

## Weathering of tin oxide coated glass with low IR emissivity

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Dedicated to Professor Oleg V. Mazurin on the occasion of his 75<sup>th</sup> birthday

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The weathering of K-glass has been studied by measuring transmission and reflection in the visible (VIS), near infrared (NIR) and infrared (IR) wavelength ranges, by chemical depth profiling with secondary neutral mass spectrometry (SNMS) and by atomic force microscopy (AFM) imaging. K-glass is a commercial tin oxide coated glass with low IR emissivity. The SnO<sub>2</sub>:F-coated side has been exposed to atmospheric conditions for up to 32 weeks and for up to two years.

It could be shown that the optical properties are only affected in the VIS range, but the visible contamination does not influence the high IR reflection. This means that the heat-insulating properties of window glazings with the K-glass coating on the surface do not degrade under atmospheric conditions.

Chemical depth profiles did not reveal major changes, except for an increase in the signals of minor elements on the surface, namely sodium, carbon and silicon. AFM showed that after 32 weeks the deep valleys of the rather rough crystalline SnO<sub>2</sub>:F are partially filled up. The high transmission of new K-glass can be regained since contamination or corrosion products can be removed by washing. The coating itself is chemically stable.

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### 1. Introduction

Modern commercial insulating window panes are coated either with so-called soft coatings based on silver or with hard coatings based on doped tin oxide (SnO<sub>2</sub>). The coatings are applied by sputtering or pyrolysis to reduce radiative heat transfer between the panes. Double glazing is assembled with the coated surfaces on the inside. One reason for this type of arrangement are the soft coatings based on silver; in spite of a combination of the metallic layers with oxidic coupling agents and protective layers they are still sensitive to scratches. They are also protected from chemical attack by atmospheric constituents.

Tin oxide coatings, however, are mechanically stable. Bulk tin oxide (cassiterite) has a Mohs hardness of 6 to 7 [1]. Dense tin oxide coatings can withstand scratches better than the uncoated float glass surface [1].

Applying these low-emitting coatings also on the outside of insulating window glazings could enhance the thermal insulation further and also reduce dewfall on the glazing [2]. This is of major interest for the development of new glazings for buildings and automobiles. To

the knowledge of the authors, the weathering behavior of tin oxide coatings under atmospheric conditions has not been reported yet.

Laboratory experience had shown that in spite of their rough surface, K-glass samples are less prone to spurious nanoscale particles, either contamination or corrosion products, compared to uncoated float glass [3]. Chemical depth profiles revealed no altered surface layer as it is known from uncoated float glass exposed to normal atmosphere [4]. To prove this experience, the coated sides of new glass samples have been exposed to atmospheric weathering in two places with different climatic conditions. One of these places was Clausthal-Zellerfeld (Lower Saxony) at 600 m above sea level with a low mountain range climate and with no large industrial emissions within 20 km. The other was Gummersbach (North Rhine-Westphalia) at an altitude of 200 to 526 m.

Transmittive, topographic and chemical properties have been recorded for exposure times of two to 32 weeks and for two years.

Close to the earth surface, organic and inorganic aerosols of natural or man-made origin like pollen, spores, bacteria, dust, smoke, salts, incineration products have a concentration of about  $2 \cdot 10^{-6}$  kg/kg air. Typical dust concentrations close to Clausthal-Zellerfeld and Gum-

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Received 19 March 2001, revised manuscript 2 April 2002.

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mersbach amount to  $< 10$  to  $30 \mu\text{g}/\text{m}^3$  and  $20$  to  $50 \mu\text{g}/\text{m}^3$  respectively (survey protocols published by the environmental authorities of Lower Saxony (<http://jupiter.nloe.de/index3.htm>) and North Rhine-Westphalia (<http://www.lua.nrw.de/luft/limes97/luxjb97c.htm>)).

## 2. Experiment

### 2.1 Samples

K-glass is the commercial name for an online CVD-coated float glass with a  $320 \text{ nm}$  thick coating of  $\text{SnO}_2\text{:F}$ . The low IR emissivity is due to the high conductivity of the coating,  $\text{SnO}_2$  with  $\text{F}^-$  anions substituted in the lattice is a good semiconductor. Underneath the tin oxide, a  $70 \text{ nm}$  thick silane-like interlayer ( $\text{SiO}_x(\text{CH}_y)_z$ ) is applied in the zone of the tin bath. It prevents sodium diffusion into the semiconductor and serves as an antireflective layer [5].

K-glass samples sized  $(20 \times 20 \times 0.4) \text{ cm}^3$  from Pilkington Deutschland AG Weiherhammer, were cleaned and mounted with silicone on larger float glass panes with the coating on the outside and installed on roofs with an inclination of  $30^\circ$ , similar to skylights. For comparison, unexposed samples were kept in a desiccator at room temperature. At the start of the experiments, all samples were cleaned by brushing with warm water and a commercial tenside and by rinsing with deionized water and acetone. Before analysis, the weathered samples were not cleaned.

### 2.2 Analysis

After exposure for 2, 4, 8, 16, and 32 weeks (Clausthal-Zellerfeld) and after two years (Gummersbach), direct and diffuse transmission and reflection were measured in different wavelength regions, chemical surface profiles were recorded by secondary neutral mass spectrometry (SNMS) and the topography was imaged by atomic force microscopy (AFM).

In an SNMS the sample surface is sputtered with krypton ions from a plasma and the secondary neutral particles are analyzed. In the high-frequency mode (HFM, SPECS GmbH, Berlin), an alternating rectangular potential of  $0$  to  $-500 \text{ V}$  and  $800 \text{ kHz}$  is applied between plasma and sample. The low potential of  $-500 \text{ V}$  provides a high depth resolution, during the zero voltage phase electrons from the plasma can discharge the sputtered surface. On float glass, the sputter balance is established after about  $50 \text{ s}$  [6]. Actual measurements showed that in the K-glass coating, it is established almost instantaneously, as expected for conductive materials.

For more instrumental details see table 1 and [4 and 7].

## 3. Results

### 3.1 Emissivity and reflection

The most important property of an insulating coating is its low emissivity  $\epsilon$  for heat radiation, which can be calculated from the reflection  $R$  in the infrared wavelength range:

$$\epsilon = 1 - R.$$

For all samples under investigation,  $\epsilon$  was almost constant during exposure. That means, corrosion and contamination did not affect the performance of K-glass as a good mirror for infrared radiation. In a former study, after two years of exposure,  $\epsilon$  increased by  $0.02$ , cleaning restored its initial value, however [8].

At the maximum intensity of heat radiation at  $10 \mu\text{m}$ , the direct reflection of all samples is above  $80 \%$  ( $82$  to  $84 \%$ ), which corresponds to  $\epsilon \leq 0.2$ .

In the IR reflection spectra of K-glass the following characteristic peaks can be identified (see figures 1a and b):

- a broad peak at  $1100$  to  $880 \text{ cm}^{-1}$  (maximum at  $1020 \text{ cm}^{-1}$ ) due to asymmetric ( $\text{Si}=\text{O}-\text{Si}$ ) and symmetric ( $\text{Si}-\text{OH}$ ) vibrations in the float glass substrate;
- peaks at  $730$  to  $595$  (maximum at  $622 \text{ cm}^{-1}$ ),  $500$  to  $400$  (maximum at  $467 \text{ cm}^{-1}$ ), and  $705 \text{ cm}^{-1}$  due to ( $\text{O}-\text{Sn}-\text{O}$ ) and ( $\text{Sn}-\text{O}$ ) vibrations in crystalline cassiterite [9];
- the band at  $2350 \text{ cm}^{-1}$  is due to sample to sample variations of  $\text{CO}_2$  adsorption during measurement and varies strongly from measurement to measurement.

There are no bands as for OH-groups or  $\text{H}_2\text{O}$  on the surface. The changes during weathering are minimal and not detectable at all before 16 weeks. The bands at  $622$  and  $705 \text{ cm}^{-1}$  join and form a shoulder and the broad glass peak around  $1020 \text{ cm}^{-1}$  decreases (see figure 1b).

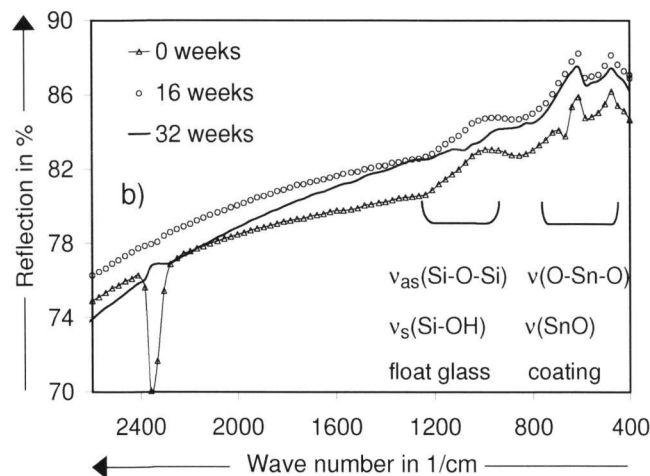
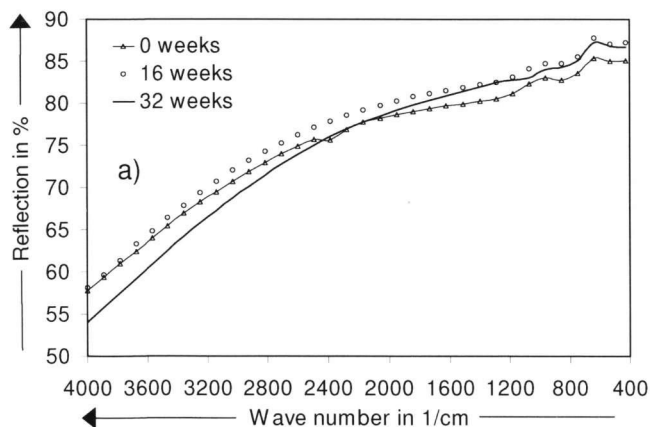
Direct transmission spectra in the  $300$  to  $2500 \text{ nm}$  range revealed no degradation until 16 weeks of weathering. After 16 weeks, the direct transmission decreases by  $2 \%$  at the transmission maximum at  $580 \text{ nm}$ . After 32 weeks, a uniform loss of direct transmission is noted over the whole UV/VIS/NIR range, with a loss of  $5 \%$  at  $580 \text{ nm}$  (see figure 2).

The loss in direct transmission and direct reflection is caused by diffuse reflection (ca.  $0.5 \%$  at  $580 \text{ nm}$  after 32 weeks) and mainly by absorption in the contamination layer (ca.  $7 \%$  at  $580 \text{ nm}$  after 32 weeks, see figure 3).

Cleaning with a mixture of alcohol and water (1:1) restores the original direct transmission as is shown in figure 4.

Table 1. Measurement methods

methods	instrument	instrument data	location of measurement
direct transmission ( $T_{\text{direct}}$ ) UV, VIS, NIR, 280 to 2500 nm	Spectrophotometer Omega, Bruins Instruments, Puchheim (Germany)	$\Delta T = 0.5\%$	Tech. University Clausthal
direct reflection ( $R_{\text{direct}}$ ) UV, VIS, NIR, 280 to 2500 nm	Spectrometer Lambda 900, Perkin-Elmer, Norwalk CT (USA)	wavelength measurement precision: $\pm 0.08$ nm UV/VIS, $\pm 0.30$ nm NIR, angle of incidence $8^\circ$	Interpane, Lauenförde
Fourier transformed IR reflection (FTIR)	ATI Mattson Genesis Series, Madison, WI (USA)	angle of incidence $26.5^\circ$	Interpane, Lauenförde
diffuse transmission ( $T_{\text{diffuse}}$ ) and reflection ( $R_{\text{diffuse}}$ ) VIS, 300 to 800 nm	Spectrometer Lambda 19, Perkin-Elmer, Norwalk, CT (USA)		Institut für Schicht- und Ionentechnik/Photo- voltaik, Forschungszentrum Jülich
secondary neutral mass spectrometry (SNMS): chemical surface profiles	INA 3, Leybold, Köln (Germany)	high frequency mode	Tech. University Clausthal
scanning force microscopy (AFM): topography	Nanoscope II, Digital Instruments, Santa Barbara, CA (USA)	contact mode, with A- and I- head, $\text{Si}_3\text{N}_4$ tips, also from Nanoscope	Tech. University Clausthal



Figures 1a and b. IR spectrum of K-glass (figure a); detail of a) with the characteristic bands for the float glass substrate and  $\text{SnO}_2$  coating (figure b).

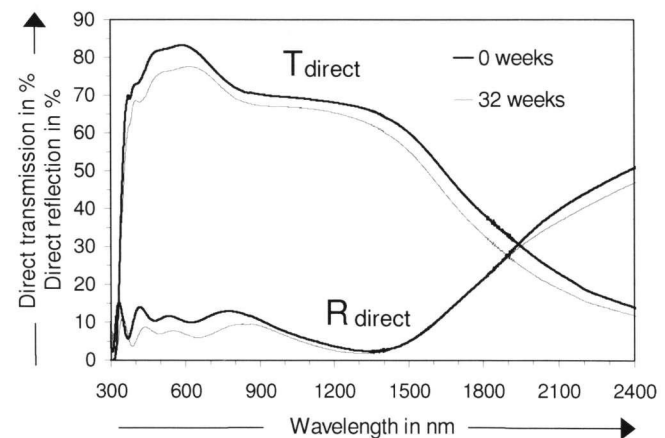


Figure 2. Direct transmission,  $T_{\text{direct}}$ , and direct reflection,  $R_{\text{direct}}$ , of K-glass before weathering and after 32 weeks under atmospheric conditions.

### 3.2 Chemical depth profiles

Figures 5a and b show the SNMS results. In the tin oxide layer, the most intense signals come from tin and oxygen. The silane interlayer is dominated by silicon and carbon. In the glass, silicon and sodium give the strongest signals. The surfaces of both the unexposed and the weathered sample are characterized by an increase of the sodium, carbon, and silicon signals within the first 150 nm (the first 50 s have been cut off in the SNMS profiles in figures 5a and b and 6). The same holds for calcium, OH, magnesium, and aluminum (not shown in figures 5a and b). In order to correctly interpret the weathering effects, sample to sample variations of the background signals have to be taken into account. Figure 6 shows the profiles of sodium after correction for

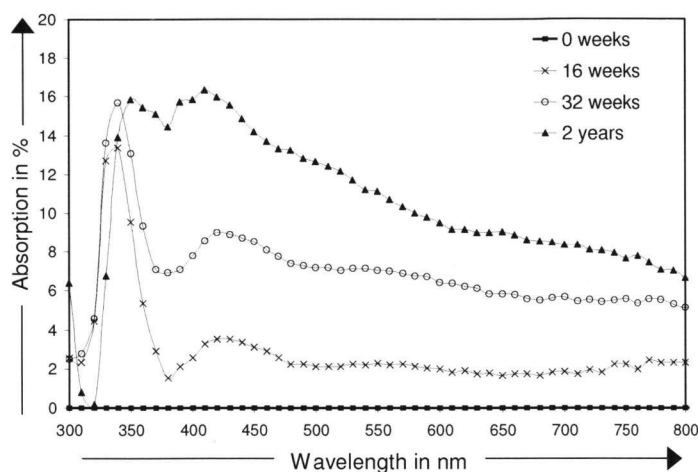


Figure 3: Absorption of the weather-induced contamination layer on K-glass, measured with a pristine sample as a reference.

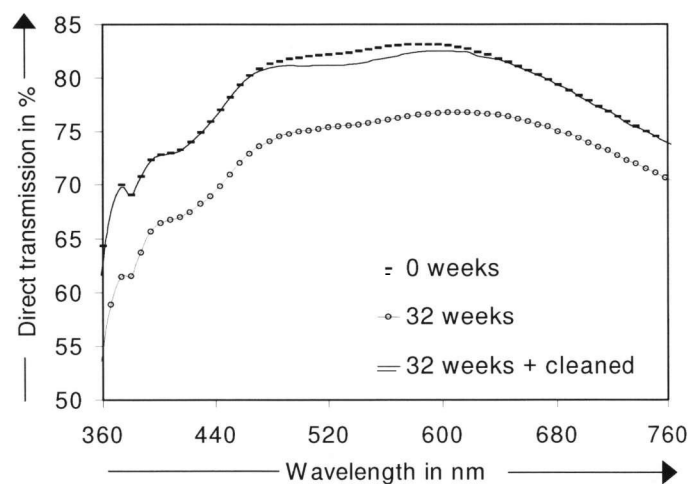
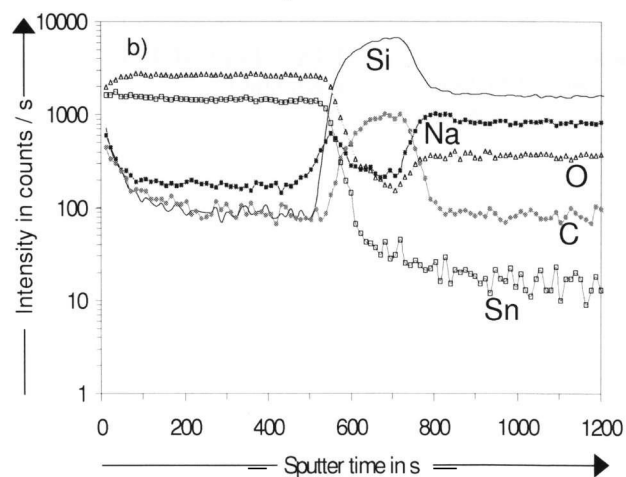
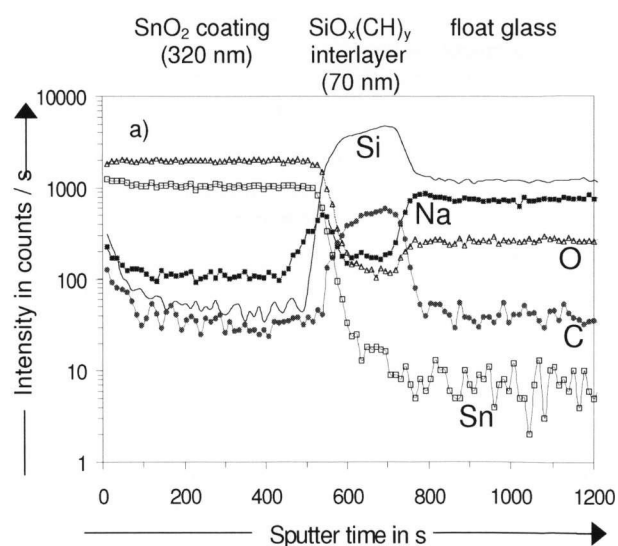


Figure 4: Direct transmission,  $T_{\text{direct}}$ , of K-glass before weathering, after weathering for 32 weeks, and after weathering and cleaning.

equal coating thickness. Within the first 150 nm, the sodium signal increases significantly. After 32 weeks of exposure, the surface signal  $I_s$  (after 50 s of sputtering) is by a factor of 3.5 higher than the background  $I_B$  in the  $\text{SnO}_2$  layer. For the unaltered sample,  $I_s/I_B$  amounts only to 2. Similar increases in  $I_s/I_B$  are detected for carbon and silicon (see table 2).

Traces of sulfur have also been detected in the coating, the signal is constant with no enhancement close to the surface. A quantification of the minor components is meaningless in this region.

The time axis cannot be linearly transformed into a depth scale as the sputter rate increases with the conductivity and decreases with the density [10]. For float glass, sputter rates amount to 0.2 to 0.3 nm/s [4 and 6]. Knowing the thickness of the coatings ( $\approx 320$  nm for  $\text{SnO}_2\text{:F}$  and  $\approx 70$  nm for  $\text{SiO}_x(\text{CH})_y$ ), the following sputter rates can be deduced: 0.6 nm/s for  $\text{SnO}_2\text{:F}$ , and 0.2 nm/s for  $\text{SiO}_x(\text{CH})_y$ .



Figures 5a and b. SNMS depth profiles of a) new, unexposed K-glass, and b) K-glass after weathering for 32 weeks. After a sputtering time of 550 s, the interface between the 320 nm thick  $\text{SnO}_2$  coating and the silane interlayer is reached (sputter rate  $(0.64 \pm 0.2)$  nm/s).

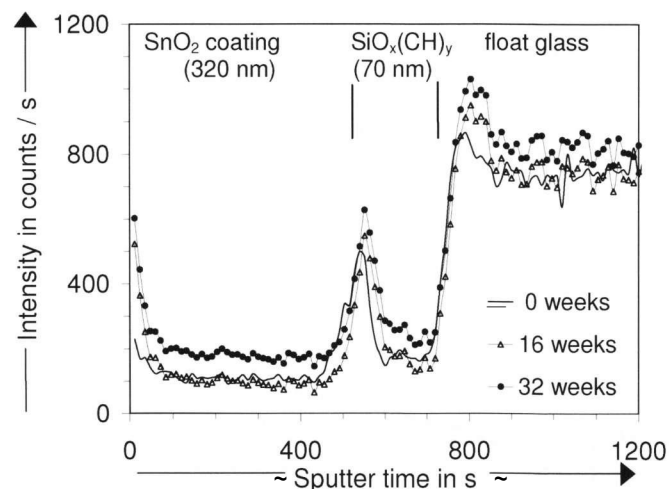


Figure 6. SNMS depth profiles of sodium in K-glass after weathering for 0, 16 and 32 weeks (corrected for different coating thicknesses).

### 3.3 Topography

Figures 7a to c show the nanoscale topography of a sample unexposed and after eight and 32 weeks of expo-

Table 2. Increase of the surface signal,  $I_S$ , compared to the background in the coating,  $I_B$

	$I_S/I_B$	
	10 weeks	32 weeks
Na	2	3.5
C	3.5	4.5
Si	5	7

sure. Please note the change of the axes, the differences in topography cannot be displayed with the same scaling.

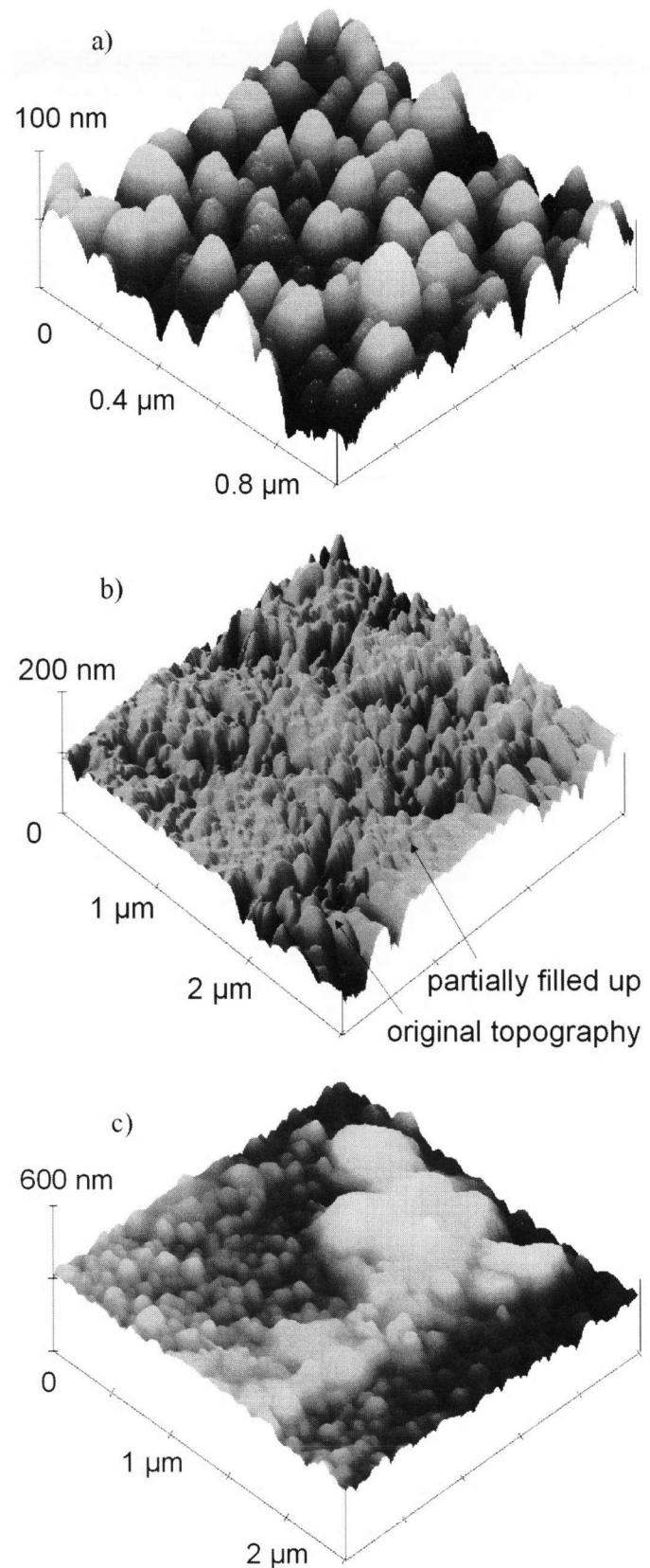
AFM images of new clean K-glass display crystal columns with typical diameters of about 100 to 300 nm and some 10 nm deep valleys between them. The root mean square (rms) roughness of  $(10 \times 10) \mu\text{m}^2$  large images amounts to  $(10 \pm 1) \text{ nm}$  and does not change with the scanning area (see table 3). In contrast to uncoated float glass stored for some weeks in laboratory air, this topography stays uniform on large areas for weeks or even months. On the weathered samples, changes could be detected not before eight weeks. As is shown in figure 7b, in some areas of the surface the valleys between the columns are partially filled up, the roughness increases slightly to  $\text{rms} = 12 \text{ nm}$ .

After 32 weeks, the surface is not uniform any more. In some  $\mu\text{m}^2$  large areas, the original topography can still be recognized. Others are partially or totally covered. The maximum scanning range of  $(100 \mu\text{m})^2$  of the AFM is not sufficient for an appropriate quantification of the coverage. Figure 7c gives an example for a region which is covered with particles that are much larger than the coating grains, with diameters of some  $\mu\text{m}$  and some 100 nm high. These particles can either be distributed randomly over the surface or they are arranged in parallel stripes as shown in figure 8.

#### 4. Discussion

The most sensitive instrument to detect the minute changes on the weathered K-glass surface proved to be the AFM. After eight weeks the covering of the coating becomes measurable. The chemical constitution of the contamination, however, cannot be revealed as the other methods do not yet note any degradation and even after 32 weeks the changes are minute. The sizes of the particles on the AFM images of some 100 nm to some  $\mu\text{m}$  are similar to the sizes of aerosol particles.

The increase in some minor elements in the surface after 32 weeks can be interpreted as surface contamination, as the profiles of the major elements and the other minor elements do not change. Probably, this contamination is mainly on the  $\text{SnO}_2$  crystal columns and



Figures 7a to c. AFM images of K-glass surfaces (note the changes of scaling), a) new, unexposed; b) after eight weeks: partially covered; c) after 32 weeks: example for an area covered by a particle some 100 nm high and some  $\mu\text{m}$  in diameter (probably an aerosol aggregate).

in the valleys between them, but not built into the crystal lattice. The depth of 150 nm of the enhanced SNMS sig-

Table 3. Root mean square (rms) roughness of unexposed and weathered K-glass (in nm), measured on different scanning areas (in  $\mu\text{m}$ )

weathering time in weeks	scanning area		
	$1 \times 1$	$10 \times 10$	$50 \times 50$
0	10	$10 \pm 1$	$11 \pm 1$
8	$13 \pm 1$	12	$12 \pm 1$
16	10 to 14	$(14 \pm 1)^{1)}$ $24^{2)}$	$(17 \pm 2)^{1)}$ $27^{2)}$
32	10	$(10 \text{ to } 33)^{1)}$ $(60 \text{ to } 120)^{2)}$	$(27 \text{ to } 35)^{1)}$ $(55 \text{ to } 110)^{2)}$

<sup>1)</sup> Without particles.

<sup>2)</sup> With particles.

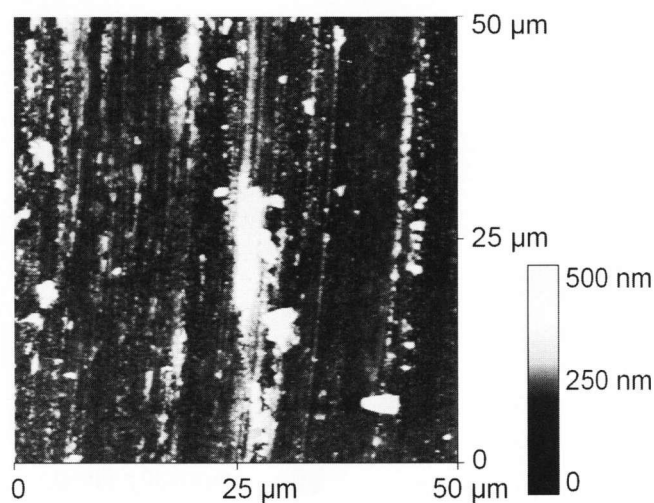


Figure 8. AFM image of a K-glass surface weathered for 32 weeks; in some regions, the contamination particles are arranged in parallel stripes.

nal fits well the AFM observation of the valley depth of new K-glass.

Two possible explanations could be found for the increase in the sodium, carbon, and silicon surface signal after exposure:

- intrinsic impurities, e.g. from the grain boundaries of the coating, from the interfaces, or glass components could diffuse to the surface and form corrosion products with air constituents;
- extrinsic contamination like hydrocarbons, and fine dust from soils and industrial emissions could accumulate on the surface.

The initial corrosion steps of uncoated alkali silicate glasses in humid air can shortly be described by an interdiffusion of alkali ions and water species and a formation of carbonates, sulfates, and hydroxides on the surface [11 to 14]. The corrosion products of the initial stages are highly soluble in water and are slowly transformed into products with low solubility. The K-glass coating contains only trace impurities of alkali and the samples have been rinsed by the rain. That is why typical

glass corrosion products like alkali carbonates/hydroxides/sulfates do not play an important role on K-glass. Only those soluble products can be found that have formed after the last rainfall. Thus, extrinsic contamination dominates the degradation. The contamination on the samples must be those fractions of environmental aerosols which are not easily dissolved in rain or recrystallize when the wet surface dries.

Stripes of particles similar to those in figure 8 have also been found on uncoated float glass after corrosion experiments. In that case, they were interpreted as wiping traces of the cleaning process before corrosion [11 to 14]. The stripes on the weathered K-glass could also be explained as traces of raindrops.

The decrease in the IR bands around  $1000 \text{ cm}^{-1}$  which are typical for Si-O-Si and Si-OH bonds in the glass is also consistent with a covering of the valleys. Sand, feldspars and clay minerals, which are components of atmospheric dust, have similar vibrations, obviously, the amount of silicates in the dust is not high enough to be detectable. No new bands arise, which could indicate C-H, C=O, C=N or other typical vibrations of hydrocarbons. Interference effects contribute to the behavior at short wavelengths below 500 nm. Filling the valleys with contamination particles changes the interference effects.

In summary, it can be stated that the weather-induced contamination slightly enhances the VIS-range absorption of the  $\text{SnO}_2$  low-emissive coating but does not affect its high IR reflection. The products which accumulate on the surface absorb visual radiation but are not IR active. They are soluble in water and alcohol and can be rinsed off. The visible degradation is reversible and does not affect the low-emissive properties of the insulating coating.

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The authors gratefully acknowledge the help by Interpane, Lauenförde, Forschungszentrum Jülich, and Pilkington Deutschland AG. The work of Anna Buksak was subsidized by an Erasmus grant.

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