

Supporting Information to Unpublished Work

In situ ATR FTIR monitoring of the formation of functionalized mono- and multilayers on germanium substrate: From 7-Octenyltrichlorosilane to 7-Carboxylsilane

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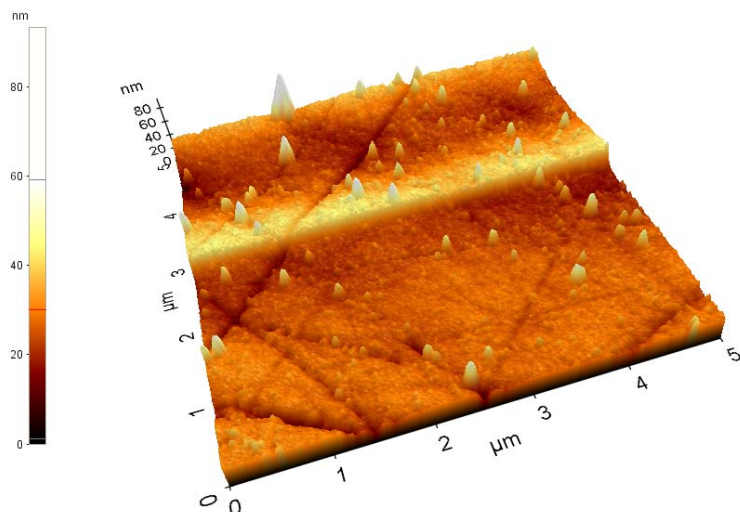
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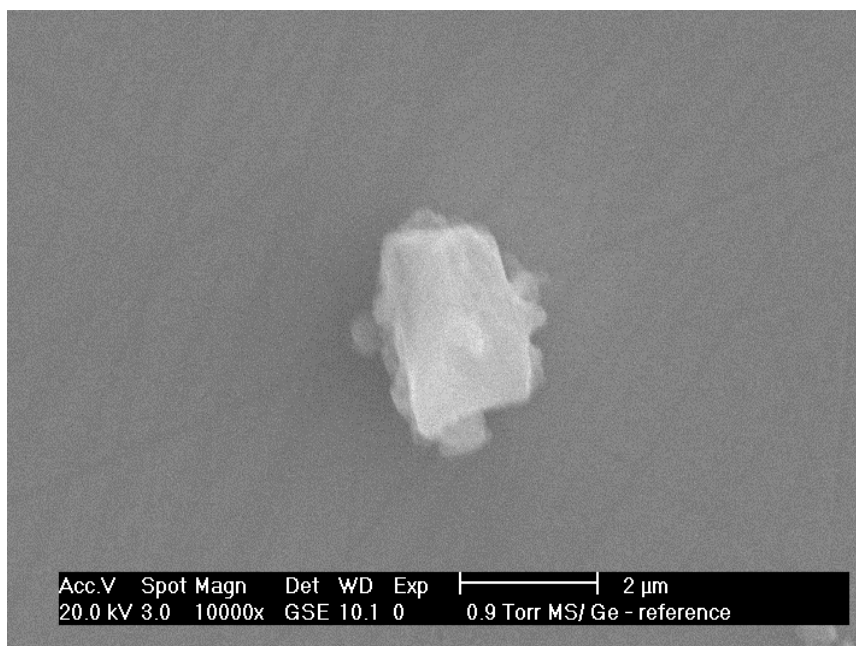
1. Ref. 36:

Matijašević J., Glowacky J., Koker T., Heissler S., Faubel W. and Fringeli U.P., *Langmuir* 2007, in preparation

In this Letter to *Langmuir* we document by AFM and ESEM the existence of nanoparticles incorporated into the surface layer. These particles turned out to be remainders from toluene drying with molecular sieve. The manuscript will be submitted within October 2007.



AFM of an octenyl-trichlorosilane (OTCS) layer on germanium. The white towers have a mean size of approximately 60nm range. Detailed analysis has shown that the particles resulted unambiguously from molecular sieve used for toluene drying. The silane layer is expected to cover the whole sample surface of the Ge MIRE.



ESEM picture from reference cuvettes exposed to toluene previously dried with molecular sieve. Remnants were qualitatively analyzed by means of Energy Dispersive X-ray Analysis (EDX). It was found that molecular sieve is present even on the surface of the MIRE in the reference channel with Al and Si atoms as the main components as well as some other traces of elements such as C, O, F, K. Measurements on the particle and on the Ge crystal area give a clear evidence, that the enhanced amount of Si, Al, K, O can be assigned to the molecular sieve remnants (e.g. zeolites).

2. Ref. 24:

Fringeli U. P., Matijašević J. and Reiter G., A new experimental and theoretical approach to in situ monitoring of surface chemical reactions by FTIR ATR spectroscopy.

Applied Spectroscopy, to be published.

This work deals with the theoretical means to overcome the following problems in ATR spectroscopy of thin layers with a highly reactive bulk solution in contact with the layer. The first problem is of general nature. Since the evanescent wave penetrates proportionally to its wavelength into the rarer medium, a bulk background may not be simply subtracted as in a transmission experiment. I would like to illustrate this fact by an example. If the real layer thickness d corresponds to about $d \approx 3 d_p$, where d_p denotes the penetration depth of the evanescent wave, the totally reflected light will no longer reach significantly the bulk background in contact with the layer. Therefore, if in the reference channel there is bulk background solution in direct contact with the MIRE, the resulting absorbance spectrum exhibits 100% overcompensation at this wavelength. Assuming that this case holds for 3 microns IR wavelength. However, since the penetration depth at 10 microns is about three times larger, background overcompensation will be less than 100%. As a consequence, if a bulk background in contact with a layer of given thickness d contributes to the ATR spectrum; accurate background compensation requires a linear scaling of the ATR spectrum of the background measured in absence of the layer. This procedure is straightforward when based

on the concept of *effective thickness* as introduced by N.J. Harrick (Harrick N.J. and du Pré F.K., Appl. Opt. **1966**, 5, 1739-1743) and further developed by myself (Fringeli U.P., *In situ* infrared attenuated total reflection membrane spectroscopy. In: Internal Reflection Spectroscopy: Theory and Applications. F. M. Mirabella Jr. (ed.), Marcel Dekker Inc. [1992], pp.255-324).

The analytical result is eq. 9 and Fig. 2 in the manuscript submitted to *Langmuir*.

The second problem is encountered in case of experiments with highly surface reactive background solutions, since layer growth starts immediately after contacting the germanium surface. The principle of calculating an ATR spectrum of a reactive background solution is described in *Sec. 2.4.1 Background Compensation* of the submitted manuscript.

The manuscript to be submitted to *Applied Spectroscopy* is still in preparation. It deals with a straightforward presentation of the applied ATR theory.