Molecular Dynamics Simulations of the First Steps of the Formation of Polysiloxane Layers at a Zinc Oxide Surface

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Summary: Three different dissolved silane molecules adsorbed at a polar ZnO surface (000$\bar{1}$) are studied by means of constant temperature molecular dynamics simulations. The adsorbed single silane molecules exhibit a different behavior depending on the chemical nature of their tail. For octyltrihydroxysilane molecules with their rather unpolar tail an orthogonal orientation at the polar metal oxide surface is statistically favored with all three polar hydroxide groups of the head being in contact with the polar ZnO surface and the unpolar tail remaining in the isopropanol phase. On the contrary, due to their highly polar tail, aminopropyltrihydroxysilane molecules show a more or less parallel orientation at the surface. Apart from some minor fluctuations two hydroxide groups as well as the amino group of the tail are in contact with the surface. The behavior of the thiolpropyltrihydroxysilane molecules is somehow located in between resulting in parallel as well as orthogonal orientations of the molecule at the surface. Though many of the results obtained for single adsorbed silane molecules can also be transferred to adsorbed silane molecules within whole layers a remarkable difference appears: Now even for aminopropyltrihydroxysilane molecules a mixture of parallel and orthogonal alignment of the molecules can be observed whereas some of the octyltrihydroxysilane molecules also show a parallel orientation.

Keywords: adsorption; coatings; molecular dynamics; polysiloxanes; surfaces

Introduction

The present study is motivated by the increasing use of polysiloxane layers for corrosion protection of metal(oxide) surfaces[1-2] by industry and the associated need for an improved understanding of the formation of polymer layers at such surfaces from its monomers, i.e. single silane molecules. Therefore, physical properties of three different dissolved silane molecules (octyltrihydroxysilane, aminopropyltrihydroxysilane and thiolpropyltrihydroxysilane) within a (mono-)layer adsorbed at a polar[3] ZnO surface are studied via constant temperature molecular dynamics simulations. A metal oxide surface instead of a pure metal

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surface is chosen to account for the fact that in contact with air many metals (like zinc, which is used for a cathodic corrosion protection of steel) are forming a thin metal oxide surface[4]. In the present computer simulation the metal oxide film is represented by a zinc oxide (ZnO) crystal, which is of wurtzite-type structure with lattice parameters $a = 0.3249$ nm and $c = 0.5205$ nm. For the surface of the zinc oxide crystal being in contact with the liquid phase containing the dissolved silane molecules the polar $(000\bar{1})$ surface with the oxygen atoms being on top was chosen.

In a previous paper single dissolved silane molecules (in isopropanol) adsorbed at a zinc oxide surface were studied[5]; in the present communication the calculations are extended to the adsorption of whole layers consisting of a large number of silane molecules. Thus, similarities as well as differences of the behavior of adsorbed silane molecules surrounded by solvent molecules only or being in contact with other silanes in addition will be analyzed. The aim is to understand the *first steps* of the formation of layers of polysiloxane molecules by studying the properties of adsorbed silane molecules. Though the polymerization process from silanes to siloxanes is not yet accounted for in the simulations the structure and morphology of (poly-)siloxane layers are, of course, determined by the orientation and physical behavior of its silane monomers. Therefore, a better understanding of the formation of such silane layers will also pave the way for an improved tailoring of polysiloxane layers.

Numerical method

Constant temperature molecular dynamics simulation at 298 K is performed following a procedure already outlined in detail in ref.[5] A simulation box (3.3×3.4×6.8 nm) with periodic boundary conditions in order to simulate a representative part of an interface devoid of any arbitrary boundary effects is used. The whole box consists of the zinc oxide surface (represented by a zinc oxide crystal of wurtzite-type structure cleaved along the $(000\bar{1})$ plane) and a liquid phase consisting of two layers for convenience. The first one (on top of the ZnO layer) contains 50 silane and 100 isopropanol molecules. The second (on top of the first) is composed of 150 isopropanol molecules and serves as an upper limit preventing any interaction of molecules in the middle layer with the second (bottom) ZnO surface due to periodic boundaries. Thus an indefinitely extended liquid phase on top of the crystal is simulated.

To save computer time the spatial positions of atoms in the the zinc oxide layer as well as the positions of molecules in the top layer are fixed throughout the whole MD simulation – all the more because one is only interested in the dynamical behavior of the "silane phase" (with a rest of some solvent), i.e. in the behavior of molecules in the middle layer.

For the whole simulation procedure the software package *Materials Studio* 2.1 (from Accelrys Inc.) was applied using the *Visualizer* module for building the metal oxide crystal and the molecules, for the combination of the layers which have been constructed with the *Amorphous Cell* tool, and for the visualization of the results obtained by *Discover* as the molecular dynamics engine. Interactions between atoms were accounted for by use of the force field COMPASS[6-8] which is a class-II force field optimized for the simulation of condensed phases including metal oxides.

Results and discussion

In the following the resulting structure and orientation of the different silane molecules forming a (mono-)layer at a zinc oxide surface are analyzed and compared to each other as well as to the behavior of single adsorbed silane molecules dissolved in isopropanol[5]. Figure 1 presents a typical end configuration of such a layer consisting of 50 octyltrihydroxysilanes after an equilibration time of 5 ns.

In accordance with the adsorbtion behavior from an infinitely diluted solution most of the adsorbed silane molecules show an orthogonal alignment at the surface and only some of them are orientated in a parallel way. Non-adsorbed silane molecules remaining in the liquid phase (i.e. isopropanol phase) show a more or less random orientation. As was shown in ref.[5] the orthogonal alignment is statistically favored for single adsorbed silanes but the parallel one is also possible (and even favored concerning the interaction energy with the surface). Therefore, the conclusion can be drawn that the results from single adsorbed octyltrihydroxysilane molecules can be also transferred to whole layers without major restrictions.

On the contrary, quite a different behavior of the adsorbed silane monomers at the metal oxide surface is observed when octyltrihydroxysilane is replaced by aminopropyltrihydroxysilane or thiolpropyltrihydroxysilane, with respect to the single chain, as well as to the behavior of the layer.

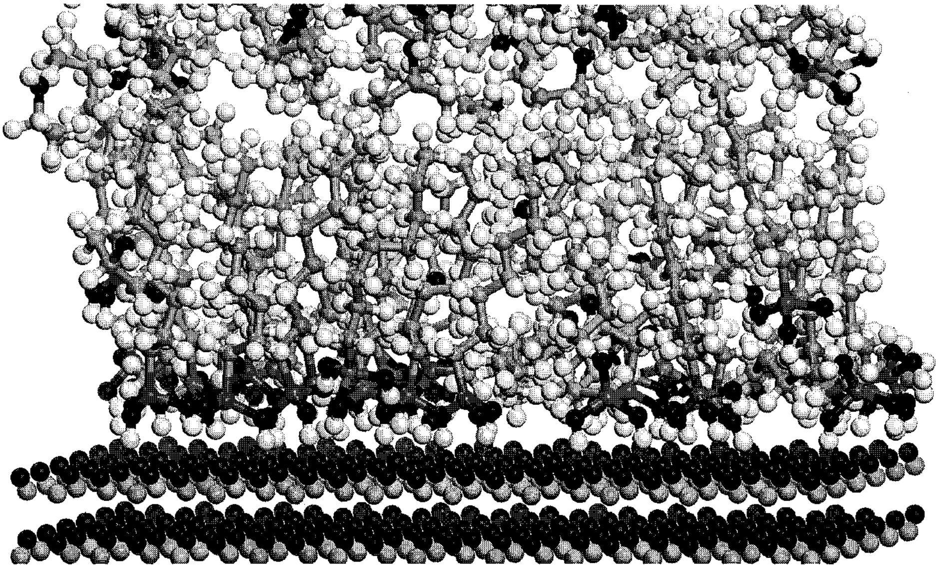

Figure 1. End configuration after an equilibration time of 5ns at 298 K of 50 octyltrihydroxysilane molecule dissolved in 100 isopropanol molecules forming an adsorbed layer at the zinc oxide surface – cut and enlarged from the overall simulation box. The different colors correspond to different atom types with white symbolizing hydrogen, black oxygen, gray carbon and dark-gray silicon (in the crystal zinc atoms are also represented by gray colors).

For an unpolar tail like the octyl group its interaction with the polar metal oxide surface merely takes place via van der Waals forces whereas now for a polar group like the aminopropyl or thiolpropyl group dipole-ion interactions between the molecule and the surface also play an important role. Therefore, strong interaction of the tail with the zinc oxide surface force a single adsorbed aminopropyltrihydroxysilane molecule into a parallel configuration (with head and tail fixed at the surface) where only slight fluctuations are possible. This picture, however, is not retained if a layer system consisting of 50 silanes is considered.

From Figure 2 a mixture of parallel *and* orthogonal orientations is observed which can be traced back to a competition between the trihydroxy and the amino groups of the aminopropyltrihydroxysilane molecules to occupy the favorite sites on the polar surface. In contrast to single adsorbed silane molecules, where only a competition between one silane molecule and the solvent (i.e. isopropanol) takes place, now a significantly increased number of polar groups competes for adsorption at the zinc oxide surface. Therefore, the orientation of the adsorbed aminopropyltrihydroxysilanes within the layer at the surface results from steric and not energetic constraints (in this case only parallel orientations should be observed).

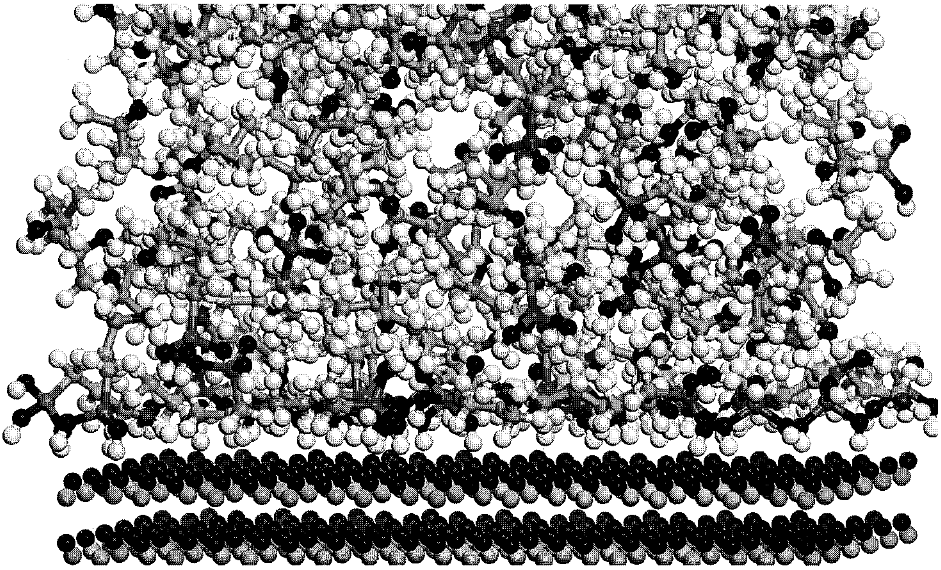

Figure 2. End configuration after an equilibration time of 3ns at 298 K of 50 aminopropyltrihydroxysilane molecule dissolved in 100 isopropanol molecules forming an adsorbed layer at the zinc oxide surface – cut and enlarged from the overall simulation box. The colors are the same as in Figure 1 with nitrogen being represented by dark-gray.

Changing the polarity of the tail by substituting the amino group by the less polar thiol group also changes the intensity of the interaction between the tail and the polar surface. The thiol group is not polar enough to exhibit such a strong interaction to the surface to force adsorbed molecules only into a single preferred orientation like that of aminopropyltrihydroxysilane in case of a dilute solution. Therefore, the physical behavior of a single adsorbed thiolpropyltrihydroxysilane molecule is somehow located in between the behavior of octyltrihydroxysilane and aminopropyltrihydroxysilane: It shows two distinct orientations at the surface though the one quite similar to that of aminopropyltrihydroxysilane (i.e. a parallel orientation) is statistically preferred. In accordance with that result an analysis of the orientation of adsorbed thiolpropyltrihydroxysilanes within a layer exhibits nearly the same picture as that of aminopropyltrihydroxysilane: Again, a mixture (like that of a single adsorbed molecule) of parallel and orthogonal orientations can be observed.

Conclusion and Outlook

The structure and orientation of adsorbed silane molecules within a whole layer forming the pre-stage to the formation of a polysiloxane layer were analyzed and compared to single adsorbed silane molecules. While the behavior of octylhydroxysilane with respect to the orientation (almost orthogonal) of adsorbed molecules is more or less independent of concentration, a clearcut tendency toward a mixture of parallel and orthogonal orientations with increasing concentration is found for silanes with polar tails. For the future an extension to other surfaces (e.g. a zinc oxide surface with vacancies) as well as to models comprising also polysiloxane molecules is envisaged.

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[1] K. Izumi, H. Tanaka, Y. Uchida, *Journal of Material Science Letters* **1993**, *12*, 724
[2] S. Hansal, W.E.G. Hansal, M. Pölzler, M. Wittmann, G.E. Nauer, *Proc. Electrochem. Soc.* **2000**, *99*, 167
[3] H. Maki, N. Ichinose, S. Sekiguchi, N. Ohashi, T. Nishihara, H. Haneda and J. Tanaka, *Jpn. J. Appl. Phys.* **1999**, *38*, 2741
[4] X. G. Zhang, "*Corrosion and Electrochemistry of Zinc*", Plenum Press, New York, 1996
[5] A. Kornherr, S. Hansal, W. E. G. Hansal, J. O. Besenhard, H. Kronberger, G. E. Nauer, and G. Zifferer, *J. Chem. Phys.* **2003**, *119*, 9719
[6] M.J. Hwang, T.P. Stockfisch, A.T. Hagler, *J. Am. Chem. Soc.* **1994**, *116*, 2515
[7] H. Sun, *Macromolecules* **1995**, *28*, 701
[8] H. Sun, *J. Phys. Chem. B* **1998**, *102*, 7338