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High intensity perrhenate anion (ReO_4^-) emitters

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Abstract

Various materials have been investigated for ReO_4^- (perrhenate anion) emission with the goal of producing a high output emitter for application as a primary ion source in secondary ion mass spectrometry (SIMS) analysis. A new emitter consisting of Re powder/$BaSO_4$ packed in Pt tubes has been found to have superior properties. This system produces in the order of 200 nA/mm^2 for over 100 h when heated between 1100 and 1300 °C. Total currents of over several hundred nano-amperes have been sustained (three orders of magnitude higher than previous emitters, >100 h). Lower currents (5–100 nA) persist for hundreds of hours. These emitters have been used in several SIMS guns for over a year, and have proven to be extremely reliable and relatively easy to operate. As the ReO_4^- ion has previously been shown to be a highly effective projectile for many SIMS applications, the development of this improved high output emitter makes it feasible to extend the range of its application to imaging and depth profiling.

Keywords: Ion emitters; SIMS; Perrhenate; Polyatomic primary ions

1. Introduction

Polyatomic primary ions are of interest in secondary ion mass spectrometry (SIMS) to take advantage of certain unique sputtering characteristics offered over monatomic projectiles. Improved performance includes increased secondary ion production, especially in static-SIMS analysis [1–8]. Of particular interest is the increase in "molecular" secondary ions, allowing the preservation of more chemical information in the sputtered ions [9,10]. Another important characteristic of polyatomic primary ions is the improved depth resolution when applied to depth profiling [11,12]. These needs have been impetus to develop a variety of polyatomic ion sources suitable for SIMS, including among others SF_6^0 (neutral) [13–15], SF_6^-, SF_5^+ [12], ReO_4^- [16], and various cluster ions [17–21].

Molecular dynamics simulations [22–24] indicate that the significant factors underlying the unique sputtering characteristics of polyatomic particles are (1) the reduced depth of the energy deposition in the sample during the sputtering event and (2) the time and space coincident coupling of energy transfer from the collision cascades of the individual atoms in the primary ion to the sputtered molecule. Depositing more energy closer to the surface, combined with time and space coincidence, enhances the probability of desorbing an adsorbed species.

Early applications of polyatomic beams for SIMS comparing a SF_6^0 source to a Cs^+ source for static-SIMS were very encouraging [6], but the SF_6^0 source utility was constrained by low output levels and focusing limitations. To retain the positive benefits of a polyatomic projectile but overcome the SF_6^0 limitations, a solid-state anion source producing ReO_4^- was developed [16]. This source provided increased output current (several hundred pico-amperes), and promised the potential for producing more finely focused ion beams. The source consisted of a mixture of barium perrhenate [$Ba(ReO_4)_2$] in a ceramic matrix of europium oxide pressed into a pellet in the end of a small rhenium tube which when heated to ∼900 °C produced the ReO_4^- ions.

These ReO_4^- ion sources have been used in our laboratory in a variety of SIMS instruments for static-SIMS analyses, and, when operated within the appropriate temperature range, they have lasted for up to 5 years (and are still operating at this writing). Their utility for producing molecular secondary ions from a broad range of sample types has been demonstrated. Most of this utility is thought to be due to the polyatomic character of the primary ion, although the negatively charged primary has the added benefit

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of greatly reducing charging problems for many types of insulating samples. This simplifies and in some cases eliminates the need for active charge neutralization. These primary ions have been used successfully for applications as diverse as the analysis of soil [25–29] and concrete [30,31] surface contaminants including chemical warfare agent detection and for the characterization of biological specimens [32]. However, a significant increase in the ReO_4^- ion output was required to extend the range of applications, in particular to provide an ability to sputter rapidly and to be able to produce a small diameter beam of adequate intensity for imaging and depth profiling applications. Reported here is the development of a new high intensity perrhenate emitter.

2. Previous experimental studies

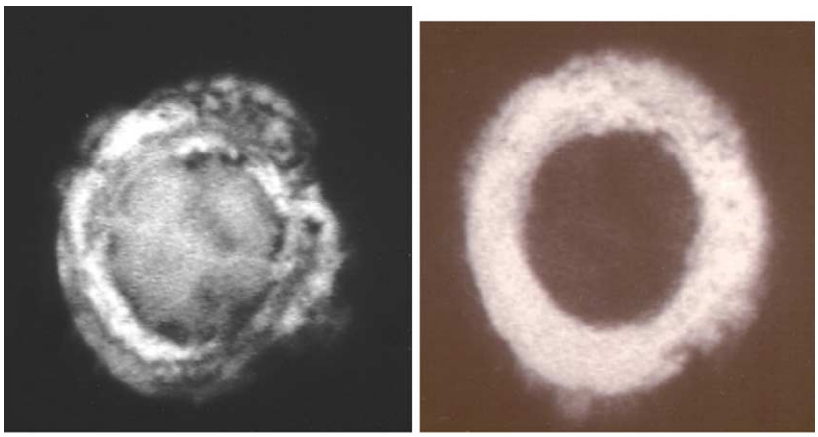
Earlier work [16,33], leading to the $Ba(ReO_4)_2$/europium oxide ceramic matrix emitter described above, consisted of testing various mixtures of perrhenate salts and rare earth oxides packed in Re tubes. These emitters were based on the idea that ReO_4^- ions are pre-formed (supplied in the matrix as perrhenate salts) and are emitted under appropriate circumstances (i.e., temperature and matrix chemistry). When further investigating the $Ba(ReO_4)_2$/europium oxide ceramic matrix emitters, it was observed that when they are run at high output continuously for several weeks, the edge of the Re tube that supports the matrix begins to emit ReO_4^- ions. As time progresses, ion production decreases from the ceramic matrix and increases from the Re tube edge. After a few weeks at high current, ion output is solely from the Re metal surface of the tube edge (see Fig. 1). The output from this donut-shaped ring is clearly less desirable compared to a small disk-shaped source for obtaining a tightly focused beam.

Production of ReO_4^- from a Re metal surface was surprising considering that bare Re filaments heated in vacuum produce no measurable ReO_4^- ion current, with or without background O_2 in the system. Some mechanism had "activated" the Re metal surface so that it would be oxidized to ReO_4^- if oxygen were available. This appears to represent ReO_4^- formed in situ by a high temperature reaction. It is believed that over time some Ba containing species migrates across the Re metal surface at high temperature and catalyses oxidation of metallic Re to produce ReO_4^-.

Other early work [34] tested perrhenate ion emission from Re metal filaments using various ceramic oxides as oxidizers, mostly rare earth oxides. While this showed that perrhenate ions could be produced in situ at high temperature from some of these systems, the output levels and lifetimes were considerably less than desirable for a sustained ion source. Furthermore, water vapor was the oxidizing species with the rare earth oxide/Re systems, while many of the other material systems investigated were sensitive to background oxygen in the system.

The discovery of relatively high output, long-lived in situ production of ReO_4^- from Re metal surfaces initiated an investigation to understand this phenomenon and to use it to produce a superior emitter. The mechanisms of this activation are being studied and will be reported separately.

It should be noted that as the output from the emitter shifts from the center region to the tube edge (Re metal surface), the ion output becomes sensitive to background O_2 in the vacuum system. This sensitivity increases with time, and O_2 is required to maintain ion production. After activation of the Re tube edge, output can be maintained for long periods at roughly the same level as initially from the ceramic matrix material alone if O_2 is maintained between 10^{-6} and 10^{-5} Torr. Without O_2 the output can drop by one to two orders of magnitude. While the mechanisms are not yet understood, apparently oxygen from either gaseous O_2



(a) (b)

Fig. 1. Surface emission images of perrhenate ions from a ceramic matrix emitter (barium perrhenate/europium oxide) in a Re tube (0.042 in. i.d. × 0.060 in. o.d.). (a) Near the beginning of emitter life, emission is from both the ceramic material in the center and the Re tube edge. (b) After several weeks the emission is from the Re tube edge only.

or from some solid compound can be used for the oxidation of Re. As oxygen from the solid state is depleted, oxygen from the gas phase becomes required.

Another important variable was the temperature of the system. ReO_4^- emission started between 700 and 800 °C and increased with temperature. However, as the temperature was raised above ∼900 °C, the lifetime of the ReO_4^- emission was greatly reduced. Since the process was not reversible (source performance did not return if the temperature was reduced) it was suspected that there was either a non-reversible chemical change or loss of a critical chemical component due to evaporation.

3. Experimental

Two basic configurations were used to test emitters, one based on a Re ribbon and the other on small refractory metal tubes (Re and Pt).

3.1. Re ribbons

The ribbon configuration was used to test materials for the direct activation/oxidation of a metallic Re surface for perrhenate emission. The filament configuration consisted of a Re ribbon, 0.0254 mm (0.001 in.) thick × 1 mm wide × ∼ 10 mm long (see Fig. 2). It was bent so that in the middle of the ribbon there was a flat emission surface (∼1 mm × 1 mm), perpendicular to the optical axis of the ion imaging system. The ends of the ribbon are spot welded to support/electrical contact posts. The ribbon is heated resistively. Materials of interest were placed on the emission surface. These were applied to the surface as powder/water slurries.

3.2. Small refractory metal tubes

Small refractory metal tube configurations consisted of a small, short tube packed flush at one end with material of interest, which was the emitting surface (see Fig. 3). Re, Pt and Pt alloy tubes of various sizes ranging from 0.381 mm (0.015 in.) to 1.32 mm (0.052 in.) i.d. and typically 3.8 mm (0.15 in.) long were used. The opposite end of the tube was spot welded to two Re filaments for mechanical support and resistive heating. These were spot welded in turn to insulated posts for mechanical support and electrical connections.

For the improved emitters presented here, the tubes were packed with a mixture of Re metal powder (635 mesh, Rhenium Alloys) and $BaSO_4$ (Fisher Scientific Company) in various molar percentages (mol%). The powders were weighed and mixed together in a vial. These mixtures were ground in a small mortar and pestle to break up the $BaSO_4$ lumps and blend with the rhenium powder. These powders were tightly compacted into the tubes.

In earlier studies the filaments used to support and resistively heat the tubes were Re ribbons (0.0254 mm (0.001 in.) thick × 1 mm wide). These were inadequate for the higher temperatures required for this work (1300 °C versus 900 °C). They would often sag, moving the emitter off center causing focusing problems and sometimes shorting. Furthermore, the higher temperatures required for operation with the $BaSO_4$ were often unattainable with the ribbons. This is due to the limited thermal conduction of the ribbons because of their small cross-section, compounded by the large surface area per unit length, which allows much of the thermal energy to be lost to radiation. Substituting Re wire as support/heater elements greatly improved this situation. To match the power supply for the greatest heat input, 0.25 mm diameter wire

Fig. 2. Re ribbon filament emitters (1 mm wide). Emission is from the square end face.

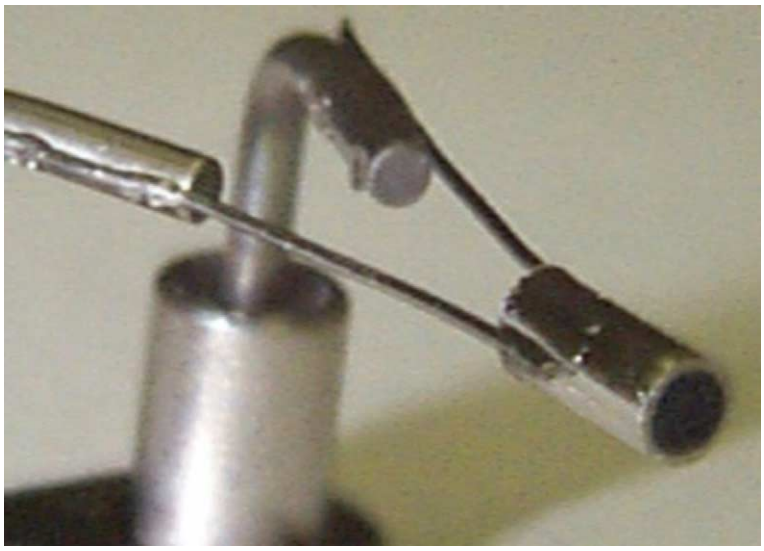


Fig. 3. Re powder/$BaSO_4$/metal tube emitters (emitter #42, 1.32 mm o.d.).

was chosen. This more robust arrangement eliminated the sagging problem and allowed operation in the desired temperature range (>1300 °C) for all but the largest diameter Pt tubes (1.32 mm i.d. × 1.57 mm o.d.). The largest diameter tubes were limited to temperatures just over 1100 °C due to the significant radiative losses from the larger surface area, combined with the limitations of the power supply (5 A). It should also be noted that the largest Pt tubes had a relatively thin wall compared to the diameter. This will lower the thermal conductivity down the length of the tube, which could result in lower temperatures at the emitting surface.

3.3. Vacuum system and measurements

These emitters are mounted in an ion gun assembly [35]. Vacuum system-based pressures were typically around 10^{-7} Torr. The lowest pressures were in the low 10^{-8} Torr range and the highest pressures were 10^{-5} Torr when oxygen or other gasses were added to the system.

The ion emitters were tested on an ion beam test stand, the predecessor of which has been described elsewhere [36]. The beam coming from the ion gun can be focused onto a faraday cup for measurement of the total ion current, or with the faraday cup retracted, on a microchannel plate (MCP) image intensifier to obtain an image of ion emission from the surface. There was no capability for mass separation in this system. A magnet could be manually held next to the vacuum chamber to deflect the beam to verify that it did not contain ions of significantly different masses. This gave an indication as to the mass purity of the beam. Emitters of a given composition were tested in a separate thermal ionization mass spectrometer to verify that the ion beam was indeed perrhenate.

Emitters were usually run continuously until their performance dropped below values of interest. Each experimental run for an emitter can take from several days for a poorly performing sample, to over 2 months. A second instrument of similar design was eventually employed to increase the number of experiments.

4. Results and discussion

4.1. Direct emission from metallic Re ribbon surfaces

Re ribbon emitters were used to investigate a variety of compounds for their capability to oxidize Re to ReO_4^- and allow its emission and also to evaluate the ribbon configuration as an emitter for ion gun applications.

Compounds tested included $Ba(OH)_2$ and $BaCO_3$, which were some of the more successful agents. There were undoubtedly waters of hydration, especially with the hydroxide. No effort was made to control the level of hydration since the materials were assumed to dehydrate when heated in vacuum. These compounds were chosen for inclusion of Ba, stability at high temperatures and for the inclusion of oxygen. Typically ReO_4^- emission occurred in the 800–900 °C temperature range.

Emission from the ribbon surfaces was non-uniform, typically exhibiting large, time and space-dependent, ion emission variations. They had regions of low emission and bright, high emission points that sometimes scintillated. This was due in part to the difficulty in uniformly applying activating/oxidizing agents to the Re ribbon surface. If sufficient agent was applied to obtain any reasonable activation, the areas with bulk material also blocked emission from those areas.

The ribbon emitters displayed wide variability in ion output between samples and treatments. Many operated from a few pico-amperes to several hundred pico-amperes and a few were in the nano-amperes range, although only for short times. Ion emission generally increased with temperature,

however as higher temperatures (generally >900 °C) were reached this effect diminished, with output increasing only slightly with increased temperature. The ribbon emitters also developed a large sensitivity to background oxygen pressure. Background oxygen in the system was required to reach and to maintain high intensity.

It became apparent that while the Re ribbon configuration was convenient for screening compounds for their ability to oxidize/activate Re for the production of ReO_4^-, it was unsuitable as an emitter for general use for the above reasons.

4.2. $BaSO_4$ as an oxidizing agent

One feature observed from the above-mentioned investigations was that oxidizing compounds containing a heavy alkaline earth cation produced longer lived, higher output ReO_4^- emission. A variety of Ba and Sr containing compounds gave by far the best results, with Ba being the preferred species. It is hypothesized that the Ba (or Sr) cation is needed to stabilize the perrhenate anion long enough for it to be emitted. It was also apparent that other important rate limiting factors included the source temperature and the availability of oxygen. A higher temperature system, and hence faster kinetics, was clearly desirable for increased ion output. It was also desirable to have sufficient oxygen available from a solid form for long-lived ion production so there would not be a dependence on gaseous O_2 (which is more difficult to control).

Barium sulfate ($BaSO_4$) was chosen as a likely candidate to meet the above requirements as an oxidizing/activating agent. It contains Ba, has a considerably higher melting point (1350 °C) than other known activating agents (for example, $BaCO_3$, melting point 811 °C) and it is known to be a powerful oxidizing agent with many oxygen atoms.

An initial test consisted of putting $BaSO_4$/water slurry directly on a Re ribbon. When heated, this immediately activated the Re and resulted in high perrhenate anion output, with a peak output of 95 nA, settling to around 60 nA for several hours, and then slowly decreasing over several days. This was without background oxygen in the system. However, as mentioned previously, the ribbon configuration resulted in very non-uniform emission across the face of the emitter, including scintillating bright points, similar to Re ribbon activation with other agents. Activation with $BaSO_4$ did not produce ReO_4^- anions until over 900 °C and produced the largest currents between 1100 and 1300 °C. These operating conditions for $BaSO_4$ activation/oxidation are several hundred degrees higher than the previous systems (800–900 °C). This verified that the higher temperature stability of $BaSO_4$ did indeed allow higher operating temperatures, which enhanced ion production.

Mass analyses of this material system ($BaSO_4$ on a Re ribbon) were performed on a high temperature Langmuir vaporization mass spectrometer (HTMS) [37] developed in this laboratory. Thermal ion emission spectra showed that the ion beam consisted of between 90 and 98% ReO_4^-, with the remainder mostly ReO_3^-, and trace quantities of Cl^-, thus verifying the predominance of ReO_4^- in the output.

The possibility of $ReSO_2^-$ existing in the emitted ion beam arises due to mass over lap with ReO_4^-. It was verified that $ReSO_2^-$ was not present in the beam in experiments using $^{18}O_2$ as a background gas in the vacuum system. $^{18}O_2$ was added to determine if ^{16}O in ReO_4^- could exchange with ^{18}O. On addition of $^{18}O_2$, the ReO_4^- thermal emission peaks split into peaks corresponding to substitution of 0, 1, 2, 3, or 4 of the oxygen atoms in ReO_4^- with ^{18}O. Under appropriate conditions all of the oxygen atoms could be replaced producing a pure $Re^{18}O_4^-$ beam. This verified that $ReSO_2^-$ did not exist in the beam.

During these experiments SIMS spectra were also taken. It is interesting to note that at temperatures below operating conditions, SIMS peaks were seen corresponding to SO_x^- ($x = 1, 2, 3, 4$). These peaks disappeared at operating temperatures. A peak at mass 32 corresponding to either S^- or O_2^- was also observed which persisted at operating temperatures. On addition of $^{18}O_2$, this peak split into peaks at mass 32, 34, and 36 corresponding to $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$, respectively, and after time (~1 h) converted completely to mass 36. Therefore, it appears that sulfur-containing species are not present at operating conditions. This was surprising as it was originally assumed that there was a direct conversion from SO_4 to ReO_4. There is also a myriad of positive peaks in the SIMS spectra, at operating temperature, corresponding to species containing various numbers of Ba, Re, and O and are assumed to be various intermediate species in the conversion to ReO_4^-.

4.3. Re powder/$BaSO_4$/metal tube emitters

It seemed logical that a system consisting of Re metal with a high surface area intimately mixed with a high concentration of $BaSO_4$ would offer distinct advantages. This would allow both $BaSO_4$ and Re to be present at the surface without blocking ion emission, and at the same time increase the rate of reaction and hence ion output due to the high surface area and increased contact between Re and $BaSO_4$. This was accomplished by mixing Re powder with $BaSO_4$ powder and packing the mixture into refractory metal tubes (Section 3.2). This arrangement was very successful. The results of the experiments performed using this arrangement are shown in Table 1.

The emitters were continuously operated from start to end, with only a few exceptions for brief interruptions due to apparatus problems. Experimental parameters (temperature profiles, addition of background O_2, etc.) were not consistently applied to the various experiments. This contributed to the considerable variability in the perrhenate ion output between emitters.

The total emitted ion current depended on emitter surface area (metal tube i.d.). The smallest tubes (Pt, 0.41 mm i.d., #40, #41) produced ion currents in the 10–50 nA range initially. The 0.84 mm i.d. Pt tubes (#44, #45) initially produced

Table 1
ReO_4^- output from Re powder/$BaSO_4$/metal tube emitters

#	Tube	i.d. (mm)	mol% $BaSO_4$	Approximate output (nA)[a]	Approximate duration (days/h)	Temperature (°C)	Output/surface area (nA/mm^2)
26	Re[b]	1.07	4.7	230–200	3/72	1150, 1180	257–223
				200–130	1/24[c,d]		223–145
28	Re[e]	0.508	4.7	50–80	14/336[f]	1140, 1200	246–394
				50–0.1[g]	21/504[c]		246–0.49
40	Pt[h]	0.41	30	10–45	36/864	1150, 1300	77–346
				20–0.5[i]	7/168[c]		154–3.8
41	Pt[h,j]	0.41	30	30–20	6/144	1200, 1265	231–154
				17–6	7/168	1260, 1270	131–46
				15[k]	1/24		115
42	Pt[l]	1.32	30	80–65[m,k]	6/144	1130[n]	58–47
43	Pt[l]	1.32	50[o,p]	160–50	1/24	1130[n]	116–36
44	Pt[q]	0.84	15	70–125–70	3/72	1080, 1185	126–226
				115–70	2/48	1250	208–126
				70–6	0.5/12		126–10
				6–3.5[k]	3/72		10–6
45	Pt[q]	0.84	30	100–125–100	7/168	1100, 1245	181–226
				100–12	3/72	1245	181–22
				12–6[k]	21/504		22–10.8
46	Pt[q,r]	0.84	30	450–500–300[s]	1/24	1250	815–906–543
				150–20	2/48		272–36
				10–5.5[k]	8/192		18–10

[a] ReO_4^- ion current measured on faraday cup (except as noted, output was from center powder region).
[b] Re, high purity CVD, Ultramet, 1.07 mm i.d. × 1.52 mm o.d. (0.042 in. i.d. × 0.060 in. o.d.).
[c] Steady drop over this period.
[d] Ribbon support heaters sagged and shorted out.
[e] Re, high purity CVD, Ultramet, 0.508 mm i.d. × 0.711 mm o.d. (0.020 in. i.d. × 0.028 in. o.d.).
[f] Over this period the output shifted from the powder in the center to the edge of the Re tube.
[g] Output was from tube edge, and required background O_2.
[h] Pt/Ru, 95%/5%, Hamilton, 22 gauge, 0.41 mm i.d. × 0.72 mm o.d.
[i] With background O_2, the output would rise back to 20 nA.
[j] Packed powder emitting surface recessed in tube approximately the same as the i.d.
[k] Emitter still performing when experiment stopped.
[l] Pt 99.9%, Johnson Matthey, 1.32 mm i.d. × 1.57 mm o.d.
[m] Initial transient 200 nA.
[n] Maximum attainable temperature.
[o] This concentration packed poorly.
[p] Emission from donut-shaped ring.
[q] Pt/Ru, 95%/5%, Hamilton, 18 gauge, 0.84 mm i.d. × 1.27 mm o.d.
[r] Large aperture, 2.54 mm (0.100 in.) in ion gun vs. 0.60 mm for all other experiments (see text).
[s] Initial transient 750 nA.

~100 nA total ion current. The larger Re tube (1.07 mm i.d., #26) produced ~200 nA.

Output from the largest Pt tubes (1.32 mm i.d., #42, #43) was ~50–100 nA. This lower output was largely due to the low operating temperature, as their large surface area had large radiation losses. 1130 °C was the maximum attainable temperature with the 5 A current limit of the power supply, while the smaller tubes were easily heated to over 1300 °C.

Ion emission per unit surface area was in the order of 200 nA/mm^2 for approximately 100 h, when the temperature was between 1100 and 1300 °C (Table 1). Some produced these high output rates for several hundred hours (#28 ~336 h, #40 ~864 h). After this initial high output period, most would produce lower ion currents for considerable periods (5–100+ nA/mm^2, often for hundreds of hours). Eventually the output would drop to lower levels, i.e., "burn out". In these experiments the temperature was often raised during the experiments (between 1100 and 1300 °C) to try to maintain higher output currents. Also it was observed that when temperatures exceeded 1300 °C these emitters would usually "burn out" in several hours to a day, depending on temperature.

A characteristic output/time profile that the emitters typically followed in various degrees is as follows. At the beginning the ion output increases with temperature starting at ~900 °C. As the temperature is raised between 1100 and 1300 °C, the output levels off and becomes considerably less sensitive to temperature. There is a slight lag in output as the temperature is raised and time is required between steps to reach a steady state. When the step to high temperature is done quickly or all at once there is sometimes an over shoot in the output that decays down to a more steady level (over seconds or minutes). When at a stable operating temperature there is a high output period in the order of

200 nA/mm^2, which usually lasts for 100 h or more. During this time the output gradually decays, but not drastically (i.e., typically 10–30%). Following this high output period there is often a significant decay period where the output drops by an order of magnitude over tens of hours to several days. This is followed by a lower output extended period that slowly decays over hundreds of hours.

With regards to beam output stability, which is important for depth profiling applications, there is some variation between emitters but once an emitter reaches stable conditions the short-term (several minutes) fluctuations are usually less than a few percent. For many emitters it is less than 0.1%. (Smaller surface area emitters have larger fluctuations than larger ones.) The longer-term drift is also generally less than a few percent per hour once steady conditions are obtained.

4.4. Tube material, oxygen sensitivity and emission uniformity

Re tubes were tried first and during operation the tube edge slowly activated while the output from the center powder area slowly diminished. The result was that after a week or two of operation the Re tube end face was emitting more than the center area, although the total output was nearly the same if background O_2 was maintained in the system. This again gave a less desirable donut-shaped emitter similar to the previous ceramic matrix emitters. Re tube emitters did show a little higher over all ion output than Pt tube emitters, but this is probably due to the increased emission surface area of the tube end.

After long run times (several additional weeks) the Re tube showed considerable erosion, with the tube becoming very thin in one particularly long run (#28). Commensurate with this was a red thin film deposit on internal parts of the ion gun that were in a direct line of sight from the emitter. Analysis in the scanning electron microscope (SEM) showed this to contain Re and O (oxygen) with ratios indicating this is probably ReO_3. This indicates that considerable amounts of Re is lost as neutral ReO_3, which deposits on the inside walls of the gun. Another observation was the slow build up of a thick porous material on the end of the emitter that seemed to block emission of ions. Its composition was not determined because it charged in the SEM. This could be scraped off, restoring it in some degree back to the higher output levels.

In an effort to eliminate emission from the tube end face, an inert yet sufficiently refractory tube material was sought. Pt tubes were tried and largely eliminated these problems. They produced high ion currents from only the powdered center region of the emitters. The tubes did not degrade with time nor did build up occur on the tube end. Under the microscope it appeared that with use there was some surface rearrangement. The Pt surfaces lost the machined appearance and became very shiny, yet had a rippled look. There was no noticeable loss of Pt tube material as there was with the Re tubes. Ion optic modeling demonstrates that positively charged secondary ions, produced when primary ions bombard the edge of the ion gun aperture, are focused right back onto the emitter. The observed polishing of the Pt tubes may be due to this positive ion sputtering effect.

As mentioned above, the activated metallic Re sources (Re ribbons or tubes) become sensitive to O_2 background levels in the vacuum over time (a day to a week). O_2 at 10^{-6} to 10^{-5} Torr becomes required to maintain the ion output levels. Without this background O_2 the output rapidly drops by over an order of magnitude or more. Output usually responds quite quickly and returns to previous levels when O_2 is restored.

Pt tube emitters (with Re powder/$BaSO_4$) show a mild reverse sensitivity to background O_2. Output typically drops by one-third to one-half with the addition of O_2. Only when the emitter is run until output has been greatly reduced (pA levels), will the output begin to show positive sensitivity to oxygen background pressure similar to the activated Re tubes or ribbons. While this behavior is not currently understood, it is a considerable improvement, as the output is less sensitive to pressure cycling and background gasses in a vacuum system. This material system (Pt tubes with Re powder/$BaSO_4$) appears to have sufficient oxygen available in some solid form to maintain long-lived perrhenate production from the high temperature oxidation of Re powder without the addition of gaseous O_2.

Fig. 4 shows a sequence of ion emission images from the surface of emitter #40. This shows that while there is some variability across the emitter surface, all the ion emission is from the center powdered region. As time goes on the images show a more uniform emitting surface and the material is observed to recede slightly into the tube over time. This possibly is due to consolidation of the material as it sinters at temperature.

On a microscopic scale there is an appreciable loss of material at these ion currents. Accounting for the loss of Re due to conversion to ReO_4^- at an emission rate of 200 nA/mm^2 and for a 50% volume packing density for the mixture, the material loss rate is calculated to be 4.1, 6.5, and 11.1 μm per day, respectively, for 4.7, 15, and 30 mol% $BaSO_4$. For 100 h at 200 nA/mm^2 the total material loss is calculated to be 17, 26 and 46 μm, respectively. This accounts only for losses due to ReO_4^-. There may be other losses due to sublimation of neutral species, etc. The Re particle size is in the order of 1–2 μm (as verified by SEM analysis). These calculated losses represent tens of layers of Re particles consumed at the surface for 100 h of operation. From these considerations it is expected that the surface (and hence the emitter characteristics) will change considerably over this time frame.

4.5. Effect of $BaSO_4$/Re ratio

A wide range of $BaSO_4$ concentrations (in the Re powder) appear to be acceptable for obtaining high perrhenate

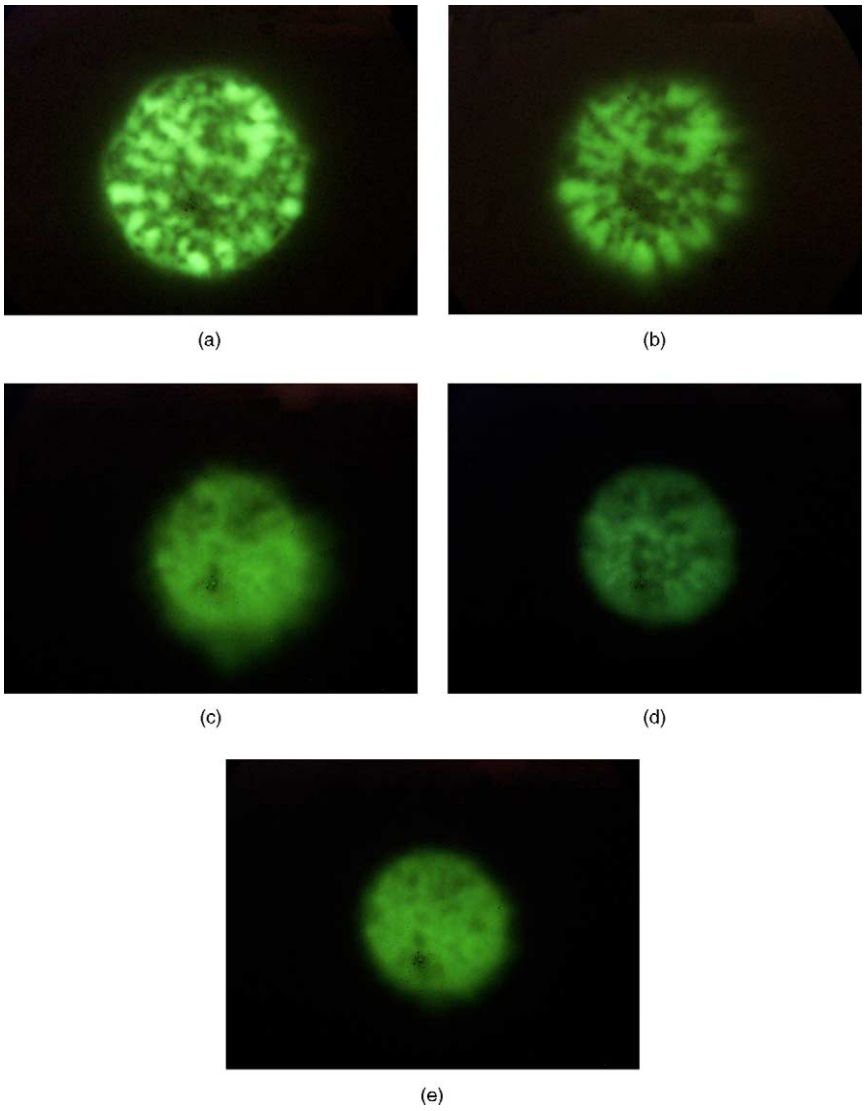


Fig. 4. Perrhenate ion surface emission images from Re powder/$BaSO_4$/Pt tube emitter (#40, 0.41 mm i.d.), at different times throughout the experiment. (a) 8 nA, 1086 °C, ~6 days (144 h); (b) 22 nA, 1156 °C, ~6 days (144 h); (c) 40 nA, 1243 °C, ~15 days (360 h); (d) 23 nA, 1235 °C, ~19 days (456 h); (e) 32 nA, 1308 °C, ~19 days (456 h).

emission. $BaSO_4$ in Re powder at 4.7, 15, and 30 mol% performed well. The 50 mol% $BaSO_4$ experiment (#43) performed poorly and it was observed that the powder mixture did not pack well, with some falling out. Calculations for the solid volume of the powder mixtures gave 22, 51, 71, and 85 vol.% $BaSO_4$, respectively, for the 4.7, 15, 30 and 50 mol% $BaSO_4$ mixtures.

4.6. Space charge issues

Later in this investigation it was suspected that space charge issues could be a problem in the ion gun at these high currents. Modeling showed that for the ion gun and settings, with an aperture of 0.6 mm (0.0236 in.), spreading of the beam was insignificant at currents below 10 nA. At 100 nA over 90% of the beam passed through the ion gun but at higher currents the beam began to be severely clipped by the aperture.

It was observed that there was a sputtered area around the aperture of the ion gun with a diameter slightly less than 2.54 mm (0.10 in.). This verified that a large portion of the beam was clipped, at least for the higher currents. Modeling further showed that the entire beam should pass through a 2.54 mm aperture up to 1000 nA. The aperture was increased to 2.54 mm in diameter. With this arrangement, a new Pt tube emitter (0.84 mm i.d., #46) gave an initial transient current of 750 nA and sustained currents for a day in the 500 nA range. This experiment verified that at high beam currents, significant clipping of the beam had occurred for the small aperture. For currents of over 100 nA analyzed with the smaller aperture, the actual emitter output may have been considerably higher than reported in Table 1 (except for #46).

4.7. Recommendations for emitters

From the above investigations the following recommendations are given in review for those interested in producing and using this Re powder/$BaSO_4$ emitter. Pt tubes are preferred (over Re tubes) for containing the emitting Re/$BaSO_4$ powder to avoid ion emission from the tube edge. For good thermal properties the tube should not be too large in diameter (<1.25 mm) and have a sufficient wall thickness (>0.2 mm). Tubes 3.8 mm long were used. Appropriately sized Re support/heater elements matched to the power supply are important. Re wire 0.25 mm diameter × ∼ 5 mm long for a 5 A power supply worked well. This will allow operation in the appropriate temperature range of 1100–1300 °C for high output emission. A small particle size Re powder was used in this work (635 mesh). While other sizes were not investigated it is believed that using as fine a Re powder as possible is important to obtain the best intimate mixing with $BaSO_4$.

Furthermore, electrons are emitted from the source at operating temperatures. These electrons will be transmitted and focused in an ion gun along with the negatively charged perrhenate ions if not properly deflected. Electron currents two to five orders of magnitude higher than the perrhenate current have been measured, some in excess of 100 μA for perrhenate currents between 1 and 10 nA. These electrons can be readily deflected using a magnetic field. In the ion guns used for this work, a simple horseshoe magnet is placed with its poles at either side of the emitter. The magnetic field easily deflects the light mass electrons while having a negligible effect on heavier ions. In this arrangement the deflected electrons strike the first aperture plate of the ion gun.

5. Summary and conclusions

Barium sulfate ($BaSO_4$) has been shown to be a superior agent for the oxidation of metallic rhenium (Re) to ReO_4^-. Based on this discovery, an improved, high output perrhenate anion (ReO_4^-) emitter has been developed for use as a primary ion beam in SIMS. The high output ReO_4^- emitter consists of Re powder blended with $BaSO_4$ packed into a platinum tube. Current densities in the order of 200 nA/mm^2 can be sustained for 100 h or more when heated between 1100 and 1300 °C. Sustained currents of several hundred nano-amperes have been produced. This output is three orders of magnitude higher than previous ReO_4^- emitters. Furthermore these new emitters show less sensitivity to background O_2 and have more uniform emitting surfaces. The ReO_4^- ion has been shown to be a highly effective projectile for SIMS applications, particularly for enhancing sputtering rates, preserving molecular information and reducing charging of insulating samples. It is anticipated that the development of this improved emitter will enable its application in imaging and shallow depth profiling.

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