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Atomic force microscopy study on the anatase crystallization of long term stored Al_2O_3-TiO_2-SiO_2 coatings on glass

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Atomic force microscopy was used to study the surface morphology of sol-gel derived Al_2O_3-TiO_2-SiO_2 coatings on microscope glasses. The coatings freshly annealed at 500 °C for 1 h were homogeneous on a nanoscale and showed typical glass pattern. After 10-month storage in air either before or after annealing, tetragonal-like crystallites were observed in coatings. The effects of chemical compositions and the storage process on the surface topography and the crystallization of anatase were studied and discussed in combination with the XRD results of corresponding annealed gels.

1. Introduction

Various crystalline and non-crystalline coatings were deposited on glass to improve the behaviours of glass, such as optical, electrical, mechanical, thermal and chemical properties, or to give glass new high performances [1–3]. TiO_2 coatings and TiO_2-containing coatings are widely used on solar reflecting glasses, on rear view mirrors, on heat mirrors, and as anti-reflective coatings. Due to their good resistance against alkaline solutions Al_2O_3-TiO_2-SiO_2 coatings are attracting the attention of many scientists. Their alkaline resistance is strongly controlled by their surface state. The recently developed atomic force microscopy is an ideal tool to study the nanoscale morphology of non-conductive solid surfaces such as the glass and the oxide coatings [4–6]. In this work, TiO_2 and various Al_2O_3-TiO_2-SiO_2 coatings were prepared on microscope slides from alkoxide solutions, their nanoscale morphologies after heat treatments were studied using atomic force microscopy. Especially the anatase-crystallization in these coatings during 10-month storage in air either before or after heat treatment was investigated and discussed in combination with the XRD results.

2. Experimental

Several solutions and gels were prepared in TiO_2 and xAl_2O_3-$yTiO_2$-$zSiO_2$ system ($x = 0$–30, $y = 25$–60, $z = 20$–65 mol %). AR grade tetraethyl orthosilicate, titanium butoxide aluminium-iso-butoxide and anhydrous ethanol were used as received. The coatings were deposited on dried microscope glass slides by dip-coating. The coatings after dried in air were heated at 1 °C/min to 500 °C and held there for 1 h. The detail of the preparation was described elsewhere [7, 8]. Some of them were stored in desicators for long time either before or after heat treatments.

The thickness of coatings was measured with a profilemeter (Long Scan Profiler P-1, Tencer, Munchen, Germany). Its accuracy is about ±10%. The topography of the coatings was investigated by AFM (Nanoscope II with A-head, Digital Instruments, Inc., Sante Barbara, CA, USA) with a maximum scanning range of 1 μm^2. Si_3N_4 tips were used. The temperature was 20 °C, the relative humidity was 40%. For any sample more than 24 points were scanned to ensure the reliability and reproducibility.

The gels were heated at 1 °C/min to the desired temperature and held for 4 h. Crystalline phase were detected by XRD (PW 1729, Philips, Kassel, Germany).

3. Results and discussion

3.1. Surface morphology of freshly annealed Al_2O_3-TiO_2-SiO_2 coatings

Table I shows the chemical compositions, thicknesses and the mean values of the AFM measured rms roughnesses (rms = root mean square) of coatings, and the crystallization status of corresponding gels.

The AFM height mode images of freshly annealed binary and ternary coatings show that A_0 to A_{10} coatings all display typical glass pattern (see Fig. 1). There is only small difference in roughness between them, for example, the surfaces of coating A_2 and A_6 are

TABLE I Designed composition, thickness, rms value of coatings and crystallization status of corresponding gels

Sample	Composition (mol %)			Thickness (nm)	RMS (nm)	Status	
	Al_2O_3	TiO_2	SiO_2			700 °C	800 °C
A0	0	35	65	80	0.56 ± 0.10	am	am
A1	10	25	65	80	0.54 ± 0.15	am	am
A2	20	25	55	70	0.54 ± 0.09	am	am
A3	10	40	50	75	0.69 ± 0.10	am	a (tr)
A4	10	50	40	75		a (tr)	a
A5	15	25	60	50	0.62 ± 0.09	am	am
A6	5	40	55	80	0.58 ± 0.08	am	a
A7	20	40	40	85	0.66 ± 0.17	am	a
A8	20	50	30	80	0.66 ± 0.11	a	a
A9	30	40	30	90	0.77 ± 0.12	a	a
A10	20	60	20	90	1.0 ± 0.20	a	a

am - amorphous, a - anatase, tr - trace.

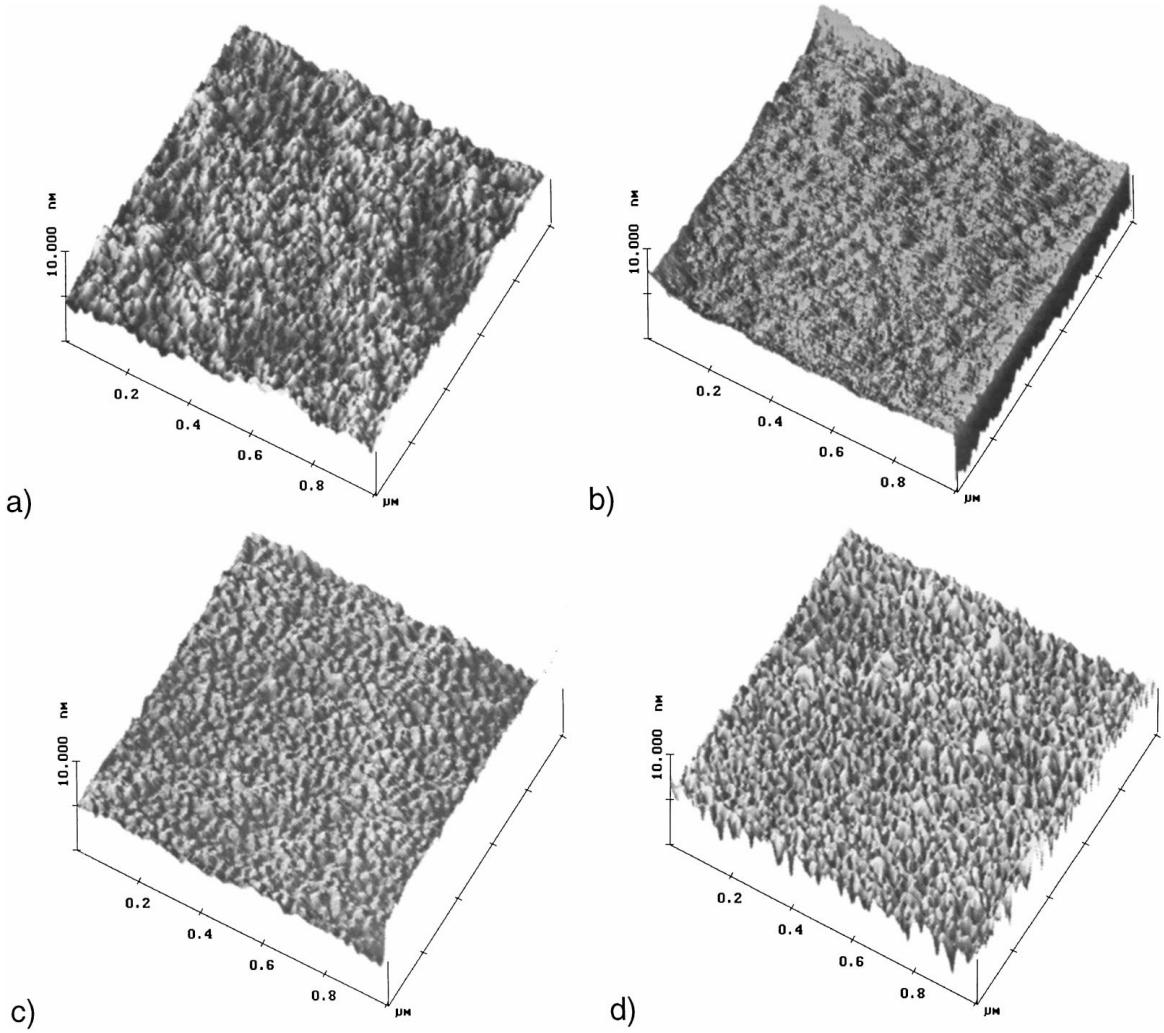

Figure 1 AFM height mode images of freshly annealed TiO_2-SiO_2 and Al_2O_3-TiO_2-SiO_2 coatings on microscope glasses (a) A_0; (b) A_2; (c) A_3; (d) A_{10}.

relative plane with small rms values 0.54 and 0.58 nm while coating A_9 and A_{10} show surfaces with sharp ripples, especially A_{10} with the greatest rms value 1.0 nm (see Table I). The surface roughness seems to be related to its chemical composition. The higher the TiO_2 and Al_2O_3 content is, the more quickly the hydrolysis and the condensation polymerization proceeds, which leads to a higher viscosity of the solution. It should be responsible for the higher rms values.

3.2. Effect of long-term storage on the surface morphology

3.2.1. 10-month storage in air after annealing

Fig. 2 displays some AFM height mode images of A_1 to A_4 coatings which had been stored in desicators under air atmosphere for 10 months after heat treatment (note the different in Z range). In Fig. 2a whose gray scale in Z is 0–30 nm, there are many granules whose size

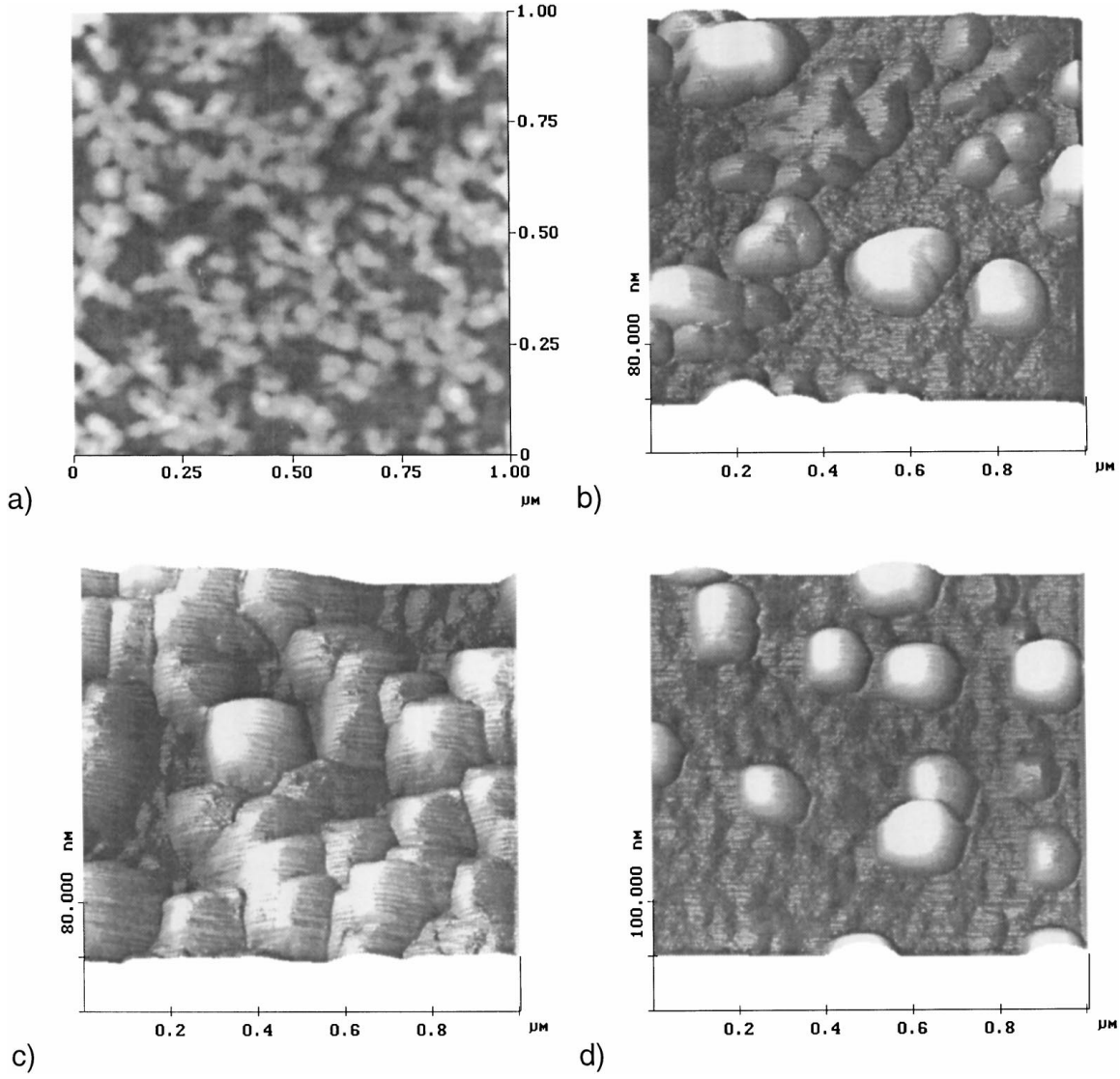

Figure 2 AFM images Al_2O_3-TiO_2-SiO_2 coatings (a), (b), (c) and (d) are A_1, A_2, A_3, A_4 coatings kept in a desiccator at room temperature for 10 months after annealed at 500 °C for 1 h.

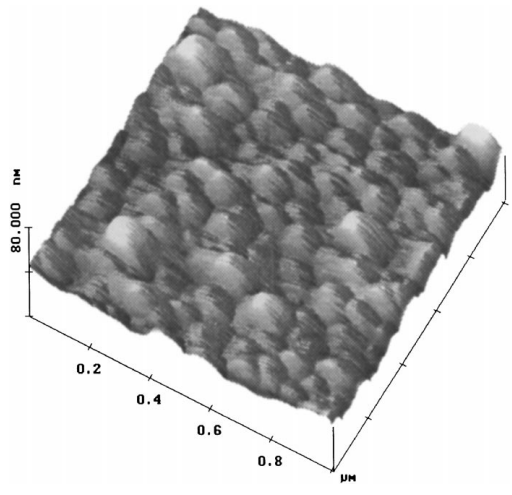

Figure 3 AFM height images of TiO_2 coatings annealed at 550 °C for 40 min.

is about 15–25 nm and height is about 5–10 nm. Their shape is some similar to those convex geometries in Fig 3b. After 10-month storage in air some tetragonal-looking crystallite were developed in A_2 coating, a few of which show clear tetragonal shape with lateral size 120–140 nm, height 5–15 nm. The shape of tetragonal crystals in A_3 coating (Fig. 2c) looks much clearer and more regular than those in A_1 and A_2 coatings. They are 100–200 nm large and 4–18 nm high, also larger and higher than those in A_1 and A_2 coatings. In A_4 coating many tetragonal crystals are detected by AFM (Fig. 2d). They are 150–200 nm large and 10–60 nm high. On its ground there are many lower tetragonal.

Fig. 3 shows the AFM hight mode images of single TiO_2 coatings. The XRD results indicates that the tetragonal crystallite is anatase [8]. By comparing Fig. 2 and Fig. 3 it could be deduced that the tetragonal crystallite in Fig. 2a–d should be anatase. It seems that anatase crystallites were formed in these TiO_2-containing coatings during long term storage. Their amount, size and perfectness degree are related to the chemical composition of the coatings, increasing in order $A_1 < A_2 < A_3 < A_4$, i.e. increasing with the TiO_2 content, which is in accordance with the crystalline status of corresponding gels displayed in Table I. A_1 and A_2 coatings contain same TiO_2 content (25 mol %), but larger anatase crystals with more regular shape

appear in A_2 which contain 10 mole % more Al_2O_3 than A_1. The presence of Al_2O_3 possibly facilitates the crystallization of anatase, which is in consistence with the results achieved by IR and XRD investigation of Al_2O_3-TiO_2-SiO_2 gels. Al_2O_3 in the Al_2O_3-TiO_2-SiO_2 gels reduces the crystallization temperature of anatase and decreases the amount of the mixed Ti-O-Si linkage [8].

3.2.2. 10-month storage in air before annealing

After dip-coating some A_5 coatings were stored in desiccator for 10 months, then annealed at 500 °C for 1 h. Fig. 4 shows the AFM image of such A_5 coating. In Fig. 4 exist a serial connected tetragonal crystallites. From right to left their size changes gradually from 50 to 100 nm, their height changes from 2 to 14 nm. Perhaps here was a surface contamination or a scratch trace, which promoted the formation of anatase nuclei during storage. They then grew up during the heat treatment.

All these indicate that during long-term storage either before or after heat treatment TiO_2 in coatings tends to crystallize as anatase, whose amount, size and perfectness depends mainly on the chemical composition of coating. The crystallization of anatase during long term storage could be attributed to the following two points.

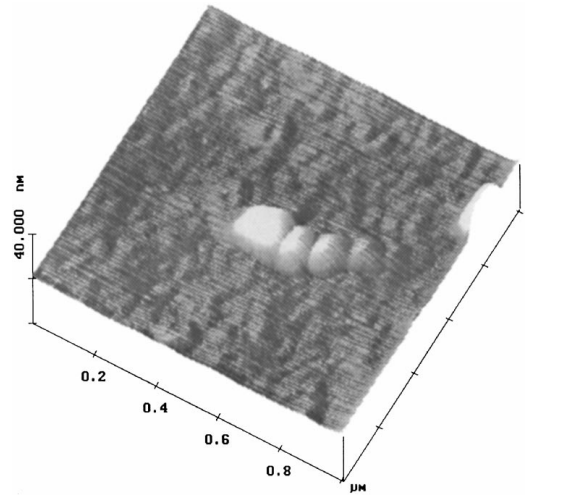

Figure 4 AFM images of A_5 coating annealed (500 °C, 1 h) after 10-month storage in a desiccator.

At first, because of the great special surface TiO_2 coatings has originally a stronger tendency to crystallize as anatase than bulk materials. TiO_2 coating on float glass (solar reflecting glasses) crystallizes completely after heat treatment [6], that is one powerful evidence. Secondary, during dip-coating and storage the surface were possibly contaminated by dusts or absorbed H_2O vapor or CO_2 and so on. They formed tiny particle clusters, which aggregated or grew up to form nuclei or acted as embryos for nucleation during the long term storage. Under appropriate condition they developed and became nuclei or crystallite which can be resolved by AFM.

4. Conclusion

The AFM study on the alkoxide-driven Al_2O_3-TiO_2-SiO_2 coatings on glass shows: 1. The nanoscale topography of various freshly annealed Al_2O_3-TiO_2-SiO_2 coatings exhibits a typical glass pattern. Their rms roughnesses are related to their chemical composition, increasing with the increase of TiO_2 and Al_2O_3 contents. 2. After 10-month storage in desiccator under air atmosphere either before and after annealing, tetragonal anatase crystallizes in A_1–A_5 coatings. Their amount, size and degree of perfectness increase gradually with the TiO_2 and Al_2O_3-content.

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