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Investigation of Siloxane Film Formation on Functionalized Germanium Crystals by Atomic Force Microscopy and FTIR-ATR Spectroscopy

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Abstract

To understand the long-time behaviour of silanes used as surface protection for cement based materials, the formation and stability of different siloxane films formed on these compounds were investigated by atomic force microscopy (AFM). Kinetics of the silane reactions were characterized by FTIR-ATR spectroscopy using a functionalized Germanium crystal as model surface. Different pH buffer solutions with a defined silane concentration were left to react with the model surface over two weeks for AFM studies, or on the functionalized Ge-crystal for time resolved reaction observation. It could be shown that the strength of the bonding between the siloxane film and the mineral surface depends on the chemical structure of the used silane, on the pH of the liquid system and on the reaction time. It is also shown that it is possible to investigate silane reactions on CSH-Gel and concrete by atomic force microscopy. To verify and complement the surface information from the AFM, investigations with a Raman-AFM combination were carried out.

Keywords: water repellent treatment, AFM, FTIR-ATR, Raman, functionalized germanium crystal

1 Introduction

Atmospheric corrosion, which is enhanced by air pollution and climate changes, causes increasing damages to concrete constructions, such as bridges or buildings [1-3]. These challenges are opportunities for the construction sector. Due to their size and relative long life of structures, the built environment has a strong impact on society, its growth and quality of life. Therefore research has a vital role to play in the field of civil engineering. The key goals are to maximize the sustainability of cement based building materials and to increase their life cycles. Concrete is the most widely used construction material. But concrete is a porous material. Therefore, harmful chemical substances, such as chloride or sulphate containing solutions can be transported into the concrete by capillarity. These chemical compounds lead to the corrosion of the reinforcement and/or to the deterioration of the concrete. Once deterioration occurs, restoration measures are necessary with both economic and ecological costs. In the hope of increasing the durability of concrete structures silicon organic compounds are used to impregnate the material against harmful substances [4].

Water plays a key role in the deterioration process. The pore and capillary structure of mineral building materials will absorb moisture during contact with liquid water. To avoid this, the water absorption capability of the construction material has to be reduced dramatically. A possible protection for this process is the hydrophobization with silicon organic compounds [5-11]. The aim of this study is to improve the understanding of the reactions and bonding mechanisms of these silicon organic compounds to the surface of cement based materials by employing very sensitive and precise analytical tools.

These compounds have been used increasingly as water repellent systems for preventive surface protection in civil engineering for many years [12-14]. However, the specific application of liquid silanes, e.g. n-propyltriethoxysilane and iso-octyltriethoxysilane, has only been in use for relatively few years. When a liquid silane is applied to the surface, the liquid is transported into the cement based material by capillarity. During this transport, the silane molecules react in a two-step chemical reaction into a siloxane compound and eventually into a silicone resin. It is important to elucidate the mechanism of the chemical reactions involved as well as the bonding between the formed silicone resin and the cement based material. However, the long-term behaviour of these compounds as well as their hydrophobic performance need to be assessed. This would allow to understand the decomposition mechanisms of the silicone resins over the years.

The present study is a sequel to a previous one where a simple silane was applied to a Si-Wafer [15]. It reports the results of experimental data obtained after the application of three different silanes to a functionalized Ge-IRE crystal. The functionalizing consisted in a sputtered pre-coating with a SiO_2 layer for the preliminary tests and a sputtered concrete coating in the subsequent studies. Different silanes were applied to these coatings and the characterization of their bonding behaviour was performed with atomic force microscopy (AFM), an analytical method useful for the examination of thin films on relatively flat surfaces [16,17,18]. As AFM is only suited to physical description of the surface, the study was complemented with a novel procedure of Fourier Transform Infra-Red-Attenuated Total Reflectance (FTIR-ATR) to obtain chemical information of the surface reactions of the silanes [19,20]. Furthermore, the polymerization of silanes on a Si wafer was investigated chemically by means of a Raman-AFM combination analysis.

2 Materials and Methods

2.1 Materials

The methyltriethoxysilane ($C_7H_{18}O_3Si$, Silane M1-Triethoxy) and the n-propyltriethoxysilane ($C_9H_{22}O_3Si$, Silane P-Triethoxy) were purchased from Wacker Chemie. The iso-octyltriethoxysilane ($C_{14}H_{32}O_3Si$, OCTEO) was purchased from Evonik. All chemicals had a purity of about 99.9 %.

For the magnetron sputtering process a 6 mm fused silica glass (Fa. Schott) and a self-made 5 mm thick concrete plate (CEM I 42,5 R Fa. Sika) were used.

2.2 Sample preparation

The studies carried out can be subdivided into two: those using a functionalized Ge-crystal; and those that complement the previous studies carried out on a Si wafer.

The first studies used a Germanium-IRE (internal reflection element) crystal, referred to as Ge crystal I. In the preliminary experiments, the crystal was functionalized by coating it with 30 nm of SiO_2. Deposition of this thin film was carried out in a Leybold Z550 sputtering facility using reactive radio frequency-magnetron sputtering with a SiO_2 target in Ar/O_2 atmosphere with 10% reactive gas. The SiO_2 target consisted of a 6 mm thick fused silica glass with 150 mm diameter. Subsequent experiments used a target of a 5 mm thick concrete plate on a standard PK150 cathode. After a cleaning procedure of the target by pre-sputtering, the germanium crystal was plasma etched to remove a thickness of 50 nm of the natural oxide from the surface and surface contaminants so as to allow sufficient film adhesion. The Si containing films were deposited by r.f. sputtering at 13,56 MHz; 0,6 Pa pressure; and, 300 W power with a deposition rate of 7,6 nm/min controlled at a partly covered silicon crystal as reference sample by a Tencor P10 surface profiler.

Subsequently, a larger Ge crystal (Bruker), referred to as Ge crystal II, functionalized in the same way, was used to continue these studies.

The three silanes were mixed in a proportion of 1:1 with a pH buffer solution (pH 4, 7, 10) to mimic realistic conditions. Then a drop of this mixture was applied to the center of the functionalized Ge-crystal, distributed and then covered with a box to avoid the evaporation of the drop during gas flushing of the spectrometer. For nearly two days, an FT-IR spectrum was collected every 10 minutes. A control run was made by applying the silane directly on to the Ge-crystal.

After collecting good spectra from the preliminary studies the Ge–IRE crystal was functionalized with a thin concrete layer as described above, to generate a realistic surface. The stepwise silane reactions on and with this surface were studied.

The second study used a Si wafer washed with ethanol and placed in a desiccator where an open beaker filled with silane had been placed. By evaporation the silane moves through the air onto the Si-Wafer and reacts forming a thin layer of polysiloxane. This was used for the Raman-AFM combination analysis.

2.3 Infrared and Raman Spectroscopy

A Bruker IFS 66/s Fourier transform IR spectrometer equipped with both a MCT and a DTGS detector, for the 4000-600 cm^{-1} and the 4000- 400 cm^{-1} spectral range, respectively, was used to obtain the IR spectra. Thirty two scans were recorded with a scanning rate of 10 kHz and a resolution of 4 cm^{-1}.

A functionalized internal reflection germanium element (Ge crystal I) coated with a 30 nm-thick layer of SiO_2 or of sputtered concrete was attached to the SPECAC horizontal ATR unit with 6 reflections under an incident angle of 45^0. Subsequently a larger Ge crystal II Bruker, functionalized in the same way, was used.

In opposition to IR spectroscopy, Raman spectra are barely affected by water bands (1400 -1800 cm^{-1} and 3200-3600 cm^{-1}). Furthermore the combination of the Raman spectrometer with the microscope provides a lateral resolved information of the sample surface in the range of a few microns.Therefore a Raman Microscope was used to prove the formation of siloxanes on the surface of the Si wafer sample to verify surface information from AFM studies and chemical information from the FTIR-ATR spectroscopy.

A Bruker SENTERRA Raman spectrometer (Bruker Optics, Ettlingen, Germany) based on an Olympus BX-51 microscope (OLYMPUS Co, Tokyo Japan) provided new insights for structures in the micron size range. A diode pumped frequency doubled Nd:YAG laser (wavelength: 532 nm) served as excitation source. The spectra were obtained with a resolution of 3 cm^{-1} at 20 mW laser power. The integration time was 30 s.

2.4 Atomic force microscopy (AFM)

The surface topography characterization of the siloxane films was carried out with a XE-100 scanning probe microscope (Park Systems Inc.) equipped with a closed-loop xy-scanner (scan range 50 µm x 50 µm) and a closed-loop z-scanner. The instrument was positioned on a home-made air-dampened platform standing on an active vibration isolation unit (MOD-1 L plus, Halcyonics GmbH). For characterization and manipulation silicon non-contact cantilevers (tip radius $\leq$ 10 nm, nominal resonant frequency 320 kHz, nominal force constant 42 N / m) were used. In all experiments the scan rate was set to 1 Hz and (256 x 256) data points were generated.

The topography visualization was carried out using true non-contact mode atomic force microscopy (AFM). After this, the surface was manipulated (scratched) using contact mode AFM (with a non-contact cantilever). Subsequently the scratched probe was characterized again with true non-contact AFM. The scan size used was bigger than that used for the manipulation (scratching) so as to visualize the manipulated and the non-manipulated surface in the same image.

3 Results and discussion

3.1 Infrared Spectroscopy

The feasibility of using FTIR-ATR to study the silane-SiO_2 reaction system, was carried out using methyltriethoxysilane (M1 triethoxysilane) applied directly on to the Ge crystal (without a SiO_2 coating). The obtained spectra are shown in Fig. 1 and indicate that polymerization of the silane occurs. During the two days of measurement the spectrum changed considerably**.** The increase of OH-vibrations at wavelength 1275 cm^{-1} assigned to δ (C-OH)$_{ip}$ in plane deformation during the first hours corresponds to the hydrolysis of alkoxy silanes to silanols with the corresponding formation of ethanol [21]. The Si-O band ν (Si-O) assigned to the Si-O stretching vibration remains sharp [22]. The C-OH, C-C and C-H_2 bands shift towards lower wavelengths and a peak broadening occurs. The CH_3 band decreases. All these observations confirm the beginning of the silane polymerization reaction to form a siloxane polymer.

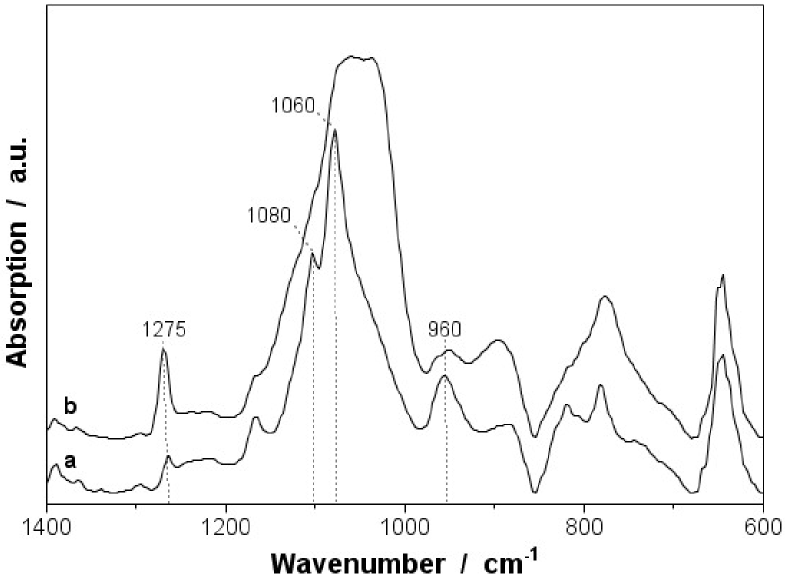

Figure 1: FTIR-ATR Mid-infrared spectra (DTGS - detector) of the polymerization of methyltriethoxysilane applied directly on the Ge crystal I (**a**= after 10 minutes; **b**= after 2 days)

Fig. 2 presents FTIR-ATR spectra of n-propyltriethoxysilane (P triethoxy) polymerization on a SiO_2 functionalized Ge crystal I. The spectra were taken at similar times as the control ones above. The film forming process by silanol condensation to a polysiloxane can be observed in the 1080–1030 cm^{-1} area through its shifting and broadening in combination with C-C and CH_2 vibrations. Typical bands featuring chemical bonding of triethoxysilanes molecules to the Ge surface and possibly triethoxysilane polymerization exhibit a broad unstructured shape between 1250-975 cm^{-1} reflecting vibrations such as ν(Ge-O-Si), ν(Si-O-Si) and ν(Si-OH) [21,23].

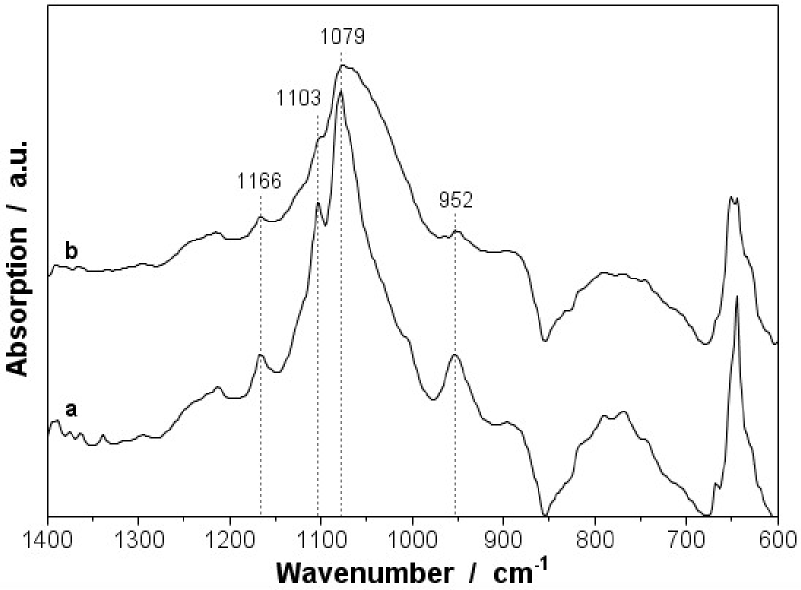

Figure 2: ATR Mid-infrared spectra (DTGS - detector) of n-propyltriethoxysilane on the SiO_2 functionalized Ge crystal I. (a= after 10 minutes; b= after 2 days)

The FTIR-ATR spectra for iso-octyltriethoxysilane on a SiO_2 functionalized Ge crystal I are shown in Figure 3. The spectra were taken at similar times as the previous examples. Small spectral shifts are observed indicating lower reactivity due to steric hindrance of the alkyl group. Similar changes as observed for the case of n-propyltriethoxysilane (compare with Fig.2) occur but apparently at a lower rate.

When using the larger Ge crystal II (Bruker) a MCT detector was used to collect the spectra. Fig. 4 shows the FT-IR spectra during polymerization of n-propyltriethoxy-silane (P triethoxysilane) on the SiO_2 functionalized Ge crystal II. The bottom spectrum shows the IR spectrum of the Ge crystal with the quartz peak (SiO_2) at 1050 cm^{-1} corresponding to the Si-O stretching vibration (ν (Si-O)). The three upper IR spectra show, besides the ν (Si-O stretch) reference peak, the increase and peak shifts of the alkyl groups with increasing time (up to 8 hours). The identified peaks are the $\delta_{as}(CH_3)$ anti symmetric deformation band at 1450 cm^{-1}; the δ_s (CH_2) symmetric deformation band at 1475 cm^{-1}; and, the δ (C-OH)$_{ip}$ in plane deformation band at 1375 cm^{-1}. The significant increase in sensitivity has allowed to see these changes thanks to the combined use of a larger crystal and the MCT detector.

3.2 Atomic force microscopy

AFM characterization of surface topography and manipulation (scratching) of the siloxane film was carried out with a XE-100 scanning probe microscope. Fig. 5 presents an AFM image of the siloxane layer on the SiO_2 functionalized Ge crystal I. A non-homogenous film covers the surface. Initially, at the beginning of the film forming process a statistically distributed carpet of polysiloxane dots can be observed. With continuing film formation, the dots first form islands and then eventually the whole surface is covered by a rough polysiloxane film formed by the joining of these growing islands.

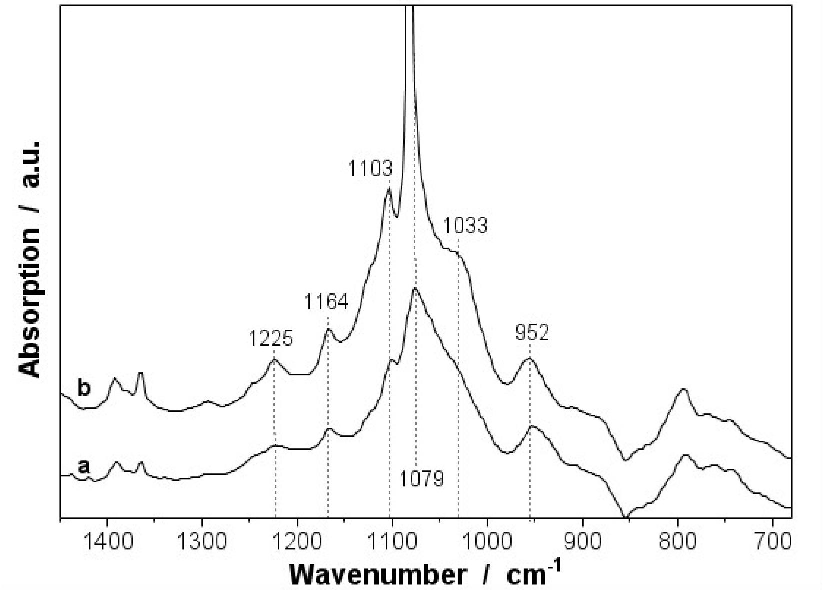

Figure 3: ATR Mid-infrared spectra (DTGS - detector) of iso-octyltriethoxysilane on a SiO_2 functionalized Ge crystal. (a= after 10 minutes; b= after 2 days)

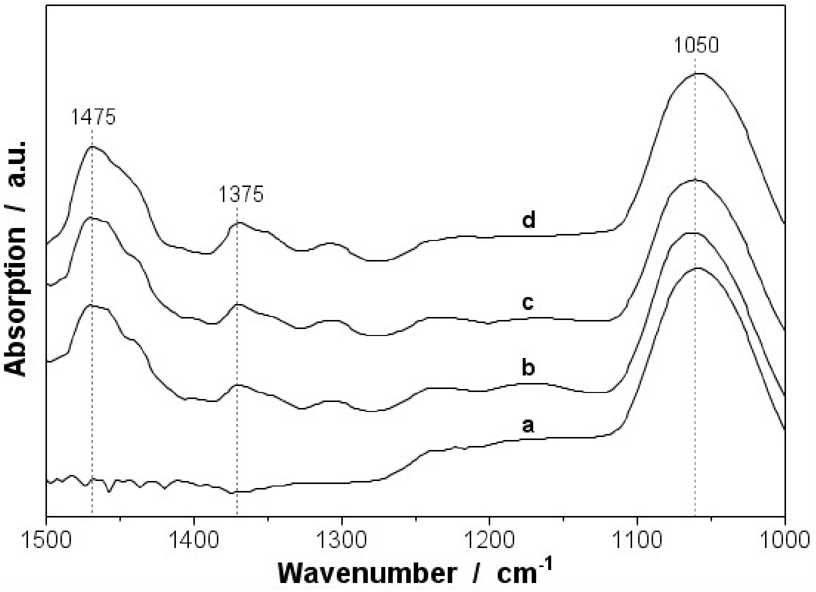

Figure 4: ATR Mid-infrared spectra (MCT- detector) of n-propyltriethoxysilane on the SiO_2 functionalized Ge crystal II. (**a**= control; **b**= 10 minutes; **c**= 1 hour; **d**= 8 hours)

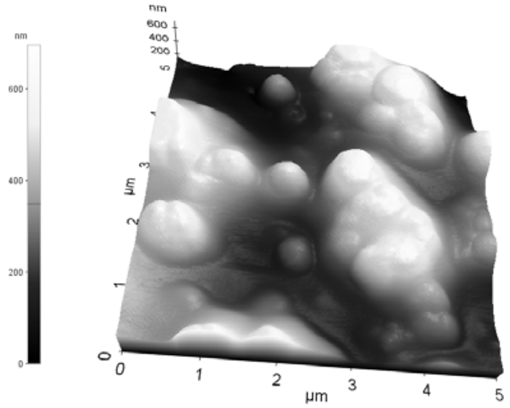

Figure 5: AFM (non contact mode) visualization of the surface topography of a siloxane film on a SiO_2 functionalized Ge crystal I at pH 10 (Scan area 5µm^2).

The influence of the chemical structure as well as the influence of the pH buffer used could also be observed for the bonding and film building process. The presented data characterize the behaviour of the silanes at pH 10 chosen because it is a more realistic system.

The results of AFM studies indicate that the bonding behaviour of iso-octyltriethoxysilane is predominantly a chemical bonding with the surface of these model substrates while for the n-propyltriethoxysilane it is primarily a van-der-Waals bonding as evidenced by the fact that the film could be scratched off the surface of the Ge crystal (Fig.6). This finding is in opposition to that of Oehmichen who reported that bonding of n-propyltriethoxysilane on concrete is stronger than that developed by iso-octyltriethoxysilane [24]. The reason for this has yet to be elucidated, however, it can be supposed that the density of terminal OH-groups on the surface and their direction plays an important role for the bonding of silanes to different substrates. Further investigations for clarifying these effects are still in progress.

3.3 Raman spectroscopy

Finally, using Raman spectroscopy it could be confirmed that a polysiloxane film had formed on the surface of a Si-wafer exposed to silanes (Fig. 7). Coupling this technique with the topographic characterization from the AFM serves to characterize in-situ the chemical composition of the visualized surface film.

3.4 Future directions

As shown above for the case of the SiO_2 functionalized Ge crystal, during an induction period statistically distributed tiny polysiloxane centers are formed on the substrate surface. So far, the fundamentals which determine the selection of these particular reactive centers are still unknown. But, with this method it should be possible to characterize first the chemical properties of the clean surface by means of Raman spectroscopy. Subsequently the distribution of the polysiloxane dots can be analysed by means of AFM. The comparison of both results will provide some information that may shed light about the mechanisms which determine the selection of the reactive centers as well as positioning and growth of the dots.

Thus, even the influence of differences in the chemical composition of the substrate, e.g., aluminate or silicate phases in the cement, on the induction period could eventually be observed. Ongoing investigations with this method will hopefully contribute to elucidate this mechanism.

4 Conclusions

The bonding behaviour of silanes on a mineral surface can be observed by using FTIR-ATR spectroscopy. For this purpose the Ge-IRE of the ATR unit could be functionalized in a magnetron sputtering process with a thin layer of SiO_2 to simulate a siliceous material. After the first successful experiments, the Ge-crystal surface was sputtered from a concrete target to better mimic a cement based material.

The technical approach used creates a special surface where reactions occurring on it can be followed by the analysis of surface reactions. The results obtained allow to characterize in-situ the reaction kinetics of the silane polymerization reaction on a mineral surface, mimicking concrete, for the first time. It was possible to indirectly detect the metastable key precursor silanol by the increased presence of ethanol during the hydrolyzis of the silanes. This is fundamental and important information for the practical use of the silanes as surface protection systems. Furthermore, the degree of bonding to the surface could also be determined. The comparison between two silanes (n-propyltriethoxysilane and iso-octyltriethoxysilane) showed the dependency of the polymerization reaction on the alkyl group in the silane. The chemical structure of this group will affect both reactivity and reaction rate.

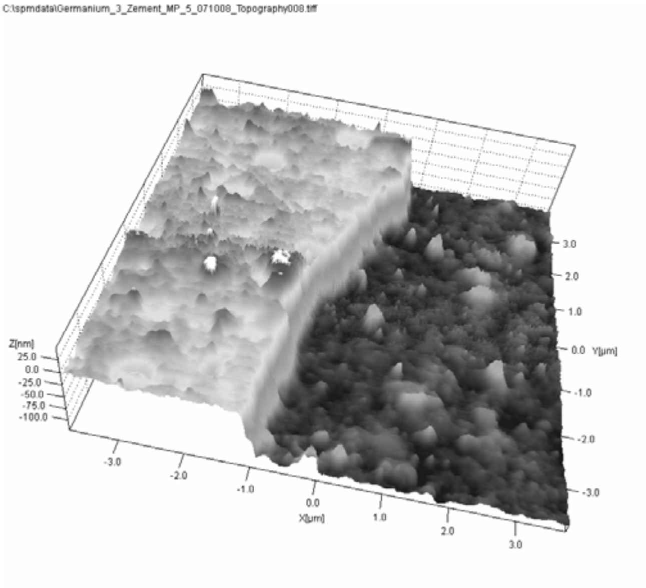

Figure 6: 3D-AFM tapping mode pictures of n-propyltriethoxysilane deposited on a sputtered concrete functionalized Ge crystal (Left). The siloxane dots (Right) on the Ge crystal surface without functionalization. Middle shows the border between sputtered part of the crystal and non sputtered part.

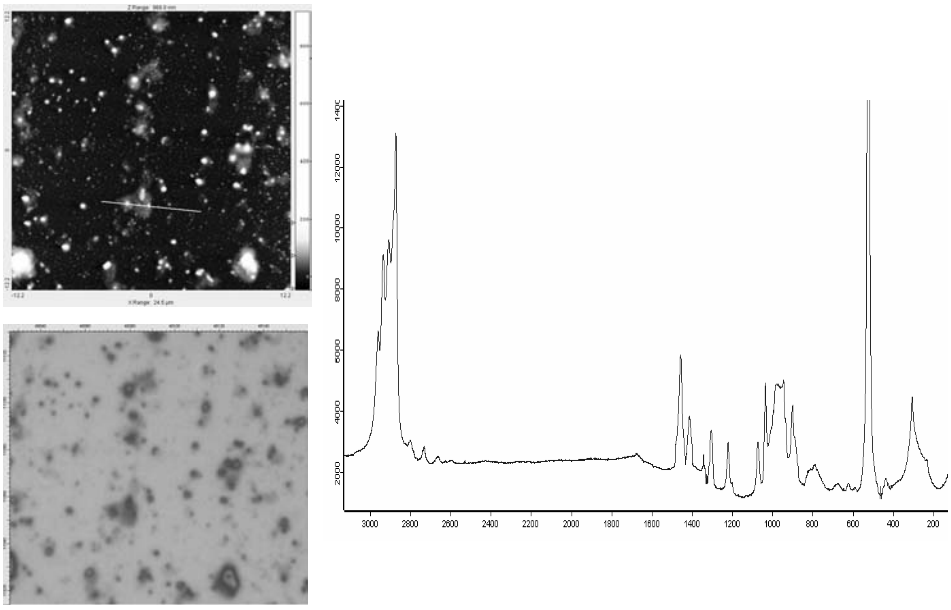

Figure 7: First measurement of n-propyltriethoxysilane on Si-Wafer with Raman/AFM coupling system showing AFM picture (top left), Raman mapping of the same area with polysiloxane dots (bottom left) and Raman spectrum of one of these polysiloxane dots (right) with CH_2, CH_3 at 2800-3000 wave numbers; C, CH_2, CH_3, Si at 850-1450 wave numbers and Si from the wafer at 470 wave numbers.

To improve the information that can be obtained from the surface reaction of a liquid solution with a mineral surface, a combination of surface observation and chemical analysis was developed. For this purpose, a combination of AFM and Raman spectroscopy was worked out so as to allow obtaining in-situ surface and chemical reaction data during reaction time. It could also be applied for the visualization of the polymer film degradation by aggressive solutions. This methodology should prove useful in the development of “tailor made” silanes for use in the construction sector and for quality control testing of products in practice.

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