

GROWTH OF MOLECULAR NANOSTRUCTURES ON Si USING SAMs OF LONG-CHAIN ALKYLTRICHLOROSILANES

Lionel Patrone⁽¹⁾, *Simon Desbief*⁽¹⁾, *Didier Goguenheim*⁽¹⁾, *Dominique Vuillaume*⁽²⁾

(1) *L2MP - Laboratoire Matériaux et Microélectronique de Provence - CNRS UMR 6137
/ ISEN-Toulon, Maison des Technologies, Place G. Pompidou, 83000 Toulon - France*

(2) *IEMN - Institut d'Electronique, de Microélectronique et de Nanotechnologie - CNRS
UMR 8520, Avenue Poincaré, BP 60069, 59652 Villeneuve d'Ascq cedex - France*

lionel.patrone@isen.fr

Controlling the preparation of smaller and smaller nanostructures is a key-point in nanotechnology. But today, limits of conventional lithography techniques as well as their costs are major obstacles to get over in order to go further in the integration of devices. A promising solution consists in using molecular self-assembly as a non lithographic approach for preparing nano-devices. In this communication, we report on a study of the growth behaviour of single and binary molecular self-assembled monolayers (SAMs) of long alkyltrichlorosilanes on Si/SiO₂ in order to get a better control of the preparation of nanostructures from such molecules on a technological substrate like silicon.

We first present the growth study of long chain alkyltrichlorosilane SAMs (16, 18, 20 and 30 carbon atoms chains) from a liquid phase on a Si surface covered with its natural oxide, at several temperatures and relative humidity values (RH). It is known that below a critical temperature increasing with the chain length, alkylsilanes are grafted nearly perpendicular to the surface following an island growth [1] up to the complete monolayer formation. Such a growth mode is driven by van der Waals intermolecular interactions. They occur during the diffusion of the molecular species on the oxide surface, which is lubricated by the presence of a natural water thin film, before grafting. Analyzing the growth kinetics of these alkyltrichlorosilanes using atomic force microscopy (AFM), ellipsometry, and contact angle measurements, we explain the behaviour of the molecules according to the deposition conditions using a model based on Diffusion Limited Aggregation (DLA). We thus show that the C₃₀ behaviour at 20°C and 40% RH is similar to that of C₁₆, C₁₈ and C₂₀ at 11°C and 40% RH. We have also established that the molecules diffusion coefficient increases with relative humidity, and surprisingly decreases with temperature. Another important result is the decrease of the growth characteristic time with the number of carbon atoms in the alkyl chain except for C₃₀. Such behaviour of the growth kinetics with the number of carbon atoms is interpreted by the competition between the molecular diffusion coefficient and the DLA capture radius, the first one decreasing with the chain length while the second increases.

In a second step, we report on the phase separation study between C₃₀ on one hand and C₁₆, C₁₈, C₂₀ on the other hand according to the deposition parameters (Fig. 1). Indeed, phase separation in such systems [2-3] is promoted by the length difference which modifies the chain to chain van der Waals interaction. In addition to the classical phase separation by islands of C₃₀ in a surrounding phase of shorter molecules, we observe a demixtion involving dendritic "filaments" of C₃₀ in a shorter molecules phase, regardless the couple of molecules studied. A third sort of phase separation also appears in the case of C₃₀/C₁₈ and C₃₀/C₂₀: formation of holes composed of islands of the shorter molecule, in a surrounding phase of C₃₀. We interpret the possibility to obtain such a demixtion using only C₁₈ and C₂₀ as short molecules with C₃₀ by the fact that we are working below the critical temperatures of C₁₈₋₃₀ molecules, which is not the case for C₁₆. To our knowledge, this is the first observation of "filaments" and "holes" structures resulting from the phase separation in a binary mixture of alkylsilanes. Furthermore, we show the composition of binary SAMs performed at low humidity (20% RH) is almost the same that the one of the silanisation solution in the case of SAMs that phase separate by islands or holes. Concerning SAMs synthesized at high

humidity (40% RH), regardless the phase separation, we note that the proportion of longer chain molecules is always lower in the SAM than in the solution. The good transfer of the solution composition to the deposition substrate at low RH conditions on one hand, and the depletion of longer chain molecules in the SAM compared to the solution on the other hand are explained within DLA growth model. Indeed, at high humidity the SAM growth is mainly driven by the diffusion coefficient, while at low humidity the deposition rate from solution is shown to be the leading parameter of the growth.

As a summary, we performed a study of the growth behaviour of long alkyltrichlorosilanes from 16 to 30 carbon atoms, in single and binary SAMs. To our knowledge, this is the first time that C_{30} alkyltrichlorosilanes have been studied so extensively and that they have been used in binary SAMs. The two relevant parameters are temperature and relative humidity. We explain the growth kinetics of individual molecules within a DLA model. As for the mixture of two alkyltrichlorosilanes of different lengths, we could obtain for the first time “holes” and “filaments” demixtion patterns. We show the SAM composition can be controlled varying relative humidity, which is explained by DLA model of growth. These results are a step forwards the preparation of size controlled nano-domains acting as a pattern for building molecular devices. For instance, modifying the functionality of the domains by changing the moieties of the grafted molecules in a selective chemical way would allow building different devices such as molecular diodes [4] and nano-transistors by grafting a conjugated oligomer (channel) on top of the alkyl chains [5]. The advantage of this Si-molecules hybrid approach of nanoelectronics is to be compatible with the well-known silicon technology regarding applications.

References:

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Figure 1. Binary SAMs : a) cross-section scheme, b) examples of demixtion patterns (AFM images).

