Address:
Glafo, PG Vejdes väg 15,
SE-351 96 Växjö
SWEDEN

Visitor's/Delivery address:
Vejdes plats 3, 352 52 Växjö

Tel: +46 10 516 63 50

E-mail: info@glafo.se

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Project leader: Peter Sundberg
Project status: Closed

CHARACTERISATION OF SOLAR CELL GLASS: A FEASIBILITY STUDY OF THE MOBILITY PROPERTIES OF ANTIMONY

The objective of the work is to investigate how leaching of antimony affects the performance of solar cell glass, and what effect the antimony has on the environment.

Background

As a result of the REACH regulation's registration of glass, one of the aspects investigated has been that of leaching of various substances out of glass. The work has been carried out in accordance with the EU Waste Regulation, investigating various types of crushed glass in water. The only substance that leached out of the samples was antimony from solar cell glass. This has created increased interest in the mobility of antimony in glass.

Glafo has previously investigated how antimony is leached out of drinking glasses exposed to climate attack. We found then that the leaching increased with severity of climate attack.

Performing the work

The study has involved a rolled solar cell cover glass containing 0,25 % of antimony (Sb_2O_5), treating the sample in boiling water in order to accelerate the reaction with moisture. The treatment was carried out at 100 °C for 100 minutes, which is equivalent to about six weeks of leaching to water at room temperature (20 °C), or even longer time at outdoor temperatures. As comparison, we have also studied an untreated glass surface. After the accelerated attack, the glass surface was analysed by a surface ablation cell (SAC) in order to see if the distribution of antimony in the surface had been affected. After the SAC analysis, the sample was examined using an optical profilometer.

This method of analysis is based on pumping an etching acid through the ablation cell to dissolve the glass. In order to obtain good resolution we used a diluted solution of etching acid. The trivalent antimony content (Sb^{3+}) and the total antimony content (Sb^{3+}+Sb^{5+}) in the etching solution were quantified by modern analysis technique.

When glass is in contact with water there is an exchange of ions in the outermost surface layer. This layer is about 200 nm deep, and is often found to have a depleted mobile ion content and, in some cases, an elevated concentration of the network-forming elements.

Distribution of antimony in the glass surface

The results from the antimony determination of two different samples in the etching solutions are shown below:

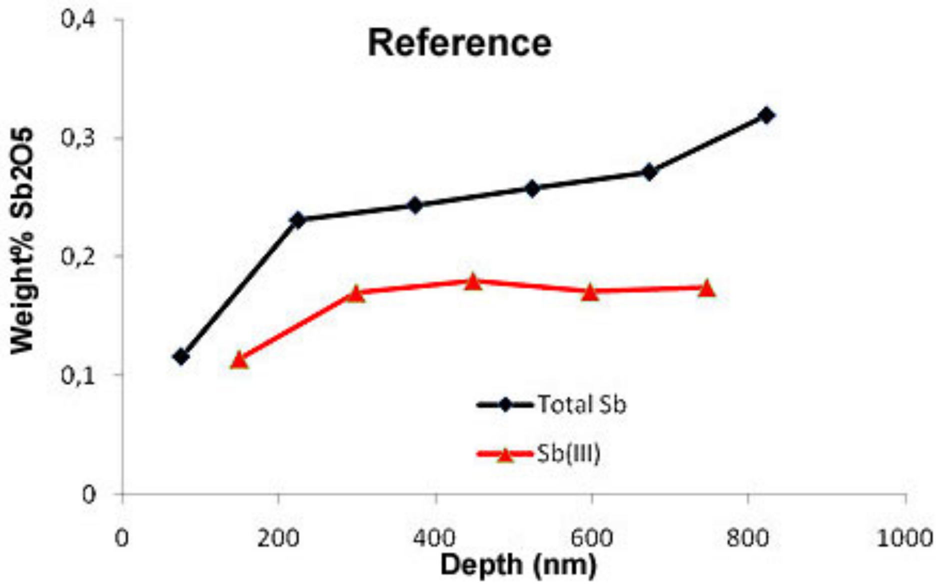

Figure 1. Rolled, untreated flat glass (reference).

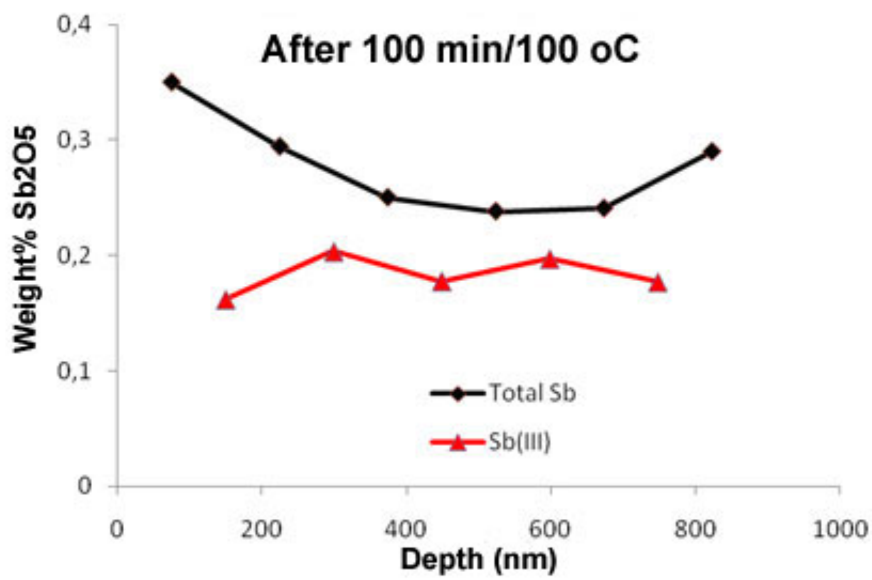

Figure 2. Rolled flat glass after exposure to boiling water for 100 minutes.

The graphs above show the antimony concentration (trivalent and total content) in the glass as a function of the calculated depth.

The total weight loss from the etching was about 6-7 mg, which means that the nominal total etched depth was about 1 micrometer (822 nm). Each etch sample is therefore equivalent to a nominal depth of about 100 nm (see also below).

The etch solutions, which contain fluoride, were also analysed for calcium. We used calcium in order to estimate how much glass was dissolved in each sub-sample. However, these results are more difficult to interpret, and evaluation is still in progress. The measurements are reproducible, but the correlation with antimony is poor. This may be due to unevenly rolled surfaces. Another working hypothesis is that calcium fluoride separates out when the measurements are made from the hydrofluoric acid solution, and that this complicates reproducible sample preparation. An alternative would be to analyse the silicon contents of the samples, but this would be difficult in an acid fluoride solution.

Leaching of antimony

Figures 1 and 2 show the antimony distribution in the glass surface. After exposure to water at 98 °C for 100 minutes there is a noticeable elevation of pentavalent antimony close to the surface of the sample. The normal condition is that mobile ions are depleted in the outermost layer of the glass.

Our preliminary interpretation is that antimony migrates as trivalent antimony, but that it is oxidised to pentavalent antimony, which is less mobile, at the surface of the glass. Such knowledge is important for such purposes as reducing leaching of antimony from glass waste disposal sites.

Appearance of the glass surface after etching in the surface ablation cell

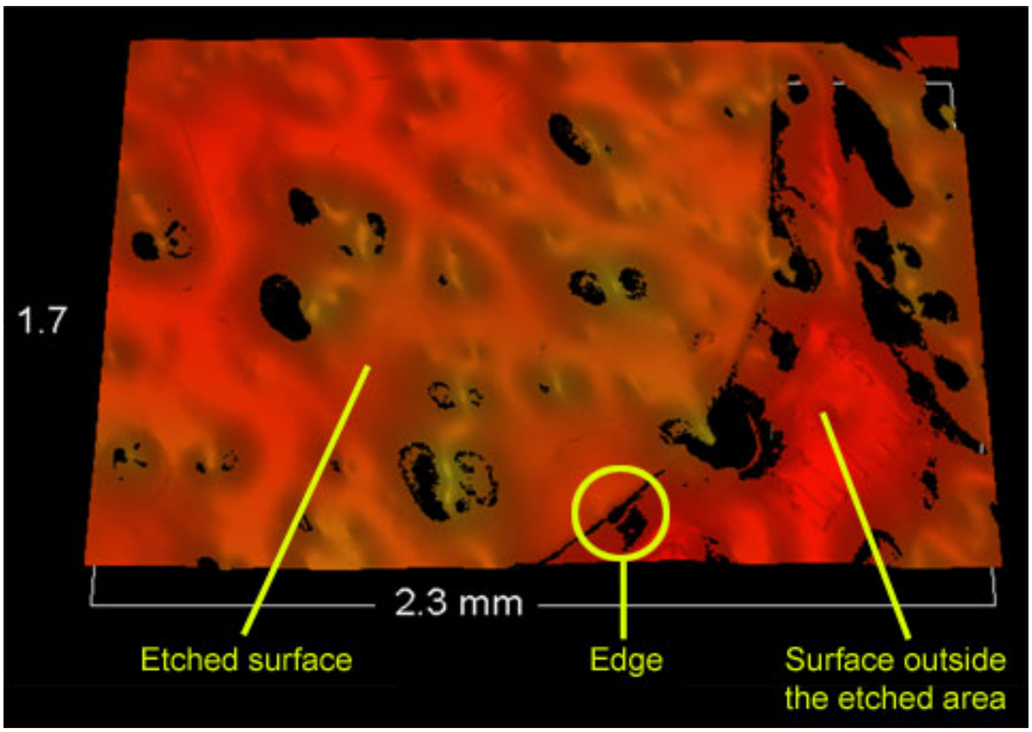

Figure 3. The surface of the glass after etching. The picture shows a faint edge from the Teflon spacer in the SAC. The glass surface is much more uneven than that of ordinary float glass.

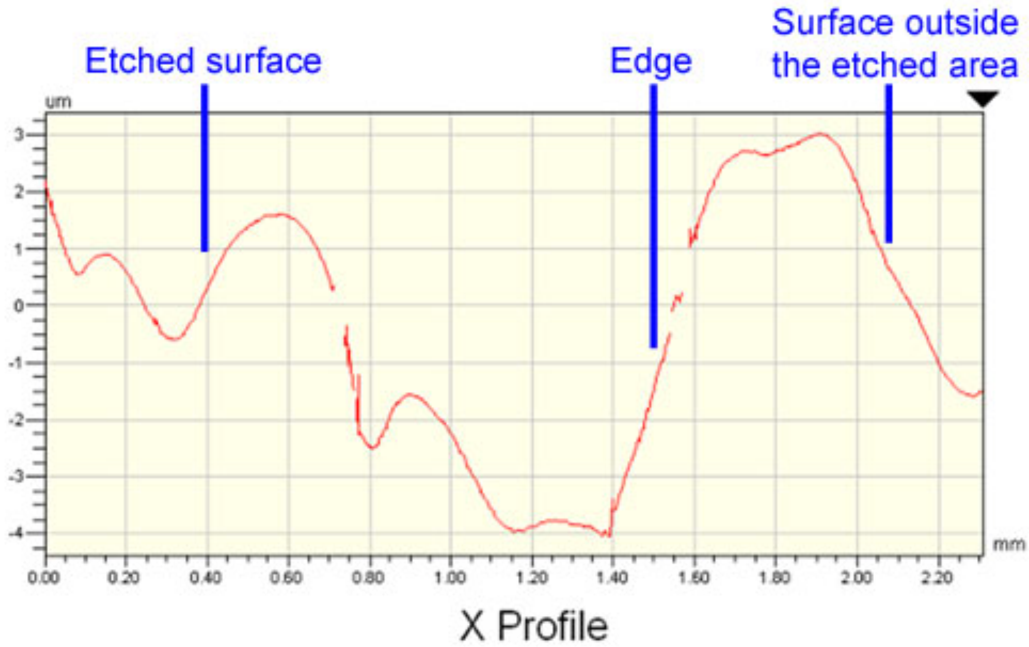

Figure 4. The surface of the glass after etching. From the X-profile, the height of the edge can be estimated as 7 micrometer. The glass surface is much more uneven than that of ordinary float glass.

The optical profilometer has given valuable information on the surface of the glass after etching. Figures 3 and 4 show the surface that was etched in the SAC. It can be seen that they are very unevenly etched, but that the untreated unetched glass surface is very uneven, and not at all like float glass. The rolled glass is therefore more difficult to study in an SAC. Etching seems largely to have occurred along the edge of the Teflon spacer. The uneven surfaces affect the result of analysis and give non-reproducible measurements. In order to optimise etching, the concentration of hydrofluoric acid should be increased, while retaining the lateral resolution of 100 nm.

To obtain best results in respect of surface composition from the SAC requires a smooth surface after etching, which was not the case here. For continued work with the cell, we need to use flat glass and a stronger etch solution.
What is the effect on the optical properties?

How are the optical properties of the glass surface affected by the leaching of antimony? This is an important question, but could not be answered in this short feasibility study.

Environmental aspects of antimony leaching
The environmental impact of antimony is still being discussed in ICG's technical committees. A current study has investigated leaching into water after 64 days' exposure. Preliminary results show that the concentrations are low, and under the detection limit of many routine instruments.

Continued work
This feasibility study has shown that antimony can be quantified directly in the etch solution, and that we can thus obtain unique results for antimony distribution in the outermost surface layer of the glass. The work also shows that the rolled glass has an unsuitable surface, and that the investigations should be performed on flatter surfaces.

The fact that leaching can be reduced by oxidising up the antimony to pentavalency should interest the art glass industry. Funding for a continued investigation of art glass should therefore be discussed with the industry. A continued investigation ought to be able to answer the questions raised by this feasibility study.

It is difficult to quantify the amounts that are leached out from glass over a long period of time. The reverse method that has been used here - of investigating the composition of the surface of the glass after leaching - should give better results. This applies particularly for the low concentrations and limit values that apply for antimony. The results of this feasibility study should be presented to some international glass conference such as ICG (International Commission on Glass) or ESG (European Society of Glass Science and Technology). Combining the use of a surface ablation cell with quantification of a substance in its various oxidation states has not previously been done.

In the longer term, we intend to continue in EU projects with these and similar studies. Being able to present a unique and relatively simple (value-for-money) method improves our chances of obtaining financing. The method can also be used for other low-concentration polyvalent elements, such as selenium and arsenic.