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An in-depth investigation into the temperature dependence of the mass spectra of an Au₈₂Si₁₈ liquid metal field emitter

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ABSTRACT The mass spectra of the beam emitted by a Au₈₂Si₁₈ eutectic molten metal ion source are investigated in detail as a function of emitter temperature. At the conclusion of the work it emerges that while Au⁺, Si⁺, and Si⁺⁺ are the result of direct field-evaporation from the liquid surface, Au⁺⁺ forms by the post-ionisation of Au⁺. Cluster ions are most probably the product of droplet break-up.

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1 Introduction

In spite of the fact that many aspects of liquid metal ion sources (LMIS) have been investigated since the late '70s, few studies exist on the temperature dependence of their fundamental characteristics and even fewer on the behaviour of their mass spectra with emitter temperature. As a matter of fact, the only systematic studies in this respect that we are aware of are by this research team [1, 2], using a Au₇₇Ge₁₄Si₉ liquid metal alloy ion source (LMAIS).

Sources producing silicon ions are useful because beams consisting of such ions can be used for direct write applications without contaminating the silicon substrate – among other applications.

At this point we must mention that typical LMIS normally consist of a solid needle (W), of a few μm's apex radius-of-curvature, wetted by a liquid metal. At a critical voltage the liquid metal film deforms and grows into a cone at the needle apex. The tip of the cone extends into a jet, the apex area of which constitutes the site of ion emission. The jet apex has dimensions of the order of 10 Å [3].

2 Experimental results and discussion

Figure 1 shows a typical current–voltage (i – V_0) characteristic of the source, whereas the inset shows the variation of the ion extraction voltage with temperature for an emission current, i , of 5 μA. The i – V_0 curve rises steeply, before it starts showing a tendency for saturation. In fact, the difference between the ion extraction voltage, V_0 , at 5 μA and the

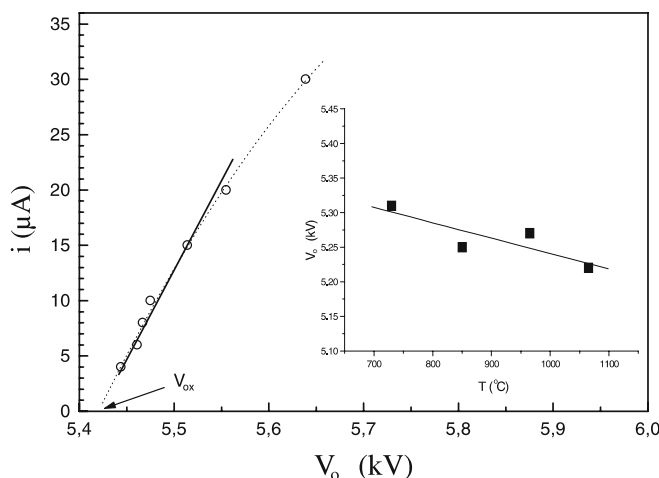


FIGURE 1 Current–voltage (I – V_0) characteristics of an Au₈₂Si₁₈ source. Inset: extraction voltage (V_0) versus emitter temperature (T)

source starting (V_{oc}) or extinction (V_{ox}) voltages is $\sim 0.5\%$. That is [1]:

$$V_0 \cong V_{ox} \cong V_{oc} = \ln \left(\frac{2h}{r_t} \right) \sqrt{\frac{\gamma r_t}{\epsilon_0}}, \quad (1)$$

where γ is the surface tension coefficient of the liquid alloy, r_t the needle apex radius-of-curvature, h the tip-to-screen distance, and ϵ_0 is the electric constant. It is seen that provided that changes in γ with temperature (T) are small – as they usually are – the behaviour of V_0 with T is translated into a similar behaviour of γ with T . Thus, in the temperature range considered, γ decreases linearly with T – as in the case of most liquid metals [4].

We now turn to the main subject of the paper, which is the dependence of the mass spectra of the Au₈₂Si₁₈ source on temperature. All measurements involving the emitter temperature were obtained at a constant emission current of 5 μA. The various ionic species were separated by an ExB filter.

Figure 2 shows a mass spectrum of the source for $T = 732^\circ\text{C}$. It can be seen that the dominant ionic species are Au⁺ and Si⁺⁺, together with the Au₂Si⁺⁺ composite (cluster) ion. For the moment, however, we shall be dealing with monatomic ions only.

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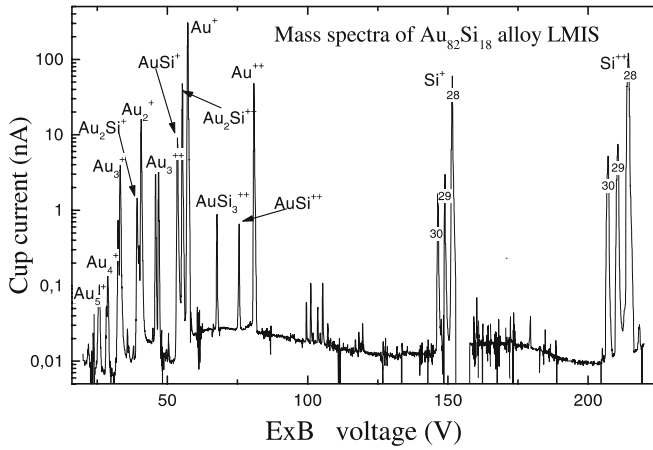


FIGURE 2 Mass spectrum of the $\text{Au}_{82}\text{Si}_{18}$ source, $i = 5 \mu\text{A}$, $T = 732^\circ\text{C}$

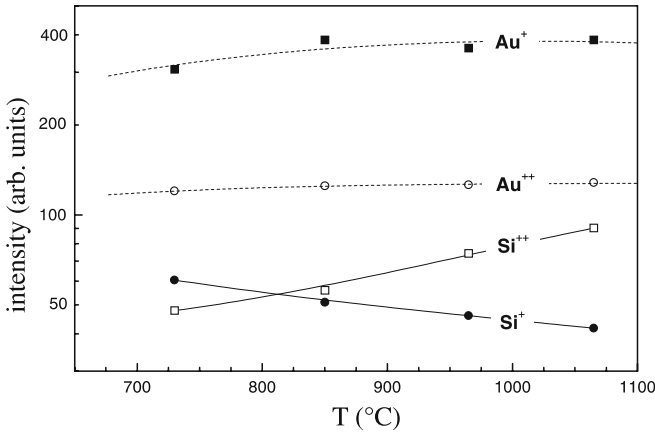


FIGURE 3 Relative abundance in the beam of Au^+ , Au^{++} , Si^+ , and Si^{++} versus T

Figure 3 shows the relative abundance of Au^+ , Au^{++} , Si^+ , and Si^{++} , whereas Fig. 4 shows the ratio of the abundance of the doubly to singly-charged Au and Si ions (I^{++}/I^+) as a function of source temperature¹. We shall discuss these figures extensively later, but for now we will concentrate on the mechanisms that control ion emission in LMIS.

According to the “image hump” model of field-evaporation [5], the current i emitted from an area containing N number of active atomic evaporation sites, is equal to:

$$i = \nu N \exp\left(-\frac{Q}{kT}\right) \quad (2)$$

ν (10^{12} – 10^{13} s^{-1}) is the vibratory frequency of the bound atom, subsequently ion, T is the temperature, and k Boltzmann’s constant. In this field-assisted thermal evaporation process, the field-reduced potential energy barrier, Q , seen by an escaping ion is:

$$Q = Q_0 - \sqrt{\frac{n^3 e^3}{4\pi\epsilon_0}} E, \quad (3)$$

where E is the field, n is the charge state of the ion, ϵ_0 the electric constant, e the fundamental electron charge, and

¹ Results in this work are within an estimated error of $\pm 5\%$.

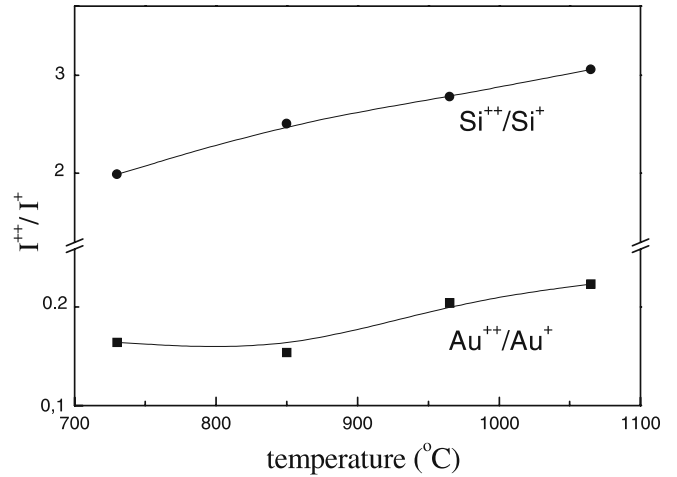


FIGURE 4 Ratio of doubly to singly-charged monomer ions (I^{++}/I^+) for Au and Si versus T

$$Q_0 = \Lambda + \sum_n I_n - n\phi \quad (4)$$

where Λ is the binding energy (heat of evaporation) of the alloy; $\sum_n I_n$ is the sum of ionisation potentials, if the ion is n -fold ionised, and ϕ is the work function of the emitter. The evaporation field is the value of E for which $Q = 0$, thus

$$E(n) = \frac{4\pi\epsilon_0}{n^3 e^3} \left\{ \Lambda + \sum_n I_n - n\phi \right\}^2 \quad (5)$$

For an ion of charge state n , Brandon’s criterion states that the value of $E(n)$ determines which ion species is likely to be expected, or dominate, in the beam [6]. If, for example, $E(2) < E(1)$ then the atom is likely to be field-evaporated as doubly-charged and vice versa. Table 1 shows the values of $E(1)$ and $E(2)$ for Au and Si. Also shown are values of the post-ionisation fields for values of I^{++}/I^+ inferred from Fig. 4, in conjunction with the post-ionisation model [7]. We recall that post-ionisation is the process by which an atom is field-evaporated as a singly-charged ion and loses one or more electrons, which tunnel back to the emitter as it moves away from the surface. The process takes place very close to the emitter. Table 1 includes values of E_{pi} derived from measurements of I^{++}/I^+ for a current range $i = 4$ – $30 \mu\text{A}$, where it was found that above $10 \mu\text{A}$, $I^{++}/I^+ = 0.25$ for Au and remains constant with i , as does I^{++}/I^+ for Si, where $I^{++}/I^+ = 10$ [8]. This implies that the field is space-charged stabilised for $i > 10 \mu\text{A}$ at about the value of the evaporation field of Si^{++} (Table 1; [8]). All E_{pi} values were extracted from Kingham [7], using our experimental values of I^{++}/I^+ .²

We take the consistency between E_{pi} for Au and $E(2)$ for Si as evidence that whereas Si^{++} is directly field-evaporated, Au^{++} forms by the post-ionisation of Au^+ . We note from

² These values, from Kingham’s “more accurate numerical approach” to post-ionisation [7] are $\leq 10\%$ lower than his original calculations (private communication to G.L.R. Mair; in [9]). The difference is not significant, and it becomes even less so, if the various approximations in both sets of calculations are considered.

Figs. 2 and 3 that, as predicted by Brandon, Si⁺⁺ dominates in the Si beam.

Let us now return to Figs. 3 and 4, starting with Fig. 4. From the curve of I^{++}/I^+ versus T for Au, we can see that the electric field remains constant for $T = 732\text{--}850\text{ }^\circ\text{C}$, since I^{++}/I^+ is essentially constant. We assume, of course, that Au⁺⁺ forms by the post-ionisation of Au⁺. Above $T = 850\text{ }^\circ\text{C}$ this ratio rises with a tendency to flatten. Presumably, at sufficiently high temperatures the field would approach a constant value, most probably equal, or very close, to the evaporation field of Si⁺⁺; i.e. $\sim 3.3\text{ V}/\text{\AA}$. Since the voltage goes down with temperature for constant current (Fig. 1; inset), the increase in electric field for $T = 850\text{--}1060\text{ }^\circ\text{C}$ must be due to the apex area of the liquid jet becoming smaller. This self-sharpening of the liquid anode would be a logical surmise: a reduced apex area entails a reduction in the number of atomic evaporation sites. Thus, the increase in electric field is offset and the total current remains constant, at $5\text{ }\mu\text{A}$, as T is raised. As shown and extensively discussed by Kingham in one of his post-ionisation papers, the probability of post-ionisation does not depend directly on temperature – although it may do so indirectly [7].

The increase in I^{++}/I^+ for Si in the range $732\text{--}850\text{ }^\circ\text{C}$, where the field is constant, is due to the increase in temperature, whereas above $850\text{ }^\circ\text{C}$ it is due to both the field and the temperature increasing. This becomes obvious if we combine (2) with (4), obtaining for $n = 1$ and $n = 2$:

$$\frac{I^{++}}{I^+} = \exp\left(-\frac{I_2 - \varphi - (\sqrt{8} - 1)\left(\frac{e^3}{4\pi\epsilon_0}\right)^{1/2}\sqrt{E}}{kT}\right). \quad (6)$$

We recall that unlike Au⁺⁺, we believe that Si⁺⁺ forms by direct field evaporation.

With regard to Fig. 3, we see that after an initial rise of T between 732 and $850\text{ }^\circ\text{C}$, from (2) we find the intensity of Au⁺ remains constant. Presumably, for $T > 850\text{ }^\circ\text{C}$ increases in temperature and electric field are offset by the diminishing number of evaporation sites, coupled to the fact that a number of Au⁺ ions are lost through post-ionisation to form Au⁺⁺. Si⁺⁺ also shows a slight rise in intensity at first, due to increasing temperature, and then it remains constant. In this case, too, temperature and field increases are counterbalanced by a reduction in the number of evaporation sites. Now, if the probability for the field-evaporation of Si⁺⁺ increases with increasing electric field and temperature, then the probability for the field-evaporation of Si⁺ must accordingly diminish – assuming, that is, that both Si⁺ and Si⁺⁺ are emitted from the same atomic sites. Bearing in mind that the number of sites also decreases, it becomes understandable that, in spite of the increase in field and temperature, the intensity of Si⁺ goes down with T .

Let us now focus our attention on Fig. 5, showing the relative abundance of cluster ions in the beam. As can be seen, in the case of singly-charged cluster ions, their relative abundance in the beam shows a slight, but steady, increase with emitter temperature. For doubly-charged clusters the intensity is essentially constant in the same range. The similarity of the curves, suggests the same creation mechanism, irre-

	Au	Si
$E(1)$	4.8	4.5
$E(2)$	5.0	3.3
E_{pi} $i = 5\text{ }\mu\text{A}, T = 732\text{--}1060\text{ }^\circ\text{C}$	3.1	2.0
E_{pi} $i > 10\text{ }\mu\text{A}, T = 850\text{ }^\circ\text{C}$	3.3	2.1

TABLE 1 Values of $E(1)$ and $E(2)$ and E_{pi} for Au and Si ($\text{V}/\text{\AA}$). E_{pi} for Au between $732\text{--}1060\text{ }^\circ\text{C}$ increases by about 2.5%, always remaining, however, around $3.1\text{ V}/\text{\AA}$ [7]. For the calculation of $E(1)$ and $E(2)$, eq. (5) was used. Values of Λ are from [4] and for φ and I_n values from [6, 10] were used

spective of the number or identity of the atoms. This immediately rules out a surface field-ionisation mechanism, like field-evaporation, since it is unlikely that, e.g., Au₅⁺ or AuSi⁺ would be field-emitted as a unit. The most likely explanation is that cluster ions are the result of droplet break-up. In support of this hypothesis is the good agreement found between a model proposed by Hornsey [11] and experimental results for the energy spread and deficit of Ga and In dimers.

In Hornsey's model a droplet becomes unstable, immediately after break-up from the tip of the jet, by capturing a sufficient number of ions. Another mechanism proposed by Joyes, and Van de Walle [12] involves droplets charged above the Rayleigh limit. These droplets break up almost immediately after emission, liberating small ion clusters, of up to about five atoms, as well as neutral atoms, near the apex region of the liquid metal emitter.

The increase in the abundance of the singly-charged cluster ions with temperature becomes understable in terms of the surface tension coefficient of the alloy decreasing with temperature, manifested by a similar decrease of V_0 (Fig. 1, inset, using (1)). The destabilising influence of decreasing γ has been established by recent experiments involving fluctuations in current, believed to arise from jet break-up with concomitant droplet emission [13]. We cannot, however, satisfactorily explain at this point the near constancy, or even slight decrease, in the abun-

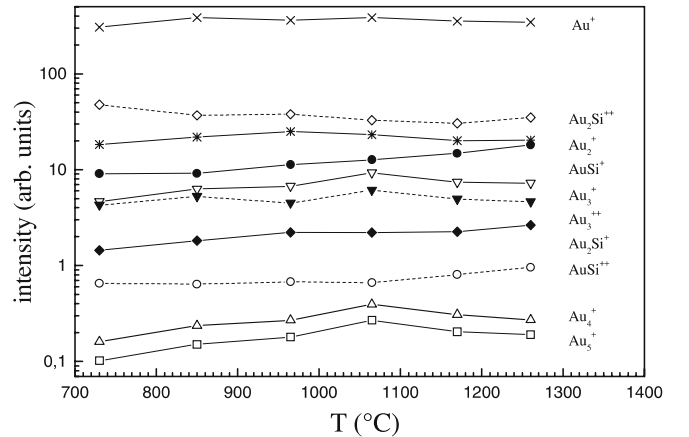


FIGURE 5 Relative abundance in the beam of some cluster ions emitted by the Au₈₂Si₁₈ source versus T . The last two points on each graph correspond to a current somewhat above $5\text{ }\mu\text{A}$ and are therefore only indicative

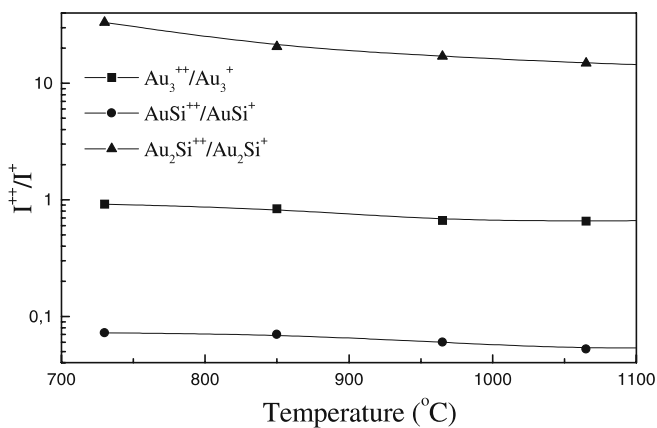


FIGURE 6 Ratio of doubly to singly-charged species for some cluster ions versus T

dance of some doubly-charged clusters, like $AuSi^{++}$ and Au_2Si^{++} .

Finally, Fig. 6 shows the ratio of the intensities of the doubly to singly-charged species for some cluster ions as a function of emitter temperature. It is seen that I^{++}/I^+ decreases with T for all three types of cluster ions. It is clear that such a decrease is precluded by (5).

Thus, in spite of the fact that the notion of an evaporation site is somewhat dubious in the case of clusters, it would seem justifiable to exclude field-evaporation as a probable cluster creation mechanism.

2.1 Conclusions

The conclusions of this study are:

1. Au^+ , Si^+ , and Si^{++} are the result of field-evaporation.
2. Au^{++} forms by the post-ionisation of Au^+ .
3. Clusters ions are liberated by droplet break-up, most probably by ion capture.

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