

The determination of surface composition profiles in glass by Auger electron spectroscopy and ion etching

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Auger electron spectroscopy (AES) combined with ion etching was used to measure compositional profiles in the near-surface regions of glass. The profiles were obtained by making a linear series of analyses along the surface of a sloping ramp etched into the glass in a separate ion bombardment operation. Composition profiles obtained in this way from the topside and underside of production float glass are described and interpreted. The advantages of this alternative method of separate ramp etching over the conventional approach of fixed beam sputtering with an *in situ* ion gun are discussed.

1. Introduction

In previously reported experiments [1] on the AES analysis of the exterior and fracture surfaces of soda lime-silica glass, it was found necessary to limit the maximum primary electron-beam current density and energy used, in order to control a progressive beam-induced depletion of the cations from the specimen surface. It was stated that thermally activated hopping of mobile species along surface and subsurface electric field gradients was the most likely cause of the depletion, but that, with appropriate beam conditions, quantitative analyses of most cation concentrations on exterior surfaces could still be obtained in timed experiments. Only in the case of sodium were the migration effects still so strong as to prevent meaningful quantitative analysis.

Although such effects can generally be minimized when making a single AES analysis at one position of fixed depth in the glass, the beam-specimen interaction can still have a deleterious effect on the accuracy of depth profiles of composition variation when the usual method of *in situ* (crater) etching is used. Thus a focused electron beam may irradiate one area of the specimen surface within the etched crater for a

considerable length of time, for example when the electron-beam diameter is comparable to the width of the bottom of the crater. However, keeping the electron beam in a fixed position will bring about a continuous alteration of surface and subsurface composition due to migration of mobile species. The depletion effect on the measured concentration profile will be cumulative, since the rate of electromigration is greater than the rate of etching, and the zone containing the electric field gradient is always many tens of nanometers in advance of the analysed surface, unless the glass contains a layer which blocks the diffusion.

In view of the problems associated with keeping the electron beam at one fixed position on the glass for too long, it was decided to work with specimens which had been ion-beam machined in such a way that a new position for the Auger analysis could be found for each depth examined. The technique of etching a 'staircase' section through the surface in an entirely separate ion bombardment operation used by Stoddart and Hondros [2] for profiling oxide films on alloys satisfied this condition and appeared suitable. The purpose of the present paper is to describe a fully developed version of this alternative approach to

composition-profiling in which continuous ramps are etched, and to illustrate the usefulness of the method in obtaining high in-depth resolution profiles of glass surfaces with minimal effects of electron-beam damage. The advantages of using separate ramp etching will also be described since this method can be more informative than the crater method on the same specimen and has potential applications for materials other than glass.

2. Experimental

2.1. Ion-etching of ramp sections

The apparatus used for ion-beam machining the ramp sections is shown in Fig. 1 and is a modified version of the G.V. Planer Ltd IB7 ion-etching equipment [3, 4]. The system is basically a d.c. triode system consisting essentially of a gas plasma generator, sample stage cathode with variable-speed shutter mechanism and an ion-beam charge neutralizing electrode for use with insulating specimens. After pump down, the system was back-filled with argon to a pressure from 0.5 to 1.6 Pa, an electron emitter and anode were activated and the plasma struck. A negative potential of typically 5 kV, with respect to the plasma, was then applied to the specimen stage and to the flat circular fine-mesh nickel gauze neutralizing electrode so that positive argon ions were extracted from the plasma and accelerated upwards to pass through the neutralizing grid. When the plasma conditions were suitably adjusted, a uniform collimated flux of argon ions and excited neutral atoms, 100 to

150 mm diameter, passed through the field-free space behind the gauze and impinged on the specimen.

The specimen consisted of a flat strip of material 100 mm × 20 mm and was held on to a rotatable water-cooled stage by a close fitting tantalum surround which also served as a permanent mask to protect a 2 mm border around the specimen from any bombardment. An important feature of the system was a second movable tantalum shutter, which initially covered the specimen completely, but was withdrawn during bombardment at a pre-determined rate so as to expose a gradually increasing area of the specimen to etching. This produced the wedge-shaped sample configuration shown in Fig. 2. Shutter drive was from an external variable-speed electric motor via a train of geared pulleys and a lead screw.

When preparing ramps on soda lime-silica glasses for subsequent AES profiling studies, normal incidence bombardment with 5 kV applied to the specimen stage and gauze was always used. With beam currents to the 150 mm diameter gauze in the range 100 mA ± 20%, sputter rates of 1.0 μm h⁻¹ ± 20% were observed. Contamination of the glass surface by material sputtered from the gauze and shutter was very light, Auger analysis showing that nickel was about 2% of the total atom concentration of an ion bombarded surface and that tantalum was less than 1%. Aluminium was just detectable. None of these elements interfered with the present profiling studies since they were either absent from the glass or undetectable

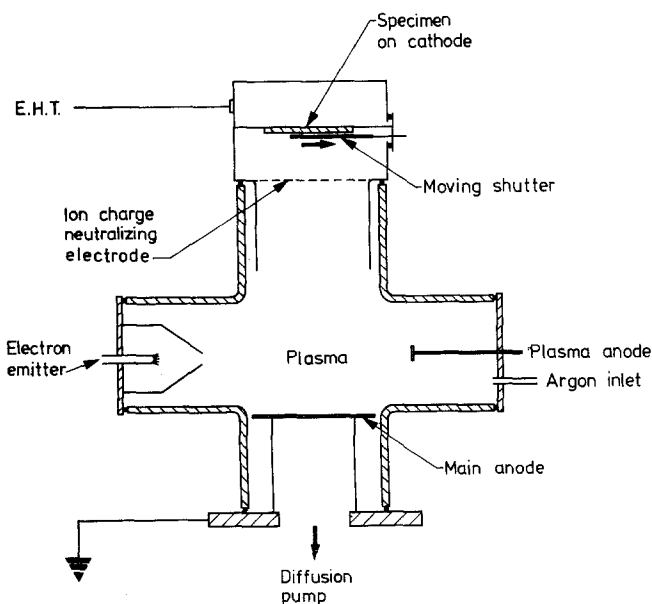


Figure 1 Ion-etching equipment for preparing ramp sections.

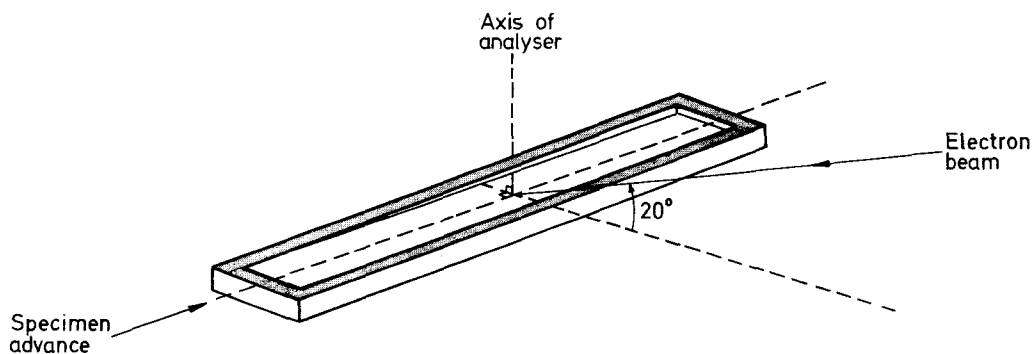


Figure 2 Disposition of primary electron beam relative to the ramp surface.

on unbombarded specimens (bulk concentration of Al in float glass = 0.4 at. %). Despite the presence of a water-cooled stage, quite high surface temperatures, considered to be at least in the range 200 to 300°C were reached when bombarding thick insulators, such as 5 mm glass under the above conditions.

2.2. Auger analysis of ramp sections

The etched specimen was transferred at room temperature through the atmosphere to a 100 mm long tray in the vacuum chamber of the Auger electron spectrometer (Vacuum Generators 4-grid retarding field analyser). This tray was mounted lengthways on to a linear motion drive of 100 mm traverse in such a way that the top surface of the specimen passed through the centre of curvature of the analyser grids. The electron beam (2.5 keV, 50 μ A) was at 90° to the line of specimen advance and was kept in a fixed orientation in space such that it struck the specimen surface on the centre line of the ramp at the analyser centre and at near grazing incidence (Fig. 2). Low angles of incidence of the primary beam to the specimen surface were necessary to prevent the specimen charging during Auger analysis [1], and were also beneficial in that high Auger electron yields were obtained. However if the angle was made too low, there was the risk of having a large off-centre component to the total signal when the beam was highly streaked across the specimen. For this reason the beam was always at 15 to 20° to the specimen with the electron gun focussed (0.5 mm diameter beam). This arrangement also had the advantage of allowing a limited amount of effective defocussing in one direction on the specimen since the area irradiated was elliptical.

Keeping the beam narrow in the direction parallel to the ramp slope is important if each

analysis is to have a depth accuracy comparable with the ultimate depth resolution of AES. Thus, within a 0.5 mm diameter beam on a sloping ramp 100 mm long, the surface falls by 0.5% of the maximum depth etched and there will be some loss of depth resolution for ramps deeper than about 100 nm. If however high depth-resolution is still required at depths greater than this from the original exterior surface, a different etching schedule can be devised whereby a shallow ramp is superimposed onto a previously uniformly etched planar surface.

The composition profile was obtained by recording a series of AES spectra from conveniently spaced positions along the ramp. This operation was particularly simple when compared with the crater-etching technique, because to arrive at any particular depth only a single adjustment to the linear motion drive was required, recording the displacement given so that the position of the analysed point on the ramp could be identified later. Since the sodium surface concentration was rapidly depleted at room temperature by electron bombardment the sodium Auger peak was measured on each new position immediately and the measurement repeated until the peak could not be detected so that an estimate of the initial concentration could be made by extrapolation. It is noteworthy that cooling the specimen to liquid nitrogen temperature was found to reduce loss of sodium from the surface during Auger analysis [5]. Similar observations have been reported by Pantano *et al.* [6, 7]. After the sodium analysis the rest of the spectrum was taken while still at the same position.

Despite the fact that the glass had been air exposed between ion bombardment and Auger analysis, no thick contamination overlayers were detected on the ramp surface. Likewise, no increase in the level of contamination on the specimen in

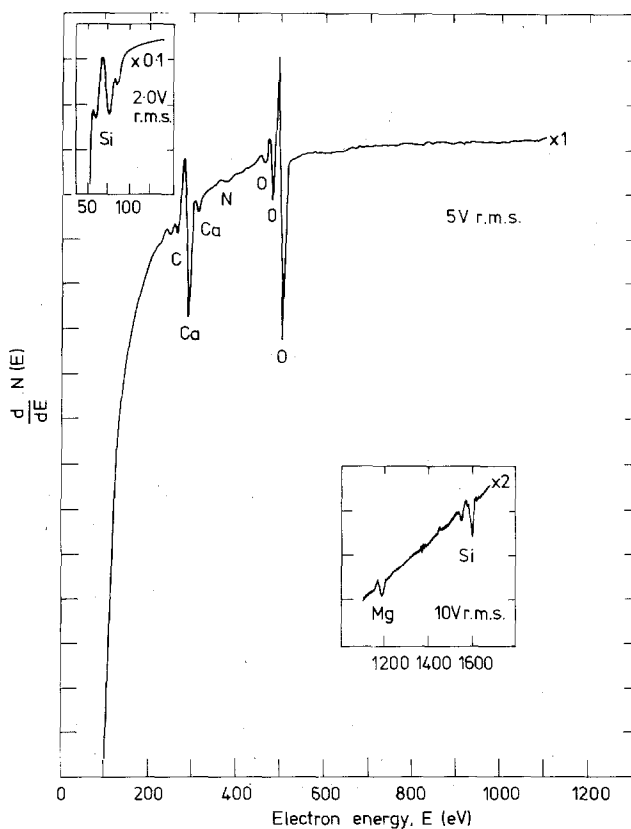


Figure 3 Auger electron spectrum of an air exposed float glass fracture surface.

the spectrometer was observed during the period (1 to 2 days) required to complete the series of measurements even at a working pressure of 1.3×10^{-5} Pa. In view of this low reactivity ultra-high vacuum was not required and a second *in situ* ion bombardment to clean the specimen prior to analysis was not necessary.

Confirmation of this low apparent reactivity of float glass to the atmosphere was obtained by comparing the AES spectrum of a glass fracture surface which had been exposed to air for a few minutes after breakage, with that obtained from an ion-etched glass surface which had been air-exposed, and then ion-bombarded again within the spectrometer (8 nm layer removed). The only difference of note between the spectra was that the air-exposed fracture surface exhibited additional peaks, due to carbon and nitrogen, but only in amounts equivalent to a small fraction of a monolayer coverage. The AES spectrum of the air exposed fracture surface is shown in Fig. 3.

2.3. Measurement of depth etched on ramp sections

Once the composition of the ramp surface had been measured as a function of distance along its

length, the depths of the points analysed below the original surface were then determined. This was done by traversing a stylus (Rank Taylor Hobson Talystep) laterally across the step at the masked specimen edge into the central etched region opposite the points analysed. For perfectly plane ramps, only a few step-measurements would suffice to determine the ramp gradient and enable the depth of each analysis point to be calculated. In practice it was found that the ramps were slightly concave and an explicit measurement of depth for each profile point was preferred. This slight concavity must arise from non-uniformity of the beam in the etching system since the specimens were plane originally and the shutter was moved at a constant rate. Fig. 4 shows a typical series of Talystep determinations of depths etched for a ramp etched into 6 mm float glass. The low scatter in the depth readings at each position and the overall consistency between readings shows that the step-depth determination was satisfactory. This step-depth at the edge of the specimen was taken to be the same as the actual depth of glass removed in the central region where composition analysis was performed. Such an assumption is justifiable within the experimental accuracy of the

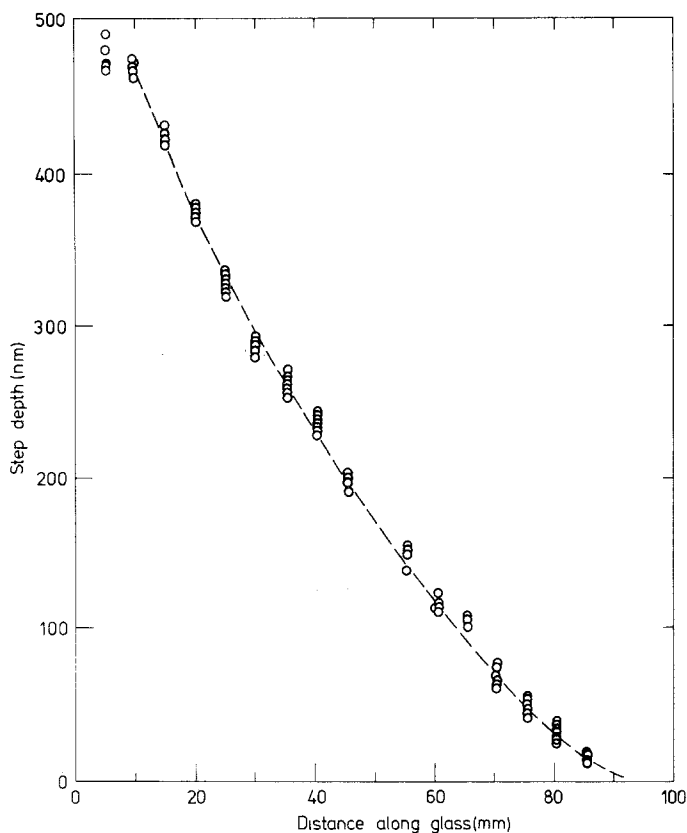


Figure 4 Talystep readings of depths etched along a typical ion etched ramp on production float glass.

step-depth determination for it can readily be shown from the data of Fig. 4, that the lateral dishing never exceeds 2 nm for ramps up to 600 nm deep in a 150 mm diameter axially symmetric argon ion column, for a 20 mm width of specimen. Likewise this lateral dishing does not affect the depth accuracy of the Auger analysis because the total length of the primary beam spot on the specimen surface seldom exceeds 10% of the specimen width.

For step-depths less than 10 nm, the Talystep method became inaccurate, but the depth could still be computed reliably. Thus for some specimens it was possible to extrapolate the experimental depth-distance curve to zero with sufficient accuracy. For others it was necessary to etch a second specimen of the same glass for a much longer time with the same plasma conditions, and make the depth measurement at an equivalent position on the deeply etched ramp. The shallow depth was then calculated by scaling the measured value with the appropriate time factor, assuming that the sputter rate at that position had remained constant.

3. Results and discussion

3.1. Element concentration profiles of float glass surfaces

Composition profiles were measured on a number of commercial float glasses by the ramp sectioning method. Two of the profiles obtained are given in Figs. 5 and 6. Fig. 5 shows the profile from the underside (i.e. the side in direct contact with the molten tin bath) of a specimen of float glass. Since the specimens were collected directly from the end of the production line and were stored in plastic boxes without any further chemical treatment, the surface condition of the glass immediately prior to ion-etching resulted only from the effects of the manufacturing process and subsequent ageing. In the Auger analysis any effects of the ion bombardment and subsequent air exposure were also detected.

It should first be noted that it was possible to obtain a sodium profile and this can be attributed directly to the fact that a new analysis position was available for each depth by this method. The special procedure used for the Auger analysis of sodium is described in section 2.2. The sodium

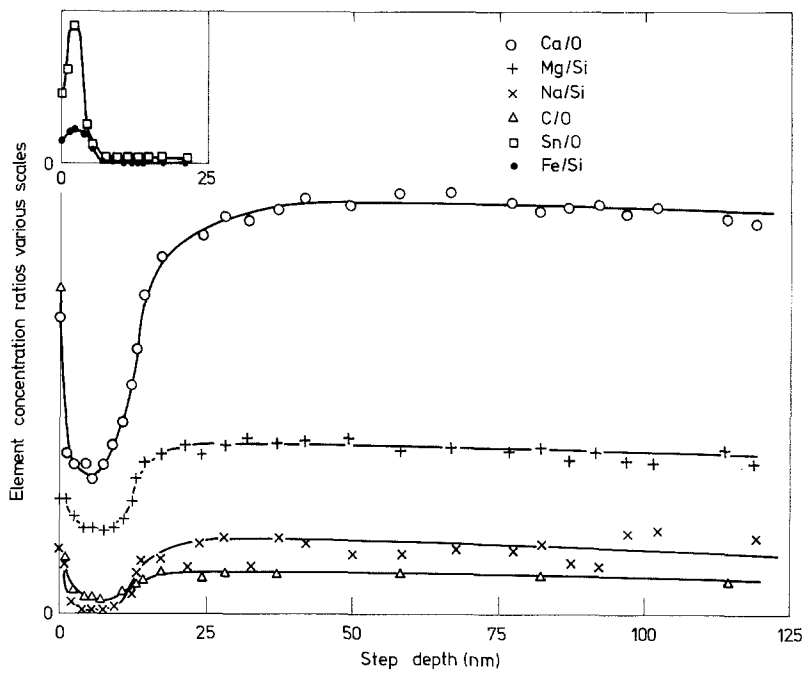


Figure 5 Element concentration profile for ex-works float glass underside.

distribution is similar to the calcium and magnesium curves. A well defined cation-deficient region was found below the original glass surface, extending to a depth of about 20 nm. In this zone, the minimum calcium and magnesium concentrations were about half those found deeper in the glass, while the minimum sodium concentration appeared to

be almost zero. Deeper into the glass, the concentrations of the three metals rose and then levelled off at values close to those found on fracture surfaces at the same angle of incidence so that it is reasonable to suppose that bulk glass concentrations had then been reached. Above the cation-deficient region, calcium, magnesium and sodium

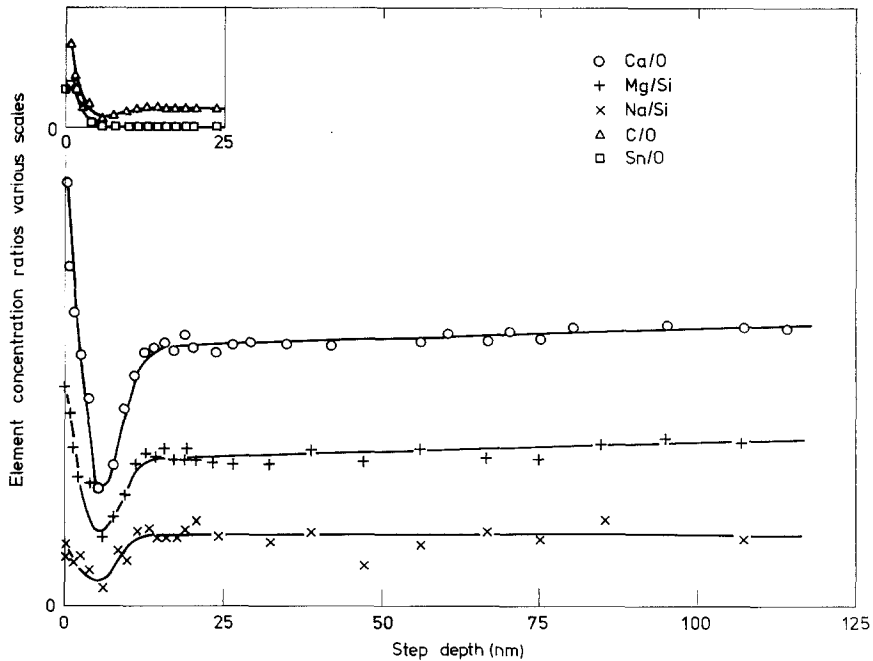


Figure 6 Element concentration profile for ex-works float glass topside.

concentrations were again high, but the carbon level was also high and the carbon Auger peak shape had a similar double peaked structure to that found in carbonates [8,9]. The process contaminants tin and iron were also found localized in this outermost region of the glass surface.

Explicit silicon and oxygen profiles have not been given in Fig. 5 because the recorded peak amplitudes for these elements were used to calculate the peak amplitude ratios that have actually been plotted. Amplitude ratios were used only to eliminate those irregularities in the profiles caused by variations in signal strength as a result of having an electron gun without beam-current stabilization. Silicon and oxygen were used as reference elements since their concentrations appeared to have remained constant along most of the ramp. Only when the carbon signal was very high, within two or three monolayers of the original "as received" exterior, were decreases in the silicon and oxygen concentrations apparent.

Fig. 6 shows the element concentration profiles from the top surface of the same glass. The essential features are very similar to those of the underside, the surface again showing a metal carbonate layer, a cation-deficient region and then unaltered glass. The thicknesses of these zones were very similar to those found on the underside and again the minimum concentrations of calcium and magnesium in the deficient region were about half those deeper into the glass. On this particular specimen, the exterior concentrations of calcium and magnesium were greater than those found beyond the cation deficient region and were also higher than the exterior concentrations shown on the underside specimen. Other analyses of virgin topside and underside specimens have however shown that these exterior concentrations of calcium, magnesium and carbon can vary considerably so that this outer carbonate zone may have an irregular distribution.

The most striking difference between the topside and underside depth distributions is the complete absence of iron from the topside profile. In fact iron analyses provide a means for determining whether a given float glass surface is topside or underside when this is not already known. Contact of the glass ribbon underside with steel rollers conveying the glass from float bath to annealing lehr is a probable source of this pick-up. Tin contamination occurs on both surfaces, but the fact that tin on the underside reaches a maximum

concentration five times greater than on the topside and that the penetration is also greater provides another means whereby the surfaces may be distinguished. The molten tin float bath is the obvious source of this pick-up.

In other respects, the topside and underside surfaces show great similarities; leached regions of comparable composition and thickness exist on both. Slow weathering due to air exposure after manufacture must have occurred, but it is also possible that previous leaching of the surfaces had taken place during an on-line water washing that the ribbon normally receives after it has emerged from the annealing lehr. The ribbon is at about 100°C when it is washed but it is difficult to say whether a few seconds of exposure to water at this temperature will bring about greater weathering than several days exposure to glass works and laboratory air. If the water washing is important in leaching the glass then one might expect the outer metal carbonate layer to consist of weathered evaporation residues.

3.2. Assessment of ramp etching method

The ramp method of profiling has the following significant advantages over the crater method:

(1) The cumulative damage created by time-dependent beam-specimen interactions may be greatly reduced. This is illustrated in Fig. 7 which compares tin concentration profiles from the underside of production float glass obtained by the ramp and crater methods. The crater profile was obtained by *in situ* bombardment with a defocused beam of 600 eV Ar⁺ ions at normal incidence and a flux density of 0.81×10^{11} ions mm⁻² sec⁻¹. Using the data of Jorgensen and Wehner [10] for low energy Ar⁺ ion bombardment of silica, and assuming that the multicomponent glass sputters at the same rate as silica a net sputter yield of 1.4 atoms per ion and a net removal rate of 1.6×10^{-3} nm sec⁻¹ were calculated. Monitoring composition at one position as a function of bombardment time showed a continuous decrease in the tin signal but it can be seen that when the electron beam was moved to a fresh position within the bombarded area a higher tin concentration than that under the stationary beam was found. For example, after 8 nm of glass had been removed, a small deflection of the beam caused the measured tin concentration to increase fourfold, and this difference could only be due to a diminution caused by the electron beam, since the use

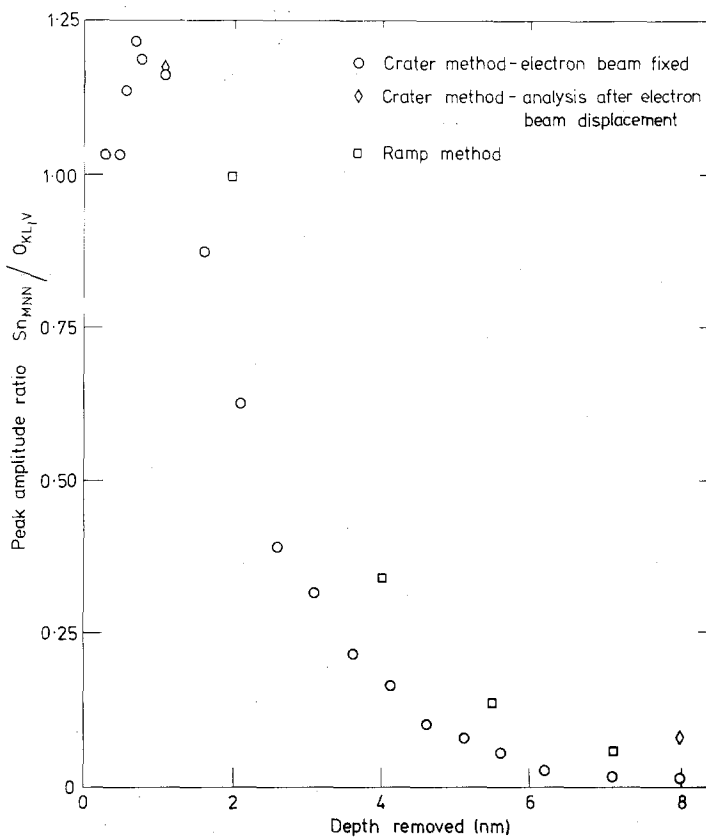


Figure 7 Comparison of tin profiles obtained from the underside of float glass by the *in situ* crater method and the ramp method.

of a defocussed ion beam and a small collimating mask at the specimen surface ensured uniform erosion over the exposed glass surface. The tin profile obtained by the ramp method gives higher tin concentrations than the crater profile at each equivalent depth etched, and approximates to the values obtained on displacing the beam in the crater method. This results from the much shorter residence time of the beam on a particular position in the ramp method. The effects of electron beam depletion are much more marked in the case of sodium than tin and it has been noted that only the ramp method allowed a sodium profile to be obtained in soda lime-silica glass at room temperature.

(2) The depth of each analysis point may be determined by metrology. Uniform sputter rates for ion milling need not be assumed. This can be an important advantage when profiling coated glasses or other glasses whose compositions change rapidly with depth.

(3) The method is non-destructive during Auger analysis. Thus the ramp surface is still available after profiling for such studies as surface roughness assessment. The effect of ion bombardment on surface topography may be measured throughout

the entire depth range. Likewise the contribution to the measured profile of preferential sputtering in multi-phase glasses may be assessed [11].

(4) A time constraint is removed from the profiling operation. Since all points to be analysed are already exposed, the AES composition data may be collected in any sequence. For example the profile may be measured from the deepest point to the original exterior. Some special feature of the profile may first be studied, afterwards returning to previous positions for further analyses. Similarly mistakes or omissions may readily be rectified and the whole experiment proceeds at a pace which is not determined by the sputter rate or the depth to be analysed.

Two disadvantages of the ramp method used in this work are the requirement for a separate etching plant and the fact that the specimen is exposed to reaction with air between etching and analysis. These disadvantages could be overcome by an arrangement in which the etching is carried out in a side chamber of the spectrometer (to avoid its contamination by sputtered deposits) and the ramp specimen then moved into the analysis position through a vacuum lock. It should be noted that the brief air exposure need not be

detrimental since any reaction layer may be removed from the ramp surface by light ion bombardment within the spectrometer prior to Auger analysis. This was not necessary in the case of the float glass surfaces, since there were no gross alterations in the concentrations of the surface species initially present after the air exposure and additional peaks due to carbon and nitrogen were always small. Thus for soda lime-silica glasses, at least, these secondary reactions have not been sufficient to obliterate the composition variations that existed along the ramp after ion etching, and the measured composition profiles agree well with those given by Pantano *et al.* [6, 7] for similar glasses. Several other profiling studies on coated and electrolytically modified float glasses have also been completed [11] where interpretation of the profiles in terms of the pre-existing structures was still possible despite air exposure of the ramp and the absence of any subsequent *in situ* ion cleaning. Only in the case where the ramp surfaces contained free metal were problems with oxidation encountered, but even here the secondary effects could still usually be distinguished and worthwhile measurements of metal concentration variations and zone thicknesses made.

There is, of course, a requirement in the ramp method as described for relatively long and preferably smooth specimens. The main application envisaged would be to materials in the form of sheet, rod (including wire and fibre) and tube. Any non-uniformity in surface composition along the length of the specimens would be indicated by a discontinuity in the profile. The shortest ramps that have been profiled with the retarding field analyser and 0.5 mm diameter electron beam have been 50 mm long with a ramp 100 nm deep. Specimens could be considerably shorter than those used here provided that the electron beam diameter was reduced to take account of the steeper slope of the ramp. For glasses or other beam-sensitive materials it would probably be necessary to reduce beam-current to avoid specimen damage. The more sensitive cylindrical mirror analyser would enable lower beam-current densities and shorter beam residence times to be used and liquid nitrogen cooling would further reduce beam damage.

In common with all ion bombardment techniques, the effects of differential sputtering in the ramp method leads to inaccuracies in the determination of relative concentrations of constituents

at any given depth. The fact that the concentration values obtained after prolonged ion-etching approximated to those of air fracture surfaces indicates that differential sputtering effects have not distorted the profiles significantly in the case of float glass. However, there is clearly a requirement for a standard of glass surface composition against which effects such as differential sputtering and air exposure can be measured. The composition of fracture surfaces prepared in ultra-high vacuum would appear to be suitable calibration standards giving the bulk glass composition providing the crack tip does not propagate by some atomically selective route. Fully quantitative profiles giving absolute values of concentration could then be obtained providing account was taken of the appropriate ranges of the Auger electrons from the different elements.

4. Conclusions

Surface element composition profiles of high in-depth resolution have been obtained by combining ion-beam machining of a ramp section with Auger electron spectroscopic analysis. The new technique offers significant advantages over the commonly used *in situ* crater-etching method for long specimens e.g. those in sheet or rod form. In particular, since a new position on the surface is used for each depth analysed, electron beam effects are reduced. The depth corresponding to each composition can also be accurately measured and no assumption or measurement of sputtering yield is required. This ramp section method is illustrated for the case of float glass surfaces where it was possible to obtain sodium profiles and locate a cation depletion region extending to a depth of about 20 nm below the original glass surface, in addition to measuring tin and iron surface contamination.

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