Original Paper

Thickness of thin films on glass – a round robin test

Report of the International Commission on Glass (ICG) Technical Committee 19 "Glass Surface Diagnostics"

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The film thicknesses of five different layer systems on glass substrates were analyzed and determined in a multi-method approach by eight different university and industrial laboratories. The total coating thicknesses varied between a few nm up to some 100 nm. The measurements give information about the chemical composition and cover a wide spectrum of typical coating application on glasses. The results of the different laboratories and methods are compared and the challenges and limits of the various analytical techniques are discussed.

1. Introduction

Modern products based on glass are often coated with functional films to optimize the performance of the surfaces. Physical as well as chemical properties are the targets. The films influence properties such as optical (reflecting, anti-reflecting, filter), mechanical (anti-scratching), adhesive (easy-to-clean), and blocking behavior (diffusion barrier). The film thickness is a key issue for all these very different functionalities. Therefore the characterization of thin films on glass – and in particular the determination of the film thickness – is a very important topic. All members of the thin film community, i.e. the producers, vendors and customers, prove this specification in general with different analytical equipment, because up to now surface and thin film analysis is not a characterization technique with a fixed and globally accepted standardized procedure.

The Technical Community 19 "Glass Surface Diagnostics" of the International Commission on Glass (ICG) has a vision "to establish the best and most effective methods of characterizing the topology, chemical composition, and reactivity of the surface and subsurface of glass (down to nm scale)". Pursuing this vision, it was a logical step to test the available equipment of the members of TC 19 in a round robin investigation on samples produced in their industrial facilities, so that the samples are of actual relevance and not optimized reference systems without practical use. The task was to determine the total thickness of the various samples with available methods in the different laboratories and then to compare the quality of the results. The measurement parameters and the preparation techniques were free of choice. The aim was to prove the accuracy and comparability of results delivered from diverse laboratories being familiar with the insulating substrate material glass.

This communication reports on investigations of five different samples coated with typical functional film systems, which are produced with industrial equipment. Nine different types of analytical techniques are used. The results obtained on inorganic single, double and triple layer systems and one single organic layer on glass are described in detail, and the advantages and disadvantages of the various techniques for investigating the various layer systems are discussed.

2. Experimental details

2.1 Samples

The samples were produced in five different university and industrial laboratories. All coated samples of each type were

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Table 1. Samples investigated

sample no.	substrate	film system	deposition techniques	producer	number of layers	layer thickness in nm
1	float glass	TiN	DC-SP	Sisecam	one	100
2	alumino silicate glass	C / Ti	DC-SP	Hoya	two	12, 20
3	float glass	SnO_2 / SiO_2 / SnO_2:F	CVD	Pilkington	three	600, 25, 25
4	float glass	SiOC	CVD	Hoya	one*)	≈ 40
5	borosilicate glass	polyimide	CVD	Trent Univ.	one	300

*) Inhomogeneous layer.

manufactured under identical conditions. Both, thin single layers and multilayer coatings were deposited with different composition types, which varied over the inorganic and organic material spectrum. As substrate material, soda-lime, borosilicate and alumino silicate glasses were employed. The samples are summarized in table 1.

The samples were distributed to the members of Technical Committee 19 "Glass Surface Diagnostics" to perform a round robin investigation.

2.2 Instruments

Each participating laboratory was allowed to analyze the samples according to its own quality regulations and with a free choice of employed techniques. Thus nine different techniques and different instruments were used to perform the measurements. A brief overview of these techniques can be found elsewhere [1 to 3]. A detailed description of every parameter set in this paper would not be target group oriented. Therefore, only the employed techniques are shortly described.

2.2.1 Secondary ion mass spectrometry (SIMS)

For depth profile measurements, dynamic secondary ion mass spectrometry (SIMS) (Cameca 3F) and time-of-flight (TOF)-SIMS equipment (Ion-TOF, Physical Electronics) were employed. All the systems used ion bombardment to erode the films, followed by a profiling technique to determine the sputter crater depth/erosion rate.

2.2.2 Grazing incidence X-ray analysis (GIXA)

Grazing incidence X-ray analysis (GIXA) provides three types of information, which can be extracted from the reflectivity versus angle of incidence curves:

- density δ of the coated layers and of the substrate,
- thickness d of the layers,
- surface and interface roughness σ (rms value).

Commercially available systems were used (X'Pert/Philips; D5000, Siemens).

2.2.3 X-ray induced photo-electron spectroscopy (XPS)

For the X-ray induced photo-electron spectroscopy (XPS) technique different commercial XPS instruments are available for characterizing the surface composition. Two methods, "angle variation of the incident X-ray beam" and "ion bombardment for sputter erosion" were employed to determine the film thicknesses. The results reported in this paper were gained with XSAM 800, AXIS 165 (Kratos) and PHI 5400MC, PHI Quantum 2000, PHI 5500 (Physical Electronics).

2.2.4 Scanning electron microscopy (SEM/EPMA)

The surface topographies and thicknesses were determined by analyzing cross sections of the coated samples with scanning electron microscopy ((SEM), LEO DSM 982, LEO 1550). The cross sections of the samples were prepared by breaking or polishing techniques and coated with monolayers of a conducting film to avoid charging effects.

2.2.5 Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) was also applied by using a 200 keV instrument, JEM-2000EX (JEOL), after applying thinning preparation techniques.

2.2.6 Rutherford backscattering (RBS)

The Rutherford backscattering (RBS) experimental conditions were: E_a = 2.2 MeV, Θ_s = 160°, normal incidence.

2.2.7 Glow discharge optical emission spectroscopy (GD-OES)

Glow discharge optical emission spectroscopy (GD-OES) analyses were performed using a HORIBA-GDOES (JY-5000RF). The samples were sputtered in an argon atmosphere of 400 Pa by applying an R.F of 13.56 MHz and a power of 30 W. Light emission of characteristic wavelengths associated with the sputtered species was monitored throughout the analysis to obtain depth profiles.

3. Results

3.1 Sample 1: TiN on soda-lime glass

This single-layer sample was investigated in eight different laboratories. The thickness and the material composition

Table 2. Thickness values of sample 1 (TiN/glass) in nm, determined with several different analysis techniques

laboratory	XPS	GIXA	Profil	SEM	GDS	RBS	SIMS	TEM
Schott	126	103						
Pilkington	110				105			
Saint-Gobain						77*)	112	
Padua Univ.		97		104			104	
Hoya								100
Asahi			100					
Penn State Univ.		98	98	100			98	
Trent Univ.	172*)							

*) Outlier.

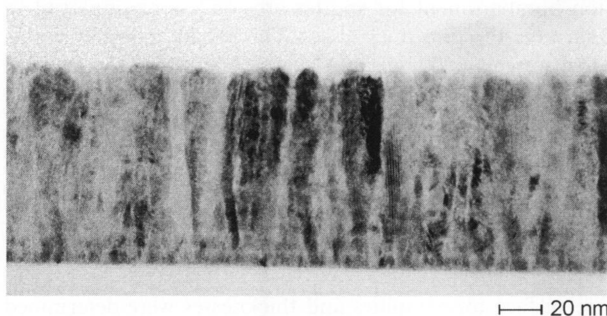

Figure 1. TEM image of a cross section of sample 1 (TiN on soda-lime glass).

are closer to "standard samples", so there are many results, gained with up to nine different methods.

The sample producer specifies the TiN layer thickness to be 100 nm.

The data listed in table 2 show the results. Measurement techniques that are able to deliver the thickness information directly (such as SEM cross sections, GIXA, mechanical profilometer) are closer to the specification than the other analysis techniques. From all measurements, a mean value of 103.9 nm was calculated with a standard deviation of ±7.8 nm. This is in a good agreement with the specified value and indicates that single-layer determination on flat glass belongs to state-of-the-art analysis. Two of the results are marked as "outliers". In both cases the thickness was calculated using theoretical values for stopping powers and sputter yields.

The drastic mismatch is related to inadequate material parameters, which had been determined for different chemical matrices. The film morphology is depicted in figure 1, which shows a TEM cross section of the film and the substrate. The film has grown into a column-like structure. Due to the flat substrate-film interface, the layer thickness was easily determined and found to be 100 nm.

3.2 Sample 2: Double layer on alumino silicate glass

Sample 2 was a two-layer coating with producer-specified parameters: 15 nm carbon on 20 nm titanium, followed by an alumino silicate substrate. Five laboratories analyzed the sample with six different techniques (table 3).

Table 3. Total thickness values of sample 2 (C/Ti on glass), determined with several different analysis techniques

laboratory	XPS	SIMS	SEM	GIXA	EPMA
Schott	41				
Padua Univ.		30	40	36	41
Hoya	33				39
Penn State Univ.		44[2] 36[3]		37	
Trent Univ.	24[1] 63[1]				

[1] Outlier.
[2] Mechanical proof.
[3] Optical proof.

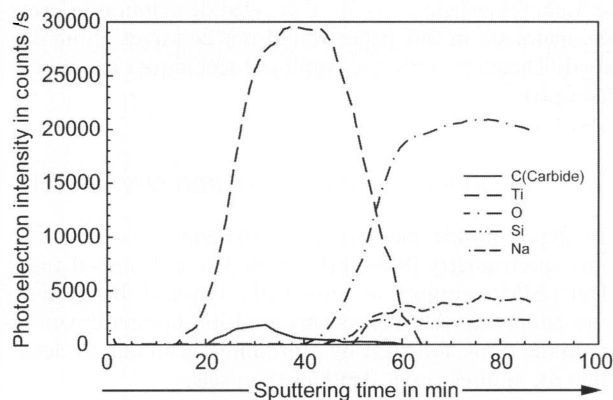

Figure 2. XPS depth profile of sample 2 (C/Ti on glass).

XPS results of Trent University laboratory were calculated by using sputter yields and density values of the literature (the same as for sample 1). The mean value of the data (not including outliers) is 37.7 nm with a standard deviation of ±4.2 nm. The measured results are in good agreement with producer's specification. GIXA, SIMS, and XPS easily determined the thickness of the single layers. In the interface region between the C and Ti layers, mixing was found which is related to TiC (binding type carbide, figure 2). The layer density varies between 1.4 g cm^{-3} for the C-layer up to 4.6 g cm^{-3} in the case of the Ti-layer.

3.3 Sample 3: Triple layer on glass

The coating of this sample type was a combination of a thick top layer (600 nm SnO_2:F) followed by two thin ones

Table 4. Thickness values of sample 3 (Sn_2O:F/SiO_2/SnO_2/glass) in nm, determined with several different analysis techniques

laboratory	XPS	Profil	SEM	GDS	RBS	SIMS	TEM
Schott	634	484	623				
Pilkington	645			682			
Saint-Gobain					470[1]	549	
Padua Univ.			550			625	
Hoya							480
Penn State Univ.			640			574[2] 545[3]	
Trent Univ.	380[1]						

[1] Outlier.
[2] Mechanical proof.
[3] Optical proof.

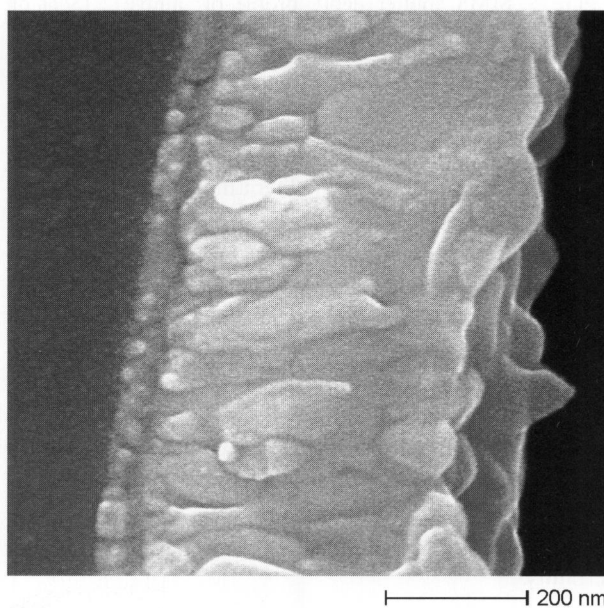

Figure 3. SEM cross section of sample 3 (SnO_2:F/SiO_2/SnO on glass).

(25 nm SiO_2 and 25 nm SnO_2). Investigations were done with seven different methods by seven laboratories (table 4). For the same reasons discussed for samples 1 and 2, the marked "outlier" results have not been not taken into account for the mean value calculation of 585.9 nm with a standard deviation of ±65.3 nm. In comparison with producer's specification, the measured film values indicate that the total film thickness must be lower than defined, but with a broad distribution of the single results. The grainy design even in the thin layers is visible in figure 3.

3.4 Sample 4: Inhomogeneous single layer on glass

The coating consisted of a single layer of SiOC and was investigated with four different methods by three laboratories (table 5). The mean value for the film thickness is 36.4 nm with a standard deviation of ±5.5 nm. The distribution of the resulting values is fairly small.

The film surface indicates (figure 4) that this coating produces an inhomogeneous topography with many small bumps. Nevertheless all the analysis methods, which are relatively insensitive to lateral resolution, yielded comparable results.

Table 5. Thickness values of sample 4 (SiOC/glass) in nm, determined with several different analysis techniques

laboratory	XPS	SEM	SIMS	GIXA
Schott	40	30[1] 28[2]		
Padua Univ.			45	37
Penn State Univ.			39[1] 34[2]	38

[1] Mechanical proof.
[2] Optical proof.

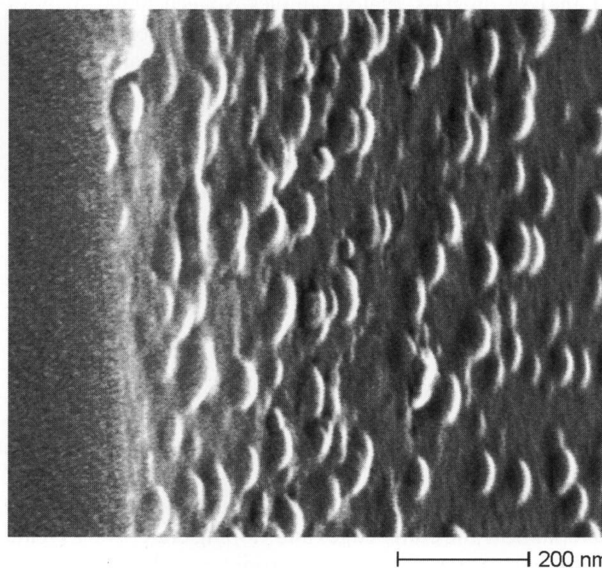

Figure 4. SEM image, depicting the surface and a part of a cross section of sample 4 (SiOC on glass) by using a tilt angle of 5°.

3.5 Sample 5: Organic layer on borosilicate glass

The last sample was investigated by three laboratories employing five different methods (table 6). The sample and

Table 6. Thickness values of sample 5 (polyimide/glass) in nm, determined with several different analysis techniques

laboratory	SIMS	SEM	GIXA	EPMA	Profil
Saint-Gobain					300
Padua Univ.	295	335 320 (BSE)	309	312	
Penn State Univ.	280[1)] 305[2)]	300			

[1)] Mechanical proof.
[2)] Optical proof.

consisted of about 300 nm of polyimide on borosilicate glass, the mean value of the layer thickness being (306.2 ± 15.6) nm.

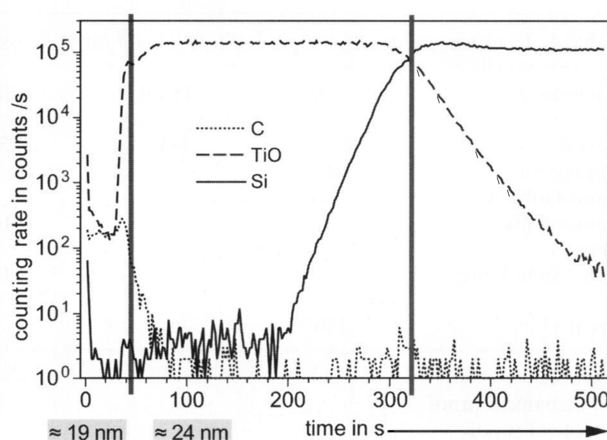

Figure 5. SIMS sputter depth profile of sample 2 (S/Ti on glass); the interfaces are additionally marked.

4. Discussions

The five different sample types represent a typical variety of films that are deposited onto glass substrates. The highly insulating substrate material requires in principle more sophisticated analyzing techniques and more operator experience. Otherwise, a lot of artefacts, for example charging effects, will hamper the quality of the results. Sample 1 with a 100 nm single TiN layer is a fine example for state-of-the-art analysis on glass-related samples. Sixteen single analyses were carried out in eight different laboratories. The mean value of 103.9 nm and the small standard deviation of only ±7.5 % demonstrate the quality of the results.

Analysis techniques such as GIXA, profilometry, SEM or TEM, which directly produce thickness values, are more accurate (mean value: (100.0 ± 2.4) nm) than sputter techniques such as SIMS, XPS, GDS (mean value: (109.2 ± 36.4) nm). These latter techniques erode the sample surface and produce a crater in the sample surface. For the thickness determination, the erosion process must stop immediately at the interface, and this position has to be determined from the detected signals (e.g. reduction of the main film element signal down to 50 % of its average value in the layer). To obtain the layer thickness, the crater depth has to be analyzed by optical or mechanical profiling systems. The results are only as good as the flatness and symmetric geometry of the crater bottom. Re-deposition of the sputtered material near the crater edges and sloping crater walls create additional measurement uncertainties. The tendency towards higher than expected thickness values shows that the operator typically stops the sample erosion too late, because the 50 % decrease of the main signal is not easy to define during the running process.

These types of measurement are not designed for determining film thickness primarily. Especially the results marked as outliers in table 1 point at inherent inadequacies. In the case of the "outlier" marked XPS measurement as well as for RBS the exact knowledge of the layer density, the chemical composition, and the total sputter yield (only XPS measurement) are needed. It is well known from the literature that the film density strongly depends on the coating techniques and the chosen parameters [4 and 5]. In the case of SiO_2 [6] the density of SiO_2 layers on glass is reported to vary between 1.82 and 2.30 g cm^{-3}, and the value for quartz glass is given in the literature as 2.20 g cm^{-3} [7].

Therefore the use of standard values for physical properties (stopping power, sputtering yield, etc.) and chemical compositions (binding energies, etc.) lead to results that are sometimes far from the real circumstances.

The design of sample 2 is more challenging because of the single-layer thicknesses of only 15 and 20 nm. The results indicate a behavior similar to sample 1: the most accurate values resulting from direct measurement methods such as GIXA.

The measurements of the two layer thicknesses confirmed the producer's specification, within experimental uncertainty.

In contrast, depth profile methods such as SIMS or XPS with sputter erosion provide additional information, for example the elemental distribution with depth, which is often more interesting than the total thickness. Figure 5 shows a SIMS depth profile of sample 2. It clearly indicates why a theoretical approach using the physical properties from literature data yields critical results. When sputter techniques are used, the measurement signals are detected as a function of time. This time scale then has to be converted to a depth scale. In the interface between the carbon and titanium layers and the interface between the titanium layer and the substrate a mixing of both interface partners exists and therefore the physical and chemical parameters have to be adapted. Furthermore, diffusion of Si into the Ti-layer is visible, which changes both the density and sputter yield of the layer. For such small single layers as used in sample 2 the interface region is comparable with the layer thickness and the determination of the exact interface is therefore critical. The drastic change of the sputter behavior is also visible: the C-layer is 25 % thinner than the Ti-layer, but the erosion time for the Ti-layer is more than six times longer.

In the case of sample 3 the thickness limit of GIXA is exceeded due to the presence of a thick top layer followed by two thin ones. The sputter techniques show the problems as discussed, so that SEM would be the best choice to obtain reliable results (see also figure 3). Even then, the morphology of the bottom layer causes slight problems in defin-

Table 7. Mean deviation (in %) of the measurement results from producer's specifications

sample 1	sample 2	sample 3	sample 4	sample 5
7.5	11	11	15	5

Table 8. Mean deviation (in %) of the measurement results from producer's specifications related to the analysis techniques

XPS	SIMS	GIXA	SEM
8.2	9.2	3.3	6.2

ing the correct interface. With sample 4 GIXA's strong points become apparent. This analytical technique integrates over a wide range (some mm), so that lateral inhomogeneities are smoothed.

Most of the above-mentioned surface analysis techniques are still appropriate for the analysis of organic material, as demonstrated with sample 5. As long as the impact energy flux is not critical for the organic film structure, any kind of charged particles (ions, electrons and X-ray photons) can be applied.

5. Conclusions

In principle, surface and thin film analysis is a commonly used approach to characterize the chemical composition, topography, and morphology of coating layers as well as elemental gradients through the films and at the interface regions. Most of the investigations are done in comparison to a reference sample, so only relative changes are taken into account for the interpretation. However, when absolute values are required, e.g. film thickness, the methods are limited, as shown in this paper. All participating laboratories were familiar with these kinds of highly insulating samples and therefore able to use their standard equipment. The measurement parameters and preparation methods were freely selected by each laboratory.

Table 7 shows the mean deviation of the measurement results from producer's specification. Homogeneous single-layer samples (no. 1 and no. 5) are easier to characterize than multilayers (no. 2 and no. 3). In general, an experimental uncertainty of 10 to 15 % has to be assumed for the analysis of unknown samples. As soon as an analytic technique can be chosen, the deviation from producer's specification can be minimized (see table 8).

Table 8 shows the mean deviation of the measurement results from producer's specification, categorized by analysis technique. For thickness determination of thin films on flat substrates GIXA has been found to be the best choice (deviation 3.3 %). SEM as a general tool produces good results for a variety of sample geometries. In this case, the preparation technique will directly influence the results and a material contrast between different layers and the substrate is necessary. XPS and SIMS are not primarily designed for thickness determination because additional analysis has to be employed to characterize the sputter crater. So two measurement techniques, both producing uncertainties, create a larger deviation value. The results obtained with the sputter techniques are fairly good, with possible deviations from the specification of ±10 %. A very clear additional result has been obtained from the study of the "outlier" examples. Theoretical physical and chemical properties of reference samples, given in the literature, often drastically differ from the values of "real" samples. So calculated approaches can sometimes produce large differences compared to real values.

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