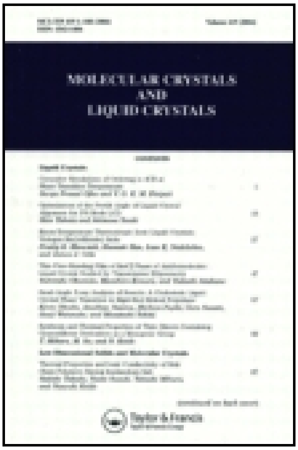

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Self-Assembly of Aminosilane Layers: Determination of Surface Density of the Amine Group Through a Reversible Chemical Reaction

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SELF-ASSEMBLY OF AMINOSILANE LAYERS: DETERMINATION OF SURFACE DENSITY OF THE AMINE GROUP THROUGH A REVERSIBLE CHEMICAL REACTION

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Abstract The surface of a fused silica and oxidized silicon wafer ($SiO_2/Si(100)$) was treated with (3-aminopropyl)triethoxysilane in solution. The silane coupling agent (SCA) produces multilayers with variable thickness (6 - 100 Å) depending upon the dipping time. The aminosilane layers were allowed to react with 4-nitrobenzaldehyde, and formation of the corresponding imine was confirmed by UV-vis spectroscopy. In aqueous medium the imine was easily hydrolyzed to regenerate the amine group and the aldehyde. Surface density of the amine was calculated from the amount of produced 4-nitrobenzaldehyde. Tilt angles of the chromophore, the imine, obtained from the surface density and A_{surf}, absorbance of the derivatized substrate, are 23 - 32°.

INTRODUCTION

The silanization, in particular aminosilanization, of hydroxyl-bearing surfaces finds numerous application in immobilization of molecules of biological interest, immobilization of inorganic catalysts, modification of electrodes, chromatography, and building foundation for self-assembly.[1-3] In all application the reactive primary amine group exposed on the surfaces is utilized.

EXPERIMENTAL SECTION

AMINOSILANIZATION

Clean substrates were immersed into anhydrous toluene solution (20 mL) containing an SCA (0.2 mL) under nitrogen atmosphere. The substrates were placed in the solution at 25 ^{O}C. The reaction time were varied from several minutes to 72 h. After the silanization they were washed with toluene, and baked for 30 min at 120 ^{O}C. Subsequently the substrates were sonicated in toluene, a mixture of toluene and methanol (v/v = 1/1), and methanol. For each sonication step 2 min was allowed. Finally the substrates were dried under vacuum.

FORMATION OF THE IMINES

The silanized substrates were immersed into anhydrous ethanol (25 mL) containing 4-nitrobenzaldehyde (10 mg) and acetic acid (0.02 mL) under argon atmosphere. The substrates were immersed in the solution at 50 °C for 3 h. After the condensation the substrates were washed with ethanol, and sonicated in ethanol for 2 min. Finally the substrates were dried under vacuum.

HYDROLYSIS

The imine-formed substrates were immersed in water (15 mL) containing acetic acid (0.02 mL), and the aqueous solution was heated at 30 °C for 1 h. Subsequently, the substrates were sonicated in the solution for 2 min. Absorbance of produced 4-nitrobenzaldehyde can be measured at this stage.

4-NITROBENZALDEHYDE *t*-BUTYLAMINE

The compound is prepared as described previously,[4] and its λ_{max} and extinction coefficient in various solvents have been measured. (λ_{max}, ε_{max}, solvent) = (282 nm, 1.56 x10^7 cm^2/mol; CH_2Cl_2); (282 nm, 1.51 x 10^7 cm^2/mol, $CHCl_3$); (282 nm, 1.55 x10^7 cm^2/mol; CH_3CN); (277 nm, 1.58 x 10^7 cm^2/mol, CH_3OH).

RESULTS AND DISCUSSION

THICKNESS

An ellipsometry showed thickness of the aminosilanized layers on silicon wafers. As in Figure 1, the reagent gives a thin layers of 6 Å thickness in 30 min. Even though the rates of film growth are different from batch to batch, the thickness of the layer invariably increases with the reaction time. Typically film of 100 Å thickness is formed in 72 h. Moreover, the ellipsometric data of the thick film formed over 10 h vary significantly (± 8 Å) from site to site. The observation reflects inhomogeneity of the thus formed thick film. It has been proposed that alkoxysilane and chlorosilane reagents hydrolyze first to form hydroxysilane compounds, and then dehydrate to form siloxane bridges not only among the hydroxysilanes but between the hydroxysilanes and the hydroxyl groups on the silica surfaces.[1] In the mechanism the trialkoxysilane compound naturally has a high chance of forming three dimensional network leading to the formation of thick films during the self-assembly.

IMINE FORMATION

Surface density of the amine group is of great concern, because it determines the other physical and chemical properties of the layer. Because the popular aminosilane density

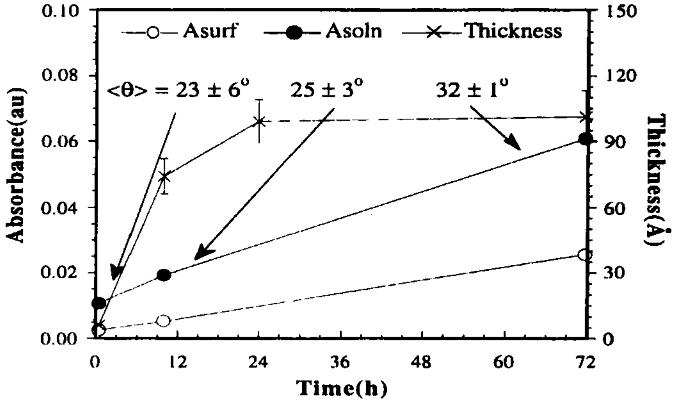


FIGURE 1 Thickness (×) of the aminosilane layers measured at various reaction time; absorbance (O) of the imine-formed substrates, converted absorbance (•) from the produced 4-nitrobenzaldehyde, and tilt angle (<θ>) of the imine at these points.

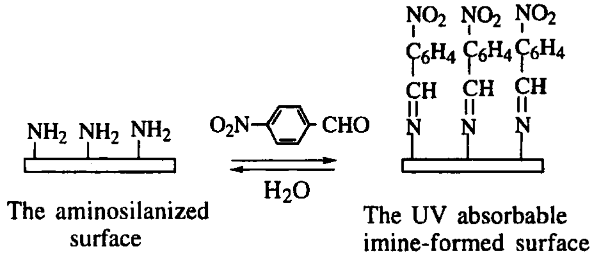
of self-assembled molecules on top of the aminosilanized layer, eventually, all reagent does not have a chromophore, measuring the surface density is no simple task. There has been strong need to establish a direct method determining density of the amine functionality exposed on the surfaces.

An imine formation (Scheme 1) between the amine group and 4-nitrobenzaldehyde was chosen to transform the nonabsorbing aminosilanized layers into absorbing layers.[5] The condensation usually can be driven by removal of water. However, use of a large excess of 4-nitrobenzaldehyde in anhydrous solvents also drives the reaction complete. Indeed, the imine formation is complete in 3 h with a large excess of 4-nitrobenzaldehyde . The absorbance of the imine dose not increase after this.

The imine shows an absorption sharp enough to assign its λ_{max} as 284 nm. These values are very close to that of 4-nitrobenzylidene *t*-butylamine in solvents of medium polarity (282 nm). As in Figure 1, relatively weak absorbance (0.0025) was observed at early stage of the reaction. The absorbance continuously increases with the reaction time.

HYDROLYSIS, DENSITY OF THE IMINE AND ITS ORIENTATION

Hydrolysis of the imine is important because it enables us to restore the analyzed surface to its original state, the aminosilanized surface for further application. Moreover, by



SCHEME 1

measuring the amount of 4-nitrobenzaldehyde from the hydrolysis, the surface density of the reactive amine group can be calculated. The surface density of the amine can be converted to a density of the imine, mathematically. Therefore, absorbance of the imine could be derived as if it were in the random orientation like in solution. When the value is designated as A_{soln}, the tilt angle from the surface normal can be calculated from the absorbance of the imine-formed substrate (A_{surf}) and A_{soln} (eq 1).[6] As in Figure 1, tilt angle of the chromophore at early stage is 23±6° and has increased to 32±1° in 3 d.

$$\sin^2\langle\theta\rangle = 2A_{surf}/(3A_{soln}) \qquad (1)$$

Therefore, the reagent produces a thin layer of 6±1 Å thickness with a density (2.1 amines/100 $Å^2$) in 0.5 h, and an inhomogeneous multilayer of 100±12 Å thickness with a relative higher density (11.8 amines/100 $Å^2$) in 72 h.

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