, alkylphosphonic acids as well as ω-substituted alkylphosphonic acids are readily accessible via Michaelis-Arbusov reaction.

Surface Characterization [3]

As substrates for this research silicon wafers coated with aluminum were used. The aluminum layer had been deposited by PVD (physical vapor deposition). Afterwards, the aluminum surface was oxidized in an oxygen plasma.
To gain a deeper insight into the structure of the metal oxide layers used in this investigation the surface of the applied alumina was characterized in detail with AFM, WAXS (Wide Angle X-Ray Scattering), and GIWAXS (Grazing Incidence Wide Angle X-Ray Scattering). The latter methods revealed dense layers of aluminum oxide (5.05 nm) and metallic Al (45.6 nm) on top of natural silicon dioxide (2 nm) followed by bulk silicon. The aluminum oxide is contaminated with some silicon dioxide. No crystalline alumina was found (Fig. 1), hence, the obtained aluminum oxide layer is amorphous.

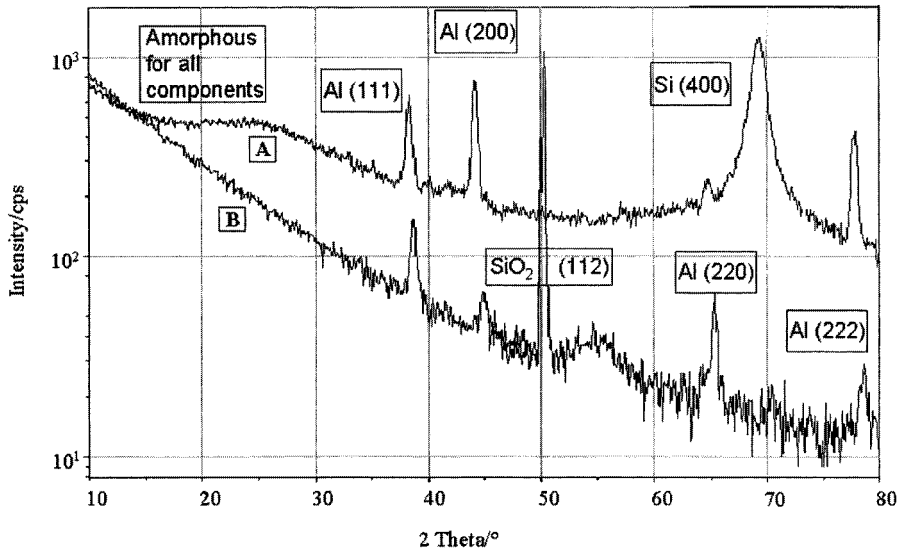

Figure 1: Comparison of WAXS (**A**) and GIWAXS ($\omega = 0.2°$, **B**) of an aluminum oxide bearing aluminum coated silicon wafer

Aluminum, which had been deposited on a silicon wafer by PVD, was oxidized in an oxygen plasma. Afterwards, the obtained aluminum oxide layer was investigated by various methods. AFM (atomic force microscopy) imaging revealed a surface covered with numerous little but singular peaks, which are depicted in white. Treatment of the Si-wafer with an aqueous ethanolic solution of phosphonic acids caused not only formation of a self-assembly layer, but also an increase in surface roughness and a pronounced increase in the number of peaks due to surface etching during the adsorption process (Fig.2).

Surface Modification [3]

Various ω-substituted dodecylphosphonic acids had been dissolved in ethanol/water 1:1 at concentrations of 1 mmol/l and were adsorbed on alumina.

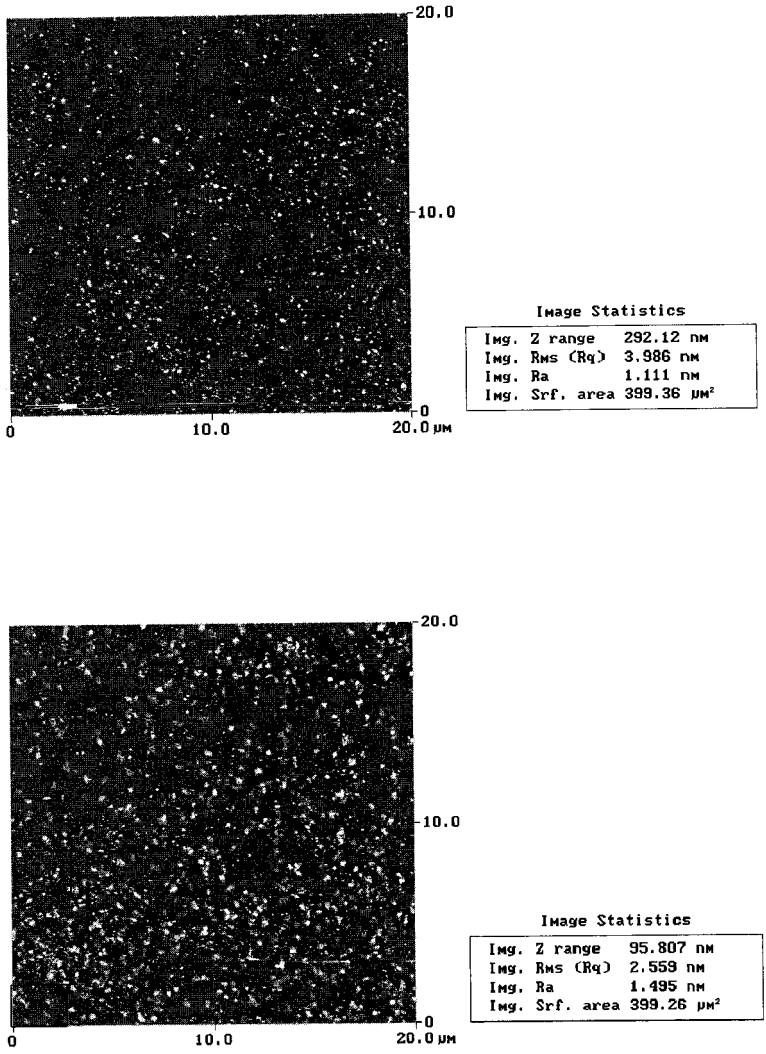

Figure 2: Time dependence of etching of the aluminum oxide layer on an aluminum coated silicon wafer. 2a) after 1 h, 2b) after 20 h

AFM investigation of 12-bromo and 12-mercapto dedecylphosphonic acid showed intense surface etching. The surface roughness increased from 1.1 nm for the untreated material to 3.1 nm for the coated wafer in the case of 12-bromo dodecylphosphonic acid and to 1.5 nm for the 12-mercapto dodecylphosphonic acid. Both, 12-amino and 12-ethylamino dodecylphosphonic acid showed much less surface etching and a surface roughness in the same order of magnitude as the untreated material. Because of the low solubility of the latter compounds due to internal salt formation the concentration in solution is to low to cause intense etching. Hence, only small amounts of these phosphonic acids were deposited on the alumina surface as confirmed by ellipsometric measurements. The determined layer thicknesses and the calculated lengths of the molecules are summarized in table 1; the error of the ellipsometric data given in table 1 is 15 %. It should be kept in mind that ellipsometry is an analytical tool with only low lateral resolution. Thus, it integrates the layer thickness over a distinct surface area. Any inhomogeneities in surface coating result in an increase or decrease in layer thickness. Therefore, layer thicknesses below the molecular length mean an imperfect coarse layer or a layer with low coverage due to angle formation between the alkyl chain and surface normal. Any tilt angle will cause a layer thickness less than the molecular length, too. Furthermore, the space filling ethyl amino group prevents formation of a dense layer, hence, the SAM of 12-amino dodecylhosphonic acid shows an even lower layer thickness than its unsubstituted counterpart.

In contrast to the amino functionalized phosphonic acids the 12-mercapto dodecylphosphonic acid forms layers more than twice as thick than the calculated molecule length. This finding can be interpreted in terms of disulfane formation during the adsorption process due to oxidation of the mercapto group or in terms of oxidative disulfane formation in the stock solution prior to adsorption.

The unexpected high layer thickness of the 12-bromo dodecylphosphonic acid can be explained by multilayer formation [4]. May be the tremendous increase in overall surface roughness influenced the measurements, too.

Table 1. Ellipsometric determined layer thicknesses of various ω-substituted dodecylphosphonic acids adsorbed on aluminum oxide.

ω-substitued dodecyl-phosphonic acid R:	Measured layer thickness/nm	Calculated molecule length/nm [7]
-H 1 h adsorption time	1.4	1.65
-H 20 h adsorption time	2.4	1.65
-Br	4.7	1.72
$-NH_2$	1.3	1.76
-NHEt	0.7	2.01
-SH	4.8	1.80

Despite the little amount of adsorbed 12-amino and 12-ethylamino dodecylphosphonic acid the obtained contact angles of the SA-layers (Table 2) show a tremendous increase in surface hydrophilicity for both compounds in comparison to dodecylphosphonic acid. The advancing contact angle decreases from 111.2° for dodecylphosphonic acid to 71.3° for ω-amino dodecyl-phosphonic acid.

With increasing hydrophilicity of the substituent the advancing contact angle decreases. The little contact angle hysteresis, which was found for dodecyl and 12-bromine dodecylphosphonic acid, suggests formation of a dense SA layer on the aluminum oxide, otherwise a greater difference between advancing and receding contact angle would have been observed.

Adsorption of alkylphosphonic acids performs via salt formation due to an acid-base reaction between the phosphonic acid and surface bound aluminum hydroxide moieties. This reaction leads to insoluble aluminum salts of phosphonic acids [5].

Table 2. Contact angles of various aluminum oxide covered Si-wafers, which are coated with ω-substituted dodecylphosphonic acids.

Substituted dodecyl phosphonic acid R:	θ_a/°	σ	θ_r/°	σ
-H 1 h adsorption time	111.2	0.3	86.4	3.8
-H 20 h adsorption time	112.5	0.6	84.1	4.9
-Br	90.4	1.4	61.9	0.8
$-NH_2$	71.3	4.2	----	----
-NHEt	74.1	1.8	----	----
-SH	74.2	0.9	----	----

θ_a: advancing contact angle, θ_r: receding contact angle, σ: standard deviation
---- Values could not be determined

SAM Modifications by Interfacial Reactions

The synthesis of functionalized alkylphosphonic acids started with the Michalis-Arbuzov reaction of 1,12-dibromododecane followed by further derivatization [6]. Details on the preparation of these and other derivatives will be described in a forthcoming paper. After deposition on aluminum oxide further modification had been carried out at the interface between solvent and solid. Here we present the nucleophilic substitution of terminal bromine by azide and rhodanide ions [7]. Successful substrate conversion was proved with diffuse reflection IR-spectroscopy (Fig. 3). After substitution of bromine by KSCN an new absorption band arose at 2155 cm^{-1}, which was attributed to the rhodano moiety [8]; after replacement of Br with NaN_3 a new absorption band appeared at 2099 cm^{-1}, which was assigned to the azide group [8].

XPS (X-ray photoelectron spectroscopy) gave further information on the reaction. In neither of the XPS spectra of both supported compounds, azide and rhodanide, residual bromine could be detected; hence, complete conversion had occurred.

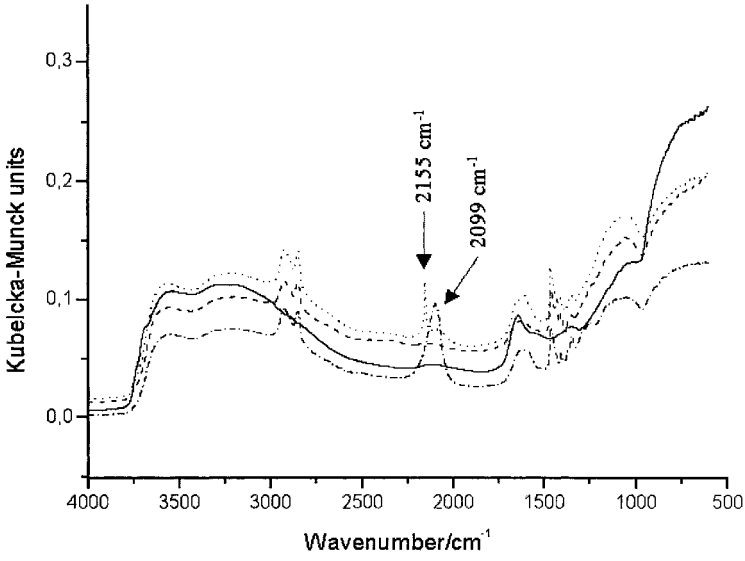

Figure 3: Comparison of the IR-spectra of supported ω-substituted dodecylphosphonic acids (Al_2O_3: ——— , $Br(CH_2)_{12}P(O)(OH)_2$: ------ , $SCN(CH_2)_{12}P(O)(OH)_2$: ····· , $N_3(CH_2)_{12}$-$P(O)(OH)_2$: -·-·-·)

Conclusion

We investigated aluminum oxide surfaces on aluminum deposited on silicon wafers. WAXS investigations confirmed the inhomogeneity of the metal oxide layer. AFM revealed a smooth surface with scattered peaks. Treatment with phosphonic acids caused etching of the aluminum oxide surface which lead to an additional formation of peaks, as was confirmed by AFM. Due to the low resolution of AFM it was impossible to detect the organic matter.

Indirectly, contact angle measurements confirmed the presence of ω-substituted phosphonic acids. With increasing hydrophilicity of the terminal functional group the contact angle dropped from 112° for dodecylphosphonic acid to 71° for 12-amino dodecylphosphonic acid.

Ellipsometric measurements, too, confirmed the existence of a thin organic layer on the aluminum oxide surface.

We successfully synthesized ω-substituted phosphonic acids with long alkyl chains. Furthermore, we could exchange terminal bromine of the adsorbed by ω-substituted phosphonic azide and rhodanide groups. Both functional groups allow further conversions and introduction of other functional moieties at the interface.

Proving functional group conversion in SA-layers requires concerted application of sophisticated analytical techniques like XPS, AFM, and diffuse reflection IR-spectroscopy.

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