AFM and XPS Study of Aminosilanes on Si

The Influence of the Number of Bonding Sites on the Polymerization

In this study APTMS and APREMS aminosilanes were used for the modification of silicon, with a purpose for using them in sensor’s applications (detection of explosives like TNT, DNT, RDX, etc.). The morphology and surface chemistry of the modified surfaces were investigated using atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). Our results show that the polymerization of aminosilanes and consequently the thickness of the aminosilane layer depend on the number of possible bonding sites of the aminosilane molecule.

Introduction

Aminosilanes are self-assembled molecules with the ability to form a durable bond between organic and inorganic materials. They are used for surface modification and adhesion promotion. A surface modified with aminosilanes has many applications (due to aminosilane’s electron donor NH₂ group), from biological studies, to attaching metal nanoparticles and sensor applications [1-4]. The silanization is usually carried out in the solution of different solvent with low concentrations of aminosilanes. There are many studies on optimizing silanization conditions (type and concentration of aminosilane, silanization time and temperature, presence of water, type of solvent...) [5, 6]. Generally alkoxysilanes, due to alkoxy groups, are capable of polymerization and hydrolyse rapidly in the presence of water to form cyclic monomers/oligomers and intermolecular cyclics [7]. In our previous study, we've shown that with APTMS modified surfaces of MEMS (micro-electromechanical systems) can be used for detection of explosive molecules (fig. 1) [8]. For the best response of the sensor (rapid response, reversibility, selectivity...) the details about optimization of the modification process are necessary.

In this study, we modified silicon surfaces with two different aminopropylsilanes (fig. 1); 3-aminopropyltrimethoxysilane (APTMS; 3 bonding sites) and 3-aminopropylethoxydimethylsilane (APREMS; 1 bonding site) in order to understand how a different number of bonding sites influences the aminosilane film.

Results
Firstly the native oxide layer on the silicon wafers has been reduced and subsequently oxidized by an oxygen plasma.

The silanization has been carried out in a 3 mM solution of aminosilane in anhydrous toluene at different temperatures and times. Using atomic force microscopy (AFM), we obtained information about the topography and the roughness of the surface. AFM imaging is a very useful method for such samples since it allows analysis of thin and soft organic materials. We performed AFM analysis on the NT-MDT Solver Pro microscope in the oscillating mode using Si-tips. From AFM results (fig. 2 a-c) we can see that aminosilanes are forming flat layers with islands. The surface of the uncoated silicon wafer (fig. 2a) is smooth, without islands, but with a surface roughness Ra=0.09 nm. Our results show that the modification with the APTMS (deposition time 6 h at 25°C, fig. 2c) leads to the formation of a relatively rough layer (Ra=0.28 nm) with a high density of islands due to polymerization. The majority of islands are from 1.5 to 2 nm in height and around 20 nm in width. We relate the flat area to a uniform array of self-assembled aminosilane molecules adsorbed on the Si-oxide surface and the islands on the flat region to the polymerization of the amnosilane molecules. In the case of the APREMS (fig. 2b, Ra=0.12 nm) coatings, obtained under the same conditions, we observed a more uniform surface with a small number of islands, revealing a height of 2 nm. For longer silanization times (22 h, AFM results not shown here), in the case of APREMS coatings, we observed even more polymerization (higher and wider islands compared to 6 h of deposition). The surface composition and chemical bonding of the coatings were characterized by the X-ray photoelectron spectroscopy (XPS), using a PHI instrument equipped with an Al-monocromatic X-ray source. The XPS method is very suitable for such investigation due to a high surface sensitivity. In the XPS spectra the present elements (Si, C, O and N) were identified and their concentrations were calculated. From the shape and shift of the XPS spectra, the chemical bonding of surface elements was inferred. Increased C concentrations and appearance of N peak in XPS spectra, compared to uncoated Si wafer, show successful bonding of the aminosilane molecules to the surface. In the case of APREMS coatings for a longer silanization time, an additional increase in C and N does not occur. The opposite was observed for the APTMS coatings, where the C and N concentrations strongly increased with the silanization time. There are more aminosilanes on the surface, particularly in the form of islands.

Typical high-energy resolution N 1s and Si 2p spectra are shown in figure 3. The spectra were deconvoluted into different components by a fitting procedure. In the
high-energy-resolution N 1s spectra (fig. 3a) we resolved two different components related to NH bonds. The component at a binding energy of 399.2 eV corresponds to -NH2 bonds and the component at a binding energy of 401.0 eV corresponds to -NH3+ bonds. The ratio of the -NH2/-NH3+ components indicates the type of interactions of the aminosilanes with the silicon substrate.

In the Si 2p XPS spectra we can recognize four different components (fig. 3b). The component at a binding energy of 99.3 and 99.9 eV corresponds to Si-Si bonds from the bulk silicon wafer beneath the oxide layer. The signal at 102.2 eV corresponds to aminosilane on the SiO2, and the signal at 103.0 eV corresponds to the SiO2 in the oxide layer. From the Si 2p spectra we estimated the relative thickness of the silicon oxide layer and the silane layer, comparing the intensities of the bulk Si components and the total Si-O components at 102-103 eV (Si atoms involved at the SiO2 interface and the Si atoms from the silane overlayer). For the thickness calculation we used equation as it was proposed in [9]. Figure 2d shows the calculated total thickness of the Si-oxide layer and the silane layer prepared at different deposition times. The thickness of (2.0±0.2) nm obtained on the uncoated wafer is related to the Si-oxide. The thickness of the APTMS layer on the Si wafer increased significantly as a function of the deposition time. This increase is mainly due to the growth of a multilayer structure of the APTMS coating, related to the polymerization. From figure 2d we estimated that after 22 h of deposition the pure APTMS layer (without Si-oxide interface) is (4.7±0.3) nm thick. The estimated thickness in case of APREMS coatings is (0.5±0.2) nm for 22 h of deposition, which is in the range of 1 monolayer, even after longer deposition times (22 hours).

Conclusions

A comparison of the composition and morphology of the silane layer on the surface gives us information about their bonding affinity. Our results show that the occupancy of the surface depends on the number of possible bonding sites of the aminosilane molecules. The APTMS molecule, with three bonding sites (3 alkoxy groups), reacted intensive with the Si-oxide layer. The APREMS molecule has one bonding site (1 alkoxy group), resulting in a more ordered layer. We also concluded that when the aminosilane molecule has more bonding sites the effect of polymerization is higher, resulting in island formation and a rougher surface. It is necessary to consider the proper preparation conditions to obtain a flat and uniform aminosilane surface; otherwise, uncontrolled silanization leads to the formation of thick and rough surface of aminosilanes.

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References

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