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High temperature Langmuir vaporization mass spectrometer

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Abstract

A high temperature Langmuir vaporization mass spectrometer (HTMS) for the analysis of solid and molten materials from room temperature up to 1700 °C was designed, built, and tested. Volatilizing species are analyzed by electron impact (EI) and by surface ionization (SI) modes. Non-volatile surface species are analyzed by the static secondary ion mass spectrometry (SIMS) mode. In addition, it is equipped with an Ar^+ dynamic SIMS gun for an elemental analysis mode and for sample cleaning. The ion source has a unified design so a single sample can be analyzed by EI, SI or SIMS modes in rapid sequence at constant or variable temperatures. The instrument and data system were designed with particular emphasis placed on the ability of the instrument to perform EI ionization of neutral species prior to condensation and reactive species prior to reaction, and on giving the user the ability to correlate data from different ionization modes with changing sample chemistry. The HTMS has been successfully applied to the analysis of ion-emitting molten glasses. Large samples mounted in small rhenium tubes have been studied at temperatures up to 1150 °C, while smaller samples on flat rhenium filaments have been analyzed at temperatures as high as 1700 °C.
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1. Introduction

When a material is heated, many processes commonly occur, such as phase changes and volatilization. Volatilization from pure materials is generally better understood than volatilization from complex materials, and volatilization of minor components from complex materials are least understood. The vast majority of volatilizing species are neutral, although a few materials volatilize appreciable fluxes of ionic species, predominantly cations with low ionization potentials and anions with high electron affinities. The volatilizing ions are typically minor components in a complex matrix, and the chemistry of this minor component in the matrix is thought to have an important role in ion emission. Understanding the chemistry of the material in the solid state prior to and during volatilization is critical to the development of an understanding of these ion-emitting materials.

In order to gain an understanding of the overall process, it is necessary to study all ions and neutrals that volatilize, as well as the condensed phase species. This has led to the development of a mass spectrometer that combines multiple ionization modes into a single instrument that can provide insights into the processes that occur as materials are heated from ambient to above the volatilization temperature of the material. Volatilizing species are analyzed by surface (thermal)

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ionization (SI) and by electron bombardment (EI) ionization of neutral species. Condensed phase species are analyzed by static and dynamic secondary ion mass spectrometry (SIMS). The EI analysis mode is for positive ions, while SI and SIMS analysis modes are for both positive and negative ions. The SI, EI, and static SIMS modes can be analyzed in a rapidly sequenced fashion. Sputtered neutrals have also been investigated but require conditions (higher fluxes of the primary ion beam and of the electron beam) that are not consistent with interspersing with the other modes.

There were a number of applications in mind when this instrument was designed, with the study of ion-emitting materials being only one. Study of the high temperature chemistry of glass-forming melts and waste materials related to the development of waste forms for the immobilization of high level nuclear waste was another important application. The instrument has the potential to be useful for the study of many high temperature processes.

Instrumentation had previously been developed in this laboratory for the analysis of SI, SIMS, and EI modes on samples as they underwent a heating cycle. However, this capability was divided between two different instruments, and data collection was too slow to allow accurate monitoring of temperature vs. ion-intensity curves for more than one ionization mode at a time [1–6]. Thus, in order for a complete analysis to be obtained, two to five samples of the same material had to be analyzed. This significantly complicated efforts to correlate temperature profiles for different ionization modes as well as introducing uncertainty due to possible sample inhomogeneity. In addition, the rate of temperature change on each instrument was manually controlled, further complicating data comparison.

When designing the present instrument, the significant deficiencies of the past instruments were addressed. The primary goal was to be able to more accurately determine changes in sample chemistry as a function of temperature. This dictated that all of the relevant ionization modes be incorporated into a single ion source in which the ionization modes could be sequenced in rapid fashion. Consistent rates of temperature change and accurate monitoring of temperature required computerized control of the current heating the sample and the readout of the thermocouple attached to the sample. Computerized data correlation was also a requirement, since in some cases weeks were required to manually work through computer files of peak heights for a single analysis.

2. Instrument design, construction, and operation

Fig. 1 shows a photograph of the instrument in relation to the electronic console. The major components of the instrument are illustrated in Fig. 2. The ion source optics focuses ions from each of the ionization modes into the mass spectrometer. The sample is mounted on the end of a probe that is inserted through the vacuum lock and docks with the end of the ion source optics. The other end of the ion source optics are integrated onto the front of the quadrupole mass spectrometer. There are two ion guns for bombarding the sample for either static or dynamic SIMS analyses. There is a custom vacuum housing for containing these components. The computer system controls the mass spectrometer and most of the associated electronics as well as collecting and analyzing data.

Design trade-offs between different types of mass spectrometers were analyzed, with quadrupole, ion trap, time of flight, and sector instruments considered. An Extrel 1000 AMU quadrupole mass spectrometer with 0.75-in. rods and C50 and C150 electronics was chosen for two main reasons. First was the ease with which this type of ion source could be interfaced to the quadrupole analyzer. It is far more difficult to interface this newly designed ion source to the other mass analyzers. It was desirable to have the sample held in place by gravity, since many materials that are melted into glasses start as powders. This constrained the sample to be held upright, which in turn requires the instrument to be mounted vertically. The quadrupole design could accommodate any geometric configuration. The second reason for this choice was that we had previously developed a highly versatile data system

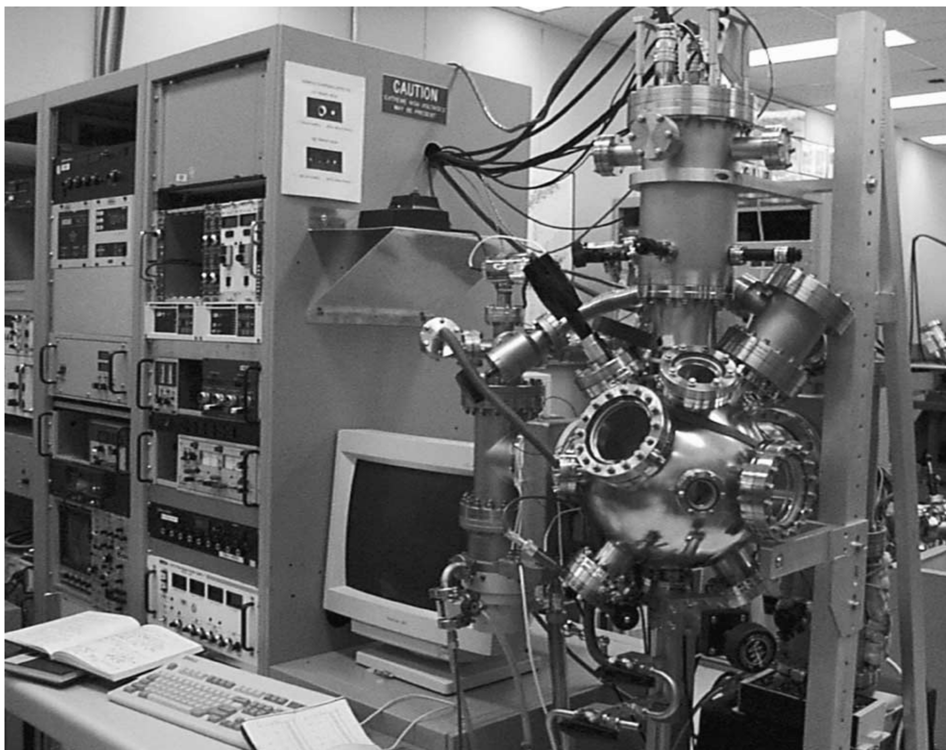

Fig. 1. HTMS instrument and peripheral electronic components.

for controlling quadrupole mass spectrometers that could be readily modified to accommodate new requirements. Data systems for the other types of mass spectrometers could not have been customized to the extent possible with the quadrupole.

The ion optics for the instrument (Fig. 3) combine all of the ion formation modes into a compact unit functioning on the same sample in rapid sequence. Many designs were modeled with the latest version of the SIMION ion optic modeling code [7], and one

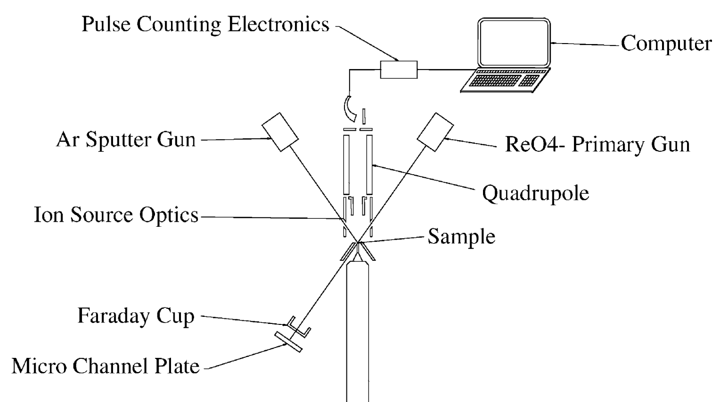

Fig. 2. Schematic view showing the major components of the high temperature mass spectrometer.

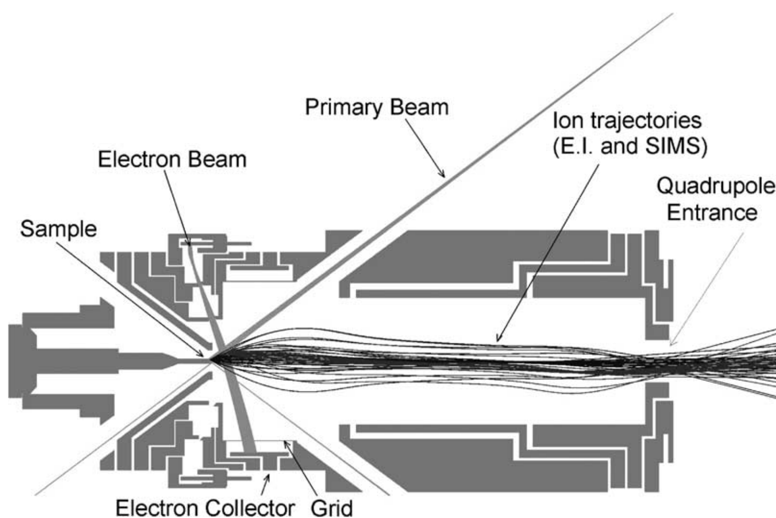

Fig. 3. SIMION-generated ion optic cross-section showing ion trajectories.

design proved to be superior both in ion optical performance and in feasibility to construct. After extensive "fine tuning" of the optics, the ion source was mechanically designed, constructed, and integrated into the instrument design. It is fully bakeable, allowing it to be used in an UHV environment. The sensitivity in all modes is quite high, especially sensitivity in the EI mode. The ion source is also unique in the way in which the various ion formation modes are integrated [8].

The cylindrical ion source, collinear with the quadrupole rods, was designed so that the face of the sample is located at the point where maximum ion transmission into the mass spectrometer is obtained when focusing conditions are optimized for ions originating from the surface. Ions are transmitted under these focusing conditions with nearly equal sensitivity even if the sample misses the optimal point by as much as ±0.5 mm along the vertical axis of the mass spectrometer. The sample must be centered to within ±0.5 mm, although reduced ion current transmission is still possible even with an uncentered sample. This provides some flexibility in sample mounting and simplifies the process of maximizing ion transmission. Sample position is readily reproduced much better than these limits, so this parameter is usually not a problem.

The electron beam for producing ions by EI is focused to converge to a point about 5 mm above the sample surface. Efficient ion transmission is still obtained for ions produced at this distance from the sample, but with a set of focusing conditions that minimize ion transmission from the surface (SI and SIMS). When analyzing SIMS and SI ions, the electron beam for EI is deflected by reversing the accelerating field for the electrons. When analyzing neutrals in the EI mode, SI ions are discriminated against by applying an appropriate leakage ring blocking voltage [9] and by altering the overall focusing conditions in the source; sputtered ions and neutrals are not produced because the primary beam is deflected away from the sample.

It is not possible to use ion optics to differentiate between SIMS and SI signals (because the focusing conditions for these two modes are essentially identical). Therefore, the net SIMS spectrum is computed from the difference between the signals detected in the "SIMS" and the "SI only" modes. This distinction is important only when the temperature is sufficiently high to produce ions by SI. When in the SI mode the primary SIMS ion beam is deflected so that only

SI ions are produced. Focusing conditions can be adjusted to minimize the contribution of SI when in the EI mode, and usually can be completely eliminated. However, it is necessary to verify that this is the situation during each analysis since the sample position may vary, which in turn may alter focusing conditions.

The ion source is enclosed except for through penetrations along five axes; a center vertical axis collinear with the quadrupole rods, vacuum lock, sample and ion focusing optics, and the other four each at 35° off vertical and 90° to each other (see Fig. 3). Ports on the spherical vacuum housing line up with the ion source penetrations. Two of the 35° penetrations are for the SIMS guns to have lines of sight to the sample and on to the opposing ports for analysis of the primary beam intensity and focusing, one for a light that shines on the sample when it is in position, and the other for viewing the sample in position. The viewport is fitted with a removable optical pyrometer. The face of the sample is located at the intersection of these five axes, which is the primary focal point of the lens and the center of the spherical vacuum housing.

The sample mounting and heating system has been evolving for many years [10], with the major difference from previous instruments being that these systems are mounted on a vacuum lock probe. Two versions are in use, one using a filament and the other a tube [10]. These are interchangeable on the end of the probe. The filament version uses a miniaturized single filament thermal ionization source, with the sample mounted on the face of the filament. The face of the filament is placed at the main focal point of the ion source. The tube version [10] has a tube mounted on rhenium filaments.

If large samples are deposited on a filament, poor sample conductivity and high sample emissivity can lower the temperature of the deposit as much as 200–300 °C below that of the supporting filament. This occurs when the bulk of the sample is larger than the bulk of the filament. This invalidates the temperature measurement made with the thermocouple, so samples of limited size must be used if an accurate temperature measurement is critical. When very thin samples are used, the temperature measured for the filament is representative of the sample temperature. When a sample is much thicker in the center and thinner on the edges, the emission profiles tend to be spread over a wider temperature range due to the varying temperature of the sample. These issues were studied by two methods. The first involved the use of the optical pyrometer focused through the viewport to measure the temperature of the face of the sample and comparing it to the filament and to the thermocouple reading. Lack of information on emissivity of the sample complicates this comparison. The second method involved comparison of the initiation of the evaporation of Ag as a function of temperature from molten glass ion emitters for thin and thick samples.

This problem with temperature gradients across a sample is inherent with Langmuir evaporation as opposed to Knudsen cell evaporation. Knudsen cell evaporation has the material in thermodynamic equilibrium and at a constant and accurately measured temperature, but cannot offer information on highly reactive species or give information on surface chemistry or of surface ions. Langmuir evaporation offers information on all species that volatilize from the surface, as well as offering SIMS, SI, and SN analysis possibilities, but does not offer information on thermodynamic equilibrium.

The tube or filament source is mounted on a 1-in. diameter vacuum lock probe that has power and thermocouple feedthroughs. This design works well due to the fact that the quadrupole does not require the ion source to be at high voltage; hence, it is practical to bring the low voltage electrical leads through a flange on the end and up the length of the probe. The probe is inserted through the vacuum lock mounted on the bottom of the vacuum housing, and the sample is positioned at the focal point of the ion source, using a docking mechanism and aided by visual observation. It takes about 5 min to insert a sample into the instrument.

The static SIMS gun uses the perrhenate anion as the primary projectile [1,5]. This primary ion is well established as an excellent probe for static SIMS analysis of electrical insulators, specifically for the analysis of molecular surface species [11–31]. The only difference between this ion gun and older

versions is the use of differential pumping. Some samples evolve gases that can poison the emitter, and differential pumping avoids this problem. The Ar^+ gun is a commercial unit and was not required for the analyses reported here, since the aim of this research was to study the top layer of the melted surface, not to sputter it clean or to perform an elemental analysis.

When static SIMS is to be used, the primary beam is accelerated to 5 kV and focused using visual observation of the image intensifier mounted on the port opposite the ion gun. During this time the sample is slightly retracted so that it does not intercept the beam. A Faraday cup is inserted, the beam intensity adjusted, and the Faraday cup retracted. Then the sample is inserted so the face is at the focal point of the lens, and the beam is positioned to silhouette the sample on the image intensifier. The beam is then deflected until the analysis is initiated so as to avoid beam damage to the sample.

The vacuum system is pumped by a turbo pump/mechanical pump combination, and by an ion pump/cryo shroud/Ti sublimator combination. Valves are used to isolate the various components. The initial evacuation is with the turbo which is sufficient for samples that do not require UHV for analysis. The ion pump is valved in when a sample does require UHV for analysis. When the ion pump is valved in, the turbo can be used to differentially pump the vacuum lock and the SIMS guns. This mode is useful if the sample is emitting gases that can poison the ion emitter in the SIMS gun since it permits differential pumping. The entire system is bakeable and pumps into the low 10^{-8} Torr range with the turbo pump and into the mid 10^{-9} Torr range with the ion pump. Samples analyzed to date have not required the cryo shroud and sublimator pump, but these are available if needed for a particularly heavy gas load or if a particularly clean vacuum were required.

The data system uses hardware and software developed in our laboratory [6]. The source code is highly modular and readily adaptable to new requirements. It controls the power supply that heats the sample and is interfaced to the thermocouple readout. The computer programs the power supplies that control the focusing voltages and thus can switch focusing conditions that have been previously optimized for the individual ionization modes. The computer also has control over the functions of the mass spectrometer and the pulse-counting detection system. The operator specifies the temperature ramp, the ionization modes and the masses to be monitored. The computer controls the parameters for scanning and for switching between ionization modes. Scanning of the specified masses for each ionization mode is initiated, and the temperature ramp is started. The computer collects data from a pulse-counting system and stores peak heights for each mode along with time and temperature in a form compatible with a spreadsheet. Specialized spreadsheets have been developed for individual applications. Alternate applications have been programmed that allow the sample to be heated to a preset temperature and the course of the reactions monitored at that temperature.

Only one peak can be measured for one ionization mode at a time, but sequencing with computer control is fast in comparison to the rate of change in the sample (data are collected for periods of about 100 ms with delay times between collections in the order of a few milliseconds). This allows data to be collected rapidly enough to track the intensity changes as functions of time and temperature. When the data is in the spreadsheet, it can be manipulated according to the needs of the analysis, with Fig. 4 giving a representative plot of the output. The plots of various ions can be examined to determine if they originate from the same parent ion. For example, the NO_2, NO, and O peaks at 46, 30, and 16 amu have identical temperature profiles in the temperature region where nitrate decomposes, so generally only the parent peak at 46 is plotted. Ion profiles from different modes can also be compared to seek clues to changes in the material with increasing temperature. When the analysis is finished, it can be compared to the results from a differential thermal analysis or another type of thermal analysis. This level of automated instrument control, data collection, and analysis allows the completion of an entire analysis in a few hours that would have required several weeks with the older instruments. In addition, the initiation of various phenomena in the sample can be correlated

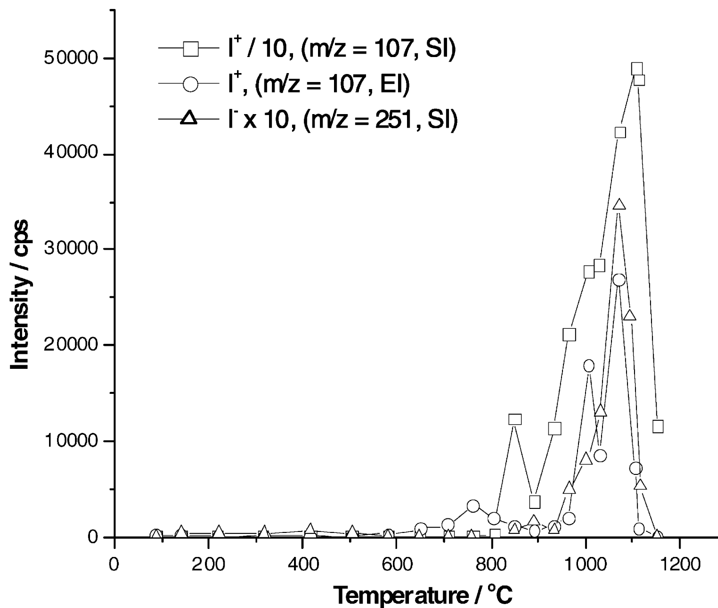

Fig. 4. Plot of Ag^+ (SI and EI) and ReO_4^- (SI) intensities vs. temperature.

with much greater accuracy due to all of the analysis modes being conducted on the same sample. Among the variables that are eliminated are: heating rates, thermocouple placement, and sample inhomogeneity.

3. Applications to ion-emitting molten glasses

During the testing of this instrument, a variety of experiments involving the Ag–borosilicate system were performed to investigate instrument performance. Ion intensities were measured in each of three data collection modes: EI, SI, and static SIMS. Physical mixtures of silver nitrate and borosilicate [4] were applied to an Re filament and inserted in the mass spectrometer. Some samples were melted by heating to approximately 900 °C for about 1 min and subsequently quenched (all while in the mass spectrometer) prior to the vaporization experiment. The resulting material was a shiny, white, and somewhat translucent glassy looking material. The sample was then heated while ion-intensity data were collected in all three modes (results are shown in Figs. 4–6).

3.1. Temperature programmed EI and SI

The major signals of interest in the EI spectrum were due to Ag^0 at $m/z = 107^+$ and 109^+. The significant signals of interest in the SI spectra were Ag^+ at $m/z = 107$ and 109, and ReO_4^- at 249 and 251. (Only the signals resulting from the most abundant isotopes of Ag and Re are included in the figures.) The feature of the analysis that is most interesting is the contrast in intensity vs. temperature for SI and EI Ag^+. The EI signal rises above the background at about 650 °C, while the SI signal begins to increase above the baseline at about 800 °C. Both signals increase until about 1070 °C, when the EI signal subsides, while the SI signal continues to grow until the temperature is above 1100 °C, before it diminishes (it is believed the sample was nearly exhausted, resulting in the dramatic intensity reduction). This behavior (reduction in EI signal while the SI signal continues to increase) was also observed in earlier studies performed in an ion/neutral mass spectrometer in our laboratory [4]. This behavior is consistent with the concept that SI ions being formed at the surface of the molten sample at the expense of

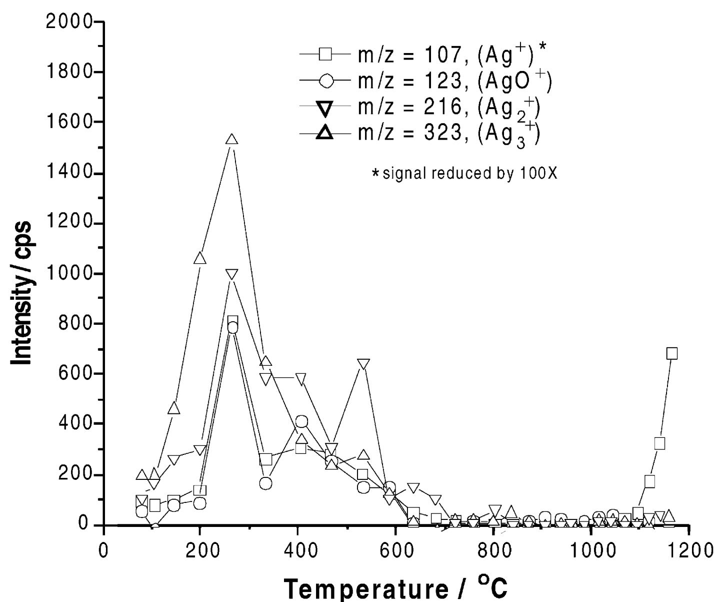

Fig. 5. Plot of Ag^+ (net SIMS) intensities vs. temperature.

Ag^0 [3]. Previous studies demonstrated that the species in the condensed phases are metallic Ag [2–4].

The appearance of ReO_4^- is indicative of the presence of an Re–O species on the surface of the molten glass [3]. It also indicates that the surface species may be ReO_4^-, which is not surprising since ReO_4^- appears to be stable at appreciably higher temperatures than the other Re oxides [1,5]. Even if the

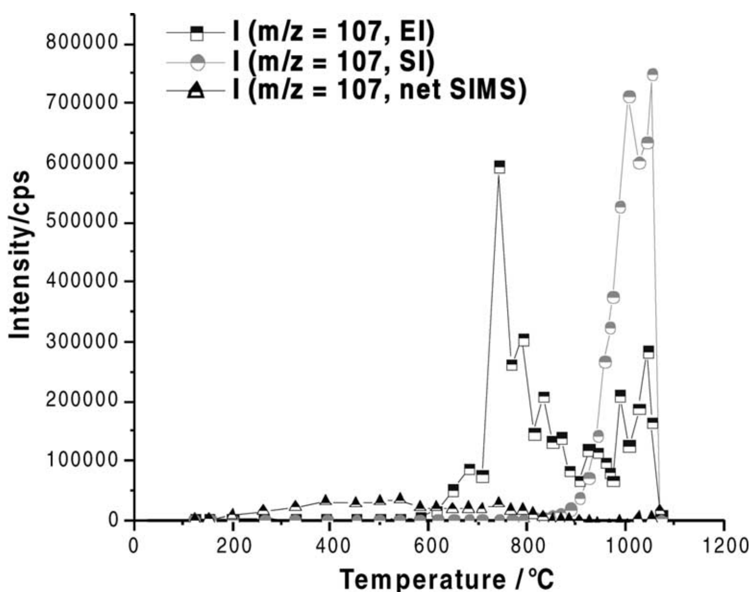

Fig. 6. Plot of Ag^+ signal intensities for all three detection modes (EI, SI, and net SIMS) vs. temperature.

absolute temperature measurement is in error, which is probably the situation with this thick sample, the relationship of the three curves to each other are accurate since all of this data was collected from the same sample. The SI ReO_4^- was observed prior to the sample being bombarded by the ReO_4^- primary beam, demonstrating that this species did not originate from ion implantation, but rather comes from reaction between the molten glass and the Re filament.

The ionization potential of Ag is 7.45 eV, which is relatively high and will cause the ion formation process to be inefficient unless there is a very high work function on the surface. This is consistent with the hypothesis that an Re oxide species forms on the surface of the molten glass, since an oxidized Re surface has been shown to have a work function that ranges as high as 7.2 eV [32,33]. It is recognized that an oxidized Re filament may be much different than an Re oxide on the surface of a molten glass, but nevertheless offers a provocative possible correlation.

3.2. Temperature programmed static SIMS

Fig. 5 presents the static SIMS temperature profile data for Ag-bearing species detected from an Ag–borosilicate sample supported on an Re filament. The Ag monomer, dimeric and trimeric Ag clusters, and a Ag monoxide, are clearly present in the SIMS spectra at temperatures below the melting point of the sample. The molecular species, present at levels about two orders of magnitude below the intensity of the atomic species, were not detected in previous studies [4] due to lower instrumental sensitivity. After the material has melted, all Ag species are essentially undetectable until Ag starts to volatilize. At this point the Ag^+ SIMS signal starts to increase, but not the molecular or cluster species. This indicates that molecular and cluster Ag species are broken down into monatomic species dissolved in the melt.

Fig. 6 presents data from another thick sample for Ag from EI, SI, and SIMS. There is significantly different behavior for each mode below the initiation of SI at about 1000 °C. EI exhibits the highest Ag^+ intensities in the 700–900 °C region, in contrast to the data in Fig. 4. This difference between the analyses in Figs. 4 and 6 is thought to be due to size and heating rates. A slower heating rate and larger sample size allows more Ag to volatilize prior to being solubilized in the molten glass. Ag^+ from SIMS starts to increase at about 200 °C, peaking at just below the melting temperature of the sample, and dropping essentially to zero by 1000 °C, and then increasing along with the other species as the temperature was increased further. This figure also demonstrates the intensity differences between the SIMS mode and the EI and SI modes.

An additional experiment was conducted in which a sample was heated to 800 °C, which is above the melting point of the material but below the volatilization point for Ag. The sample was then cooled to room temperature, and then put through another heating/analysis cycle. The same Ag clusters observed earlier were observed during this cycle, and again they disappeared when the temperature reached about 850 °C. The atomic Ag ions from EI and SI came on as usual at about the same temperature as previous runs that did not involve a preheat cycle. This observation suggests that there is some segregation of the analyte (Ag) as the liquid cools and that an analysis of the cooled material is not representative of the material while it is hot. This observation is consistent with the SEM data of Huett et al. [2].

4. Conclusions

The HTMS was designed to allow the measurement of ions by SIMS, SI, and EI under computer control in rapid sequence on the same sample, and it has performed up to the design criteria. Sputtered neutrals have also been detected, but under conditions not compatible with interlacing with the other modes. The capabilities of this instrument have allowed the development of improved techniques for analyzing the high temperature chemistry of condensed phase materials. These techniques allow the convenient measurement of reactive gases and condensable vapors prior to their reacting or condensing as they evolve

from a material undergoing thermal processing. At the same time the user can detect changes in surface chemistry using SIMS and SI.

This instrument is currently being used to gain new insights into molten glass ion emitters, and is demonstrating that a mixture of ions and neutrals are being emitted from these materials. The ion and neutral flux started and ended at similar temperatures, indicating that they originated from the same condensed phase species, even though there was a dramatic shift in the ion/neutral ratios. It is speculated that this increase in ion/neutral ratios may correspond to the formation of a high work function surface on the molten glass.

Acknowledgements

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