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X-Ray Reflectivity Investigations of Glass Surfaces Produced by Float and Draw Techniques*

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Abstract. Surfaces of soda-lime glass and borosilicate glass have been investigated by grazing incidence X-ray reflectivity (GIXR). Characteristic differences are obtained in dependence on the fabrication procedure, the composition and the cleaning procedure. Strong variation is recorded between the two soda-lime float glass surfaces while minor differences are analysed between the top and bottom side of borosilicate float glass. This is attributed to the reduced amount of tin diffused into the bottom side of the borosilicate glass surface. Different cleaning procedures generate characteristic changes on the glass surfaces which can be verified by GIXR. The results indicate that borosilicate float glass combines the merits of the good surface quality of float glass with the high chemical resistivity of borosilicate glass.

Key words: float glass, cleaning, X-Ray reflectivity

Surface properties of primary flat glass are mainly a function of composition, method of forming, chemical interaction with an environment containing reactive gases such as H_2O, CO_2 or SO_2 and cleaning procedure. In the float glass process, today's predominant process for flat glass, the bottom surface of the glass ribbon remains in direct contact with molten tin for several minutes. Under this condition, tin from the float bath can diffuse into the underside of the glass ribbon and affects the quality of the glass surface. The most relevant oxides of the glass melt are not involved in the heterogeneous reaction occurring in the molten glass/liquid tin interface, whereas sodium may be transferred from the glass melt to the metal phase, and tin may be oxidized and dissolved as SnO or SnO_2 in the glass melt [1, 2].

In the past, the fabrication of flat glass has been restricted mainly to soda-line glasses which have typically compositions of approximately 72% SiO_2, 14% $Na_2O + K_2O$, 10% CaO, 3% MgO, 1% Al_2O_3. Traditionally, various drawing techniques are used for the production of the chemically resistant borosilicate glasses which have typically a composition of about 75% SiO_2, 10% B_2O_3, 6% $Na_2O + K_2O$, 5% Al_2O_3. Fairly recently SCHOTT, Jena, succeeded in the fabrication of flat borosilicate glass with a special float technique. Since 1994 the advantages of the float techniques are used for the production of borosilicate glass which allows the fabrication of flat glasses in large dimensions, combined with fast and inexpensive production of plane and smoothed surfaces.

In addition to the interaction in the molten glass/liquid system, chemical reactions with the atmosphere take place, e.g. during the transport and cooling of the glass ribbon or during cleaning. Deviating conditions on both sides may increase the differences in the properties, too. For the drawing process the influence of the Sn bath is absent, but comparable reactions may occur in the drawing equipment in which similar atmospheric conditions prevail as in the cooling zone. Subsequent contact with water, detergents and packaging materials may further influence the surface conditions of primary flat glass. Especially, for subsequently coated glass the cleaning procedure with various chemical interactions with the glass surface plays a dominant role and may be different on both glass sides.

In this short contribution the surface properties are analysed by means of grazing incidence X-ray reflectivity for two classes of glass: for soda-lime glass and borosilicate glass, both of which are produced by two surface forming processes: by float and draw tech-

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niques. Additionally, the influence of different cleaning procedures on the different glass types and glass sides is studied. Typical variations for top and bottom sides are obtained in the density of the surface region and surface roughness.

Experimental

At grazing incidence all X-ray techniques become surface sensitive. Far below the angle of total reflection the X-ray penetrate only 2–7 nm into condensed matter. It turns out that grazing X-ray reflectometry is the right technique to match the demands of thin layers on glass surfaces and their interfaces [3, 4].

The technique used is based on the reflection of X-rays by flat surfaces. This reflection follows the classical optical principles of refraction and reflection with optical indices related to the wavelength used and to the properties of the medium X-rays are refracted according to Snell's law when they cross the interface of two media. In the hard X-ray range the index of refraction, n, is a complex number with a real part slightly smaller than 1 [5]. It can be written as $n = 1 - \delta + i\beta$. δ and β are positive and of the order of 10^{-5} to 10^{-6}. The absorptive correction $\beta = \mu\lambda/4\pi$ is proportional to the coefficient of linear absorption, μ, and the photon wavelength, λ. The dispersive correction, δ, is proportional to λ^2, to the mass density, ρ, and the real part $(Z + f)$ of the atomic form factor. Since n is smaller than one $(1 - \delta)$, the beam is refracted away from the surface normal when it enters into the matter. Therefore, there exists a critical angle, θ_{1c}, for the incident beam at which the angle of the refracted beam, $\theta_2 = 0$. Below θ_{1c} the beam is totally reflected. When absorption can be neglected this occurs at $\theta_{1c} = \sqrt{2\delta_2}$. In the hard X-ray range this angle is below 0.5° for most materials. The determination of the critical angle gives the mass density of the reflecting medium. In reality, however, θ_{1c} cannot be determined in a simple way from the reflectivity because the drop in reflectivity at the critical angle is smeared out by absorption and by surface roughness. The latter is taken into account by an exponential Debye-Waller-type factor to the Fresnel reflectivity derived from the model of Névot and Croce [6]. For more details on X-ray reflectivity see [7, 8].

The information which can be extracted from the reflectivity versus angle of incidence curves includes: 1) the density ρ of the substrate and of the thin surface layers, 2) the thickness of the layers d, 3) the interface roughnesses σ.

The information quoted above are extracted by fitting of the experimental data with the program GIXA [9], which is based on the transfer matrix method [10] and uses the simplex-algorithm in combination with simulated thermal annealing [11]. The accuracy of the parameters depends on the quality of the samples and on the accuracy with which the angle of incidence is determined. Flat substrates such as float glass are well suited. The data analysis needs values for the dispersive correction to the atomic scattering factor f(E). These data were taken from calculation [12, 13]. The accuracy for the determination of the density is proven to be within $\pm 1\%$. The thickness of the surface layers can be determined within ± 0.1 nm. The rms-values of the interfaces are reproducible within $\pm 3\%$. The weighted chi-square values for the fits are between 0.8 and 0.4, which indicates that the measured curves are described exactly by the calculated curves.

The measurements were performed by an instrument based on a standard Philips diffractometer with PW1830 generator and optically encoded PW3020 goniometer (using a step size of 0.001° in θ). The X-ray source was a sealed tube with copper anode and long-fine-focus of height 40 µm. An 1/30° divergence slit and two parallel receiving slits of 100 µm were used in a parallel beam configuration. A graphite monochromator was placed before a gas proportional counter. The direct beam intensity at 40 kV/40 mA reached $> 1*10^7$ cps. Since the dynamic range of the X-ray detector is limited to $5*10^5$ cps for reflectivity curves, an attenuator (Ni-foil, factor 235) was used at high intensities, which increased the dynamic range by over 7–8 decades. The underground counting rate is typically 0.3–0.6 cps. The sample stage is motorized and allows the adjustment of the sample in the direct beam with an accuracy in height of 1 µm and a tilt angle of 0.01°. The precise adjustment of the incident and reflected beam with an accuracy of better than 1 arc sec is done just below the critical angle by rotating the sample with fixed source and detector, as in the "rocking curve experiment". The Rutherford Backscattering Spectrometry (RBS) measurement are performed with the Van der Graff accelerator of the University Frankfurt/Main which are described in detail elsewhere [14].

The samples analyzed are commercially available:

- soda-lime float glass (FLACHGLAS AG, Gelsenkirchen),
- borosilicate float glass (SCHOTT, Jena),
- Tempax (SCHOTT, Mainz).

All samples had a thickness of 4 mm and were measured at the top side (which is in contact with the atmosphere above the tin bath) and the bottom side (which is in contact with the tin bath during solidification), except Tempax, which was analyzed only at one side, because both sides are equivalent. Two cleaning procedures have been applied for sample preparation and are summarized in Table 1. The so-called "standard cleaning" is a typical cleaning procedure which is performed in commercial production before coating. The "HF cleaning" is typically used for small scale preparation in laboratories. The main difference between both procedures consists in the first cleaning step. Due to the application of fluoride acid in the HF cleaning procedure a dissolution of the glass structure takes place at the surface of the glass and material is washed away.

Results and Discussion

Figure 1 shows the reflectivity data taken with Cu Kα radiation from a soda-lime float glass on the top and bottom sides prepared with the standard cleaning procedure given in Table 1. The reflectivity has been recorded over 7 orders of magnitude. At the critical angle it can be recognized that the bottom side has the higher density. From the shape of the curve it can be concluded that the bottom side possesses a smoother surface and differs clearly from the top side. The results of the fit are summarized in Table 2. Two surface layers have to be assumed in order to describe the data of both sides in a satisfactory way. The need for a second layer with low density is seen in the experimental data by the pronounced minimum at about 1.5° for the top side and the structure between 2° and 3.5° for the bottom side. The first surface layer at the top side (leached layer) has a density (2.38 g/cm^3) considerably smaller than the bulk glass (2.48 g/cm^3). The bottom side has a higher density of 2.52 g/cm^3. Here, the surface layer is thicker (14.3 nm) and possesses a den-

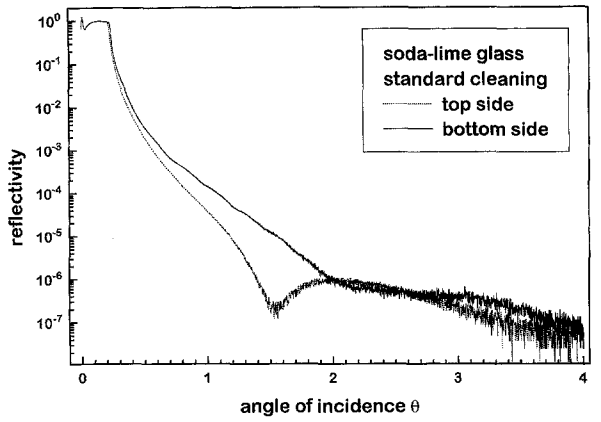

Fig. 1. Reflectivity versus angle of incidence from both sides of soda-lime float glass prepared with the standard cleaning procedure

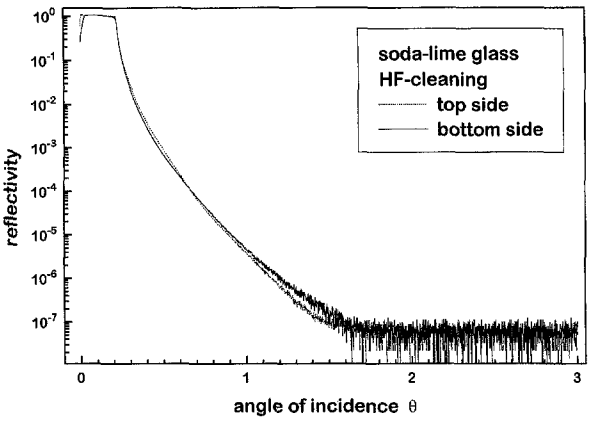

Fig. 2. Reflectivity versus angle of incidence from both sides of soda-lime float glass prepared with the HF cleaning procedure

Table 1. Used cleaning procedures

	Standard cleaning	HF-cleaning
1. Cleaning	40% HNO_3, 40 °C, 4′	HF + HNO_3, RT, 1′
Rinse	water	dm-water
2. Cleaning	Det., 40 °C, brush, 1′	Det., 40 °C, US, 4′
Rinse	water	dm-water
3. Cleaning	Det., 40 °C, brush, 1′	H_3PO_4, RT, US, 4′
Rinse	dm-water	dm-water
Drying	IR	IR

RT = room temperature, US = ultra sonic, IR = infra-red, dm = demineralized water, Det. = detergence, X′ = time in min.

sity of 2.55 g/cm^3, which causes the oscillations in the experimental data between 1° and 2°. The reason for the higher density at the bottom side is the well known diffusion of tin into the glass surface and the enrichment of iron in the surface. X-ray fluorescence measurements [5] show that the Sn Kα fluorescence is about 75 times stronger at the bottom side than on the top side. Also strong differences for the iron concentration are found with a strong enrichment at the bottom side. A very thin surface layer with low density and a strongly hydrated (gel-layer) is found which causes the unusual shape of both curves.

Figure 2 exhibits the reflectivity data of soda-lime glass surfaces prepared with HF cleaning. This cleaning procedure destroys the differences between top and bottom side of soda-lime float glass (Table 2). The influence of tin is reduced and results in a higher density of the bulk only. At the surface a leached layer with a pronounced density gradient grows up. The increased roughness of the surface (rms = 1 nm) can be attributed partially to the gradient. From the gel layer there is nothing left. HF cleaning is an etching method. Glass is not only leached at the surface region but also dissolved and washed away. The enrichment of tin and iron in the surface of the bottom side is removed and both sides equalized.

The experimental data of borosilicate float glass prepared by standard cleaning are shown in Fig. 3 and the results of the fitting procedures are summarized in Table 3. No influence of tin on the density of the

Table 2. Fit parameter for the reflectivity data of soda-lime float glass

		Standard cleaning		HF-cleaning	
		Top side	Bottom side	Top side	Bottom side
Bulk glass	ρ [g/cm^3]	2.48	2.52	2.47	2.52
(soda-lime)	σ [nm]	0.6	0.4	0.5	0.5
	ρ [g/cm^3]	2.38	2.55	2.45–2.18	2.49–1.93
Leached layer	d [nm]	2.7	14.3	8.0	10.5
	σ [nm]	0.3	0.2	1.0	1.0
	ρ [g/cm^3]	1.42	1.85	-/-	-/-
Gel-layer	d [nm]	1.4	1.0	-/-	-/-
	σ [nm]	0.4	0.3	-/-	-/-

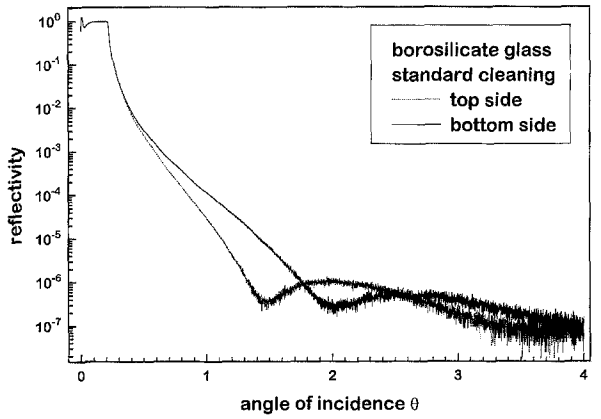

Fig. 3. Reflectivity versus angle of incidence of both sides of borosilicate float glass prepared with the standard cleaning procedure

Table 4. Fit parameter for the reflectivity data of Tempax produced with a drawing technique

		Standard cleaning	HF-cleaning
Bulk glass	ρ [g/cm^3]	2.24	2.24
(Tempax)	σ [nm]	0.5	0.7
	ρ [g/cm^3]	2.25–2.28	2.23–2.18
Leached layer	d [nm]	15.7	20.0
	σ [nm]	1.0	1.1
	ρ [g/cm^3]	1.41	-/-
Gel-layer	d [nm]	1.5	-/-
	σ [nm]	0.5	-/-

bottom side can be detected for borosilicate glass. On both sides a density for the bulk glass of 2.23 g/cm^3 is determined. A thin, 4.6 nm thick, leached surface layer with lower density (2.21 g/cm^3) has to be assumed at the bottom side. A very thin gel layer is found on both sides. The difference in the thickness of this layer between top and bottom side is obvious in the experimental data from the position of the remarkable minimum in the curves at 1.5° and 2°, respectively.

Because of chemical resistivity of borosilicate float glass the cleaning with the HF procedure doesn't dramatically change the surfaces properties. The results of the fit are summarized in Table 3. The difference in the density of the bulk glass is small and lies within the experimental precision. The leached layer is relatively thin on both sides and reveals at the top side a slightly lower density (2.20 g/cm^3) than at the bottom side (2.3 g/cm^3). This is attributed to the influence of the tin, which was not dissolved during the cleaning procedure and is now enriched in the surface of the bottom side. At the top side an additional thin layer with a density of about 2.0 g/cm^3 is detected.

The surface quality of Tempax (drawed borosilicate glass) given in Table 4 is significantly worse in regard of flatness and roughness in comparison to borosilicate float glass. Both cleaning procedures produce a relatively thick leached layer (15.7 nm and 20.0 nm) with a gradient in density. A difference between the two cleaning procedures was found in the direction of the gradient. For the standard cleaning the density increases slightly from the bulk to the surface, whereas for the HF cleaning the density decreases. A gel layer at the top of the surface was found only for the standard cleaning. Compared to borosilicate float glass, Tempax reveal a slightly weaker chemical resistivity in the course of cleaning.

Tin depth profiles measured with RBS from the bottom side are depicted in Fig. 4 in order to enlighten the different behaviour of the both sides of borosilicate float glass and to soda-lime float glass. The depth scale is calculated assuming a density of 2.50 g/cm^3 for soda-lime glass and 2.25 g/cm^3 for borosilicate glass [16]. The enrichment of tin in the surface of both glasses is

Table 3. Fit parameter for the reflectivity data of borosilicate float glass

		Standard cleaning		HF-cleaning	
		Top side	Bottom side	Top side	Bottom side
Bulk glass	ρ [g/cm^3]	2.23	2.23	2.23	2.24
(borosilicate)	σ [nm]	0.2	0.3	0.6	0.5
	ρ [g/cm^3]	-/-	2.21	2.20	2.3
Leached layer	d [nm]	-/-	4.6	3.0	2.1
	σ [nm]	-/-	0.3	0.4	1.9
	ρ [g/cm^3]	1.7	1.6	1.96	-/-
Gel-layer	d [nm]	1.6	1.1	2.0	-/-
	σ [nm]	0.5	0.3	0.9	-/-

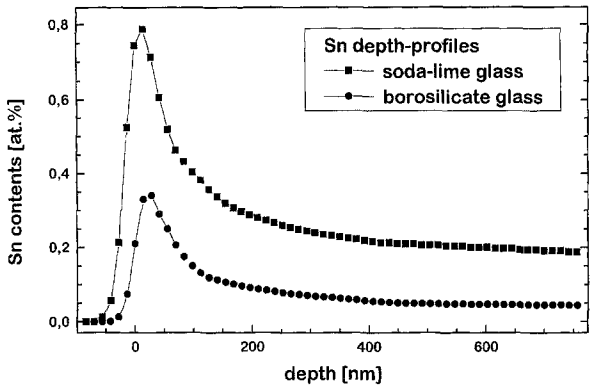

Fig. 4. Depth profiles of Sn from RBS measurements. The depth scale is calculated for a density of 2.5 g/cm^3 for soda-lime glass and 2.25 g/cm^3 for borosilicate glass

clearly visible. The profiles in Fig. 4 indicate that the different behaviour of the bottom sides of both glasses is evoked by the different amount of diffused tin into the bottom side which is much weaker for borosilicate glass than for soda-lime glass. Additionally, borosilicate glass contains no impurities of iron, which is enriched in the surface of soda-lime glass [16].

Conclusion

It is demonstrated, that X-ray reflectivity at grazing incidence (GIXR) is an excellent tool in surface and thin film analysis and enables to probe subtile details of surfaces and thin layered structures on surfaces. The analysis provides the reflectivity measured over a wide angular range (8° in 2θ) and over at least six or seven orders of magnitude in dynamic range. Differences in the influence of cleaning procedures on the surfaces of soda-lime glass and borosilicate glass are demonstrated. The top and bottom side of soda-lime float glass differ clearly due to the tin content at the bottom side of the glass. The limited chemical resistivity causes an equalization of both sides by the HF cleaning. Due to the minor tin content in the bottom side, borosilicate float glass has two approximately equal sides. The chemical resistivity causes, that the changes during the HF-cleaning are negligible. Borosilicate float glass combines the advantages of the float process on the quality of the glass surfaces with the prominent chemical properties.

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