On the temperature dependence of the mass spectra of AuGe and AuGeSi liquid metal alloy ion sources

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Abstract. This reports on an extensive study of the characteristics of AuGe and AuGeSi liquid metal alloy ion sources as a model system for new semiconductor compatible FIB sources. Such characteristics include ion beam mass spectra. A careful investigation has been undertaken where the emitter temperature is the main variable parameter. This work concerns the temperature dependence of the mass spectra of two needle-type liquid metal alloy ion sources (LMAISs), namely Au77Ge14Si9 (Tm=364°C) and Au73Ge27 (Tm=365°C). The sources are important for producing SiGe implanted layers. The experimental results, in conjunction with existing theories, strongly points towards the co-existence of two mechanisms for the emission of doubly-charged monomer ions: direct field-evaporation and post-ionisation.

1. Introduction

Liquid metal ion sources (LMIS) are one of the key elements in focused ion beam (FIB) technology [1]. The liquid metal ion source, once just a laboratory curiosity, is now the basis of focused ion beam systems that use a variety of heavy metal ions (with currents of 1 pA - 30 nA) which can be focused into diameters smaller than 10 nm with current densities of several A/cm² [2]. They have opened up totally new possibilities for scanning ion microscopy, surface analysis, micro-machining, writing ion implantation and high-resolution ion lithography.

The predominate use of these systems has been in various aspects of IC fabrication. The two main features of the FIB tool that are most important are the capability to remove material from the sample by sputtering (micro-machining) and to add materials to the sample by ion induced reactions (deposition) at sub-micron dimensions. In this role, the FIB LMIS tool is used in failure analysis, defect characterization, design modification, and process control in a variety of industries.

The use of LMAISs is necessitated by the fact that some metals of interest are not amenable to ion source manufacture in pure form (for example, high melting point, high vapour pressure or reaction of the metal with the substrate). This study presents systematic measurements on the temperature dependence of the mass spectra of two needle-type LMAISs, namely Au77Ge14Si9 and Au73Ge27. As shown below, the two sources display entirely different temperature behaviours.
2. Experimental results
The Au_{77}Ge_{14}Si_{9} (T_m=364°C) and Au_{73}Ge_{27} (T_m=365°C) alloy sources were prepared at the Rossendorf Research Center in Dresden. The emitter beam was analysed with an ExB filter. Fig. 1 and fig. 2 show the complete mass spectra of the two alloy sources.

Before we proceed any further, let us calculate the evaporation field of the singly and doubly charged ions emitted from the source. We recall that the evaporation field is defined as the value of the electric field for which the height of the potential barrier (Q) seen by an escaping ion is equal to zero. In a thermally activated process, such as field-evaporation [4], the current \( I \) emitted by a single, atomic, evaporation site is

\[
I \approx \exp \left( -\frac{Q}{kT} \right),
\]

where \( T \) being the temperature of the emitter and \( Q \) is given as

\[
Q = Q_o - \frac{n\varepsilon E}{4\pi\varepsilon_0} - \sum I_n - n\phi
\]

with

\[
Q_o = \Lambda + \sum I_n - n\phi
\]

where \( \Lambda \) is the heat of evaporation (binding energy) of the bound atom (subsequently ion), \( \sum I_n \) the sum of the ionisation potentials, if the ion is \( n \)-fold ionised, \( \phi \) the work function of the metal (emitter), \( e \) the fundamental electronic charge, \( \varepsilon_0 \) the electric constant and \( E \) is the field acting at the emitter surface.

The evaporation field \( E(n) \) is found from equations (2) and (3), for \( Q = 0 \),

\[
E(n) = \frac{4\varepsilon e^2}{n^2}\left\{\Lambda + \sum I_n - n\phi \right\}^{\frac{1}{2}},
\]

for an ion of charge state \( n \). According to Brandon’s criterion [5], the value of \( E(n) \) determines which ion species will dominate in the beam. If e.g. the field \( E(2) < E(1) \), then the atom is likely to be directly field-evaporated as doubly charged. Table 1 shows values of \( E(1) \) and \( E(2) \) for the different atomic species emitted by the Au_{77}Ge_{14}Si_{9} source. Also shown in the post-ionisation field (\( E_{pi} \)) are values for Au, deduced from Kingham’s calculations [6] for a value of \( F^+/I^+ \) at 0.2 (Au) and 2 (Ge) (figure 3).

Table 1. Values of \( E(1) \) and \( E(2) \) for the monomer ion species of the Au_{77}Ge_{14}Si_{9} source, together with the corresponding post-ionisation field values. Value in brackets for \( E_{pi} \) for Au and for \( E_{pi} \) for Ge are from Reference [7], for \( F^+/I^+ \) at 0.2 (see figure 3); value in brackets for \( E(2) \) for Ge is for \( q=4.8 \) eV [5] instead of 4.62 eV [8]. All field values in V/Å
Table 2. Values of $E(1)$ and $E(2)$ for the monomer ion species of the Au$_{73}$Ge$_{27}$ source, together with the corresponding post-ionisation field values. Value for $E_{pi}$ for Au and for $E_{pi}$ for Ge are from Ref. [7], for $I^2+/I^+$ at 0.5 (Au) and 5 (Ge) (see Figure 3). All field values in V/Å.

|        | Au  | Ge  | Si  |
|--------|-----|-----|-----|
| $E(1)$ | 4.8 | 3.7 | 4.5 |
| $E(2)$ | 5.0 | 3.1 (2.9) | 3.3 |
| $E_{pi}$ | 3.3 (3.1) | 2.3 | 2.2 |

Table 2 shows values of $E(1)$ and $E(2)$ for the different atomic species emitted by the Au$_{73}$Ge$_{27}$ source. Also shown in the post-ionisation field ($E_{pi}$) are values for Au and Ge deduced from Kingham’s calculation [6] for a value of $I^2+/I^+$ at 0.5 (Au) and 5 (Ge) (figure 3).

For the Au$_{77}$Ge$_{14}$Si$_9$ source, the consistency between the values of $E(2)$ for Ge and Si and $E_{pi}$ for Au we take as evidence that Ge$^{2+}$ and Si$^{2+}$ are directly field-evaporated as the dominant ionic species for Ge and Si, respectively, Au$^{2+}$ is formed by the post-ionisation of Au$^+$. (see Table 1)

For the Au$_{73}$Ge$_{27}$ source, the consistency of the values of $E(2)$ for Ge and $E_{pi}$ for Au at 550°C, we take as evidence that whereas Ge$^{2+}$ is directly field-evaporated as the dominant species of Ge, Au$^{2+}$ is formed by the post-ionisation of Au$^+$.

Figure 3. Ratio of singly to doubly charged ions of the main monomer species versus emitter temperature.

The lowering of the intensity of Au$^+$ (figure 4 and figure 5) with temperature can be explained in terms of a slight decrease of the electric field acting at the emitter, due to an increase in the apex area of the emitter. We already know that emission area increases with emission current, and that the abundance of both Au$^+$ and Au$^{2+}$, from the AuGe source, decreases with current [9]. An increase in the emission area i.e., in the number of field-evaporation sites, ensures that the total current remains constant. Since the evaporation rate is a very sensitive function of field, equations (1) and (2), only a slight change in field can result in a considerable change in the evaporation rate of an ionic species; of course, this will be partly offset by the increase in temperature. For Ge$^{2+}$ and Si$^{2+}$, however, Q at 0 and thus changes in temperature or slight changes in field strength are not likely to affect the evaporation rate of the species very much. This is in accord with the results of figure 4 and figure 5.

For Si$^+$ and Ge$^+$, Q is not zero, but it could be argued that decreases in field value are offset by the increase in temperature, and thus the intensity of these species remains approximately constant (figure 4 and figure 5).
In the case of AuGeSi source the surface tension coefficient rises with temperature up to 850°C, reaching a broad maximum at this temperature, and then it starts to decrease [10]. When liquid metal alloys behaving “normally”, e.g. AuGe source, increasing the temperature precipitates an enhancement of droplet emission, arising from the reduced surface tension coefficient which, in turn, reduces the stability of the liquid anode [11]. The opposite would happen with the AuGeSi source and thus the increased stability in this case would result in a reduced probability of jet break-up.

![Figure 4. Intensity of the various monomer ions source vs emitter temperature $I=10\mu A$.](image1)

![Figure 5. Intensity of the monomer ions by the producer by the source vs emitter temperature $I=10\mu A$.](image2)

3. Conclusions
We investigated the temperature dependence of the mass spectra of two LMAISs, AuGe and AuGeSi as a model system for new semiconductor compatible FIB sources. While Ge$^{2+}$ and Si$^{2+}$ appear to be directly-field evaporated, Au$^{2+}$ seems to be the result of the post-ionisation of Au$^+$ in both sources.

The temperature dependence of the intensity of the main species can be conceivably explained in terms of a slight decrease of the electric field acting at the emitter, due to an increase in the apex area of the emitter.

4. Acknowledgement
The authors wish to honour the long and fruitful work and collaboration in the field of investigation and understanding of LMIS with G.L.R. Mair, who died in June 2004.

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