

# Direct current and pulsed operation of contaminated liquid metal ion sources

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Gallium liquid metal ion sources (LMISs) have been exposed to common gas and liquid phase laboratory and vacuum system contaminants. Minor changes in the direct current and pulsed operation of the LMISs were observed after contaminant exposure. Time-of-flight mass analysis of the ion emission revealed that contaminant species are primarily field evaporated with the gallium substrate. Low vapor pressure contaminants have been observed to constitute a significant portion of the total emitted ion current. © 1999 American Vacuum Society. [S0734-211X(99)03206-0]

## I. INTRODUCTION

Field evaporation of ions from liquid metals is of considerable interest because it creates an exceptionally stable, high brightness, point source of ions.<sup>1,2</sup> It is these physical attributes that makes a liquid metal ion source (LMIS) particularly attractive for applications such as focused ion beam systems, secondary ion mass spectroscopy, and space propulsion.<sup>3-7</sup>

A typical LMIS is constructed by coating a sharply pointed metal wire, typically tungsten or molybdenum, with a liquid metal. The electric field that results when several kilovolts are applied to a LMIS distorts the surface of the liquid into a microscopic cone. When the cone half angle reaches 49.3°, the surface tension of the liquid and the electrostatic stress of the field balance to form a stable configuration, commonly known as a "Taylor cone."<sup>8</sup> A small, sharp protrusion at the apex of the Taylor cone generates an electric field of a few volts/angstrom that is sufficient to cause the field evaporation of the metal as positive ions.<sup>9</sup>

The field evaporation process is initiated only when the applied voltage, and hence, the electric field, reaches a critical threshold voltage ( $V_{th}$ ). The current emitted from a LMIS is typically several microamperes at the onset of ion emission and is composed primarily of singly charged monoatomic ions.<sup>10-12</sup> However, instabilities in the Taylor cone begin to cause the emission of charged droplets at ion currents in excess of  $\sim 30 \mu A$ .<sup>13</sup> The Taylor cone collapses if the applied voltage is reduced to the extinction voltage ( $V_{ex}$ ) and, as a result, causes the LMIS to stop emitting ions. There is typically a hysteresis of  $\sim 1\%$  that exists between the threshold and extinction voltages for a given LMIS so that ion emission can occur below the threshold voltage once a Taylor cone has been formed.<sup>14</sup>

LMISs have employed a wide variety of different materials such as pure metals, alloys, alkali metals, and even molten salts.<sup>15-18</sup> However, since gallium (Ga) has a particularly suitable set of physical properties, it is one of the most common materials to use for LMISs. The melting point of Ga is near room temperature (29.78 °C) and it has a very low vapor pressure ( $\ll 10^{-12}$  Torr) at temperatures below 300 °C. In ad-

dition, the current extracted from Ga LMISs is stable for thousands of hours.<sup>19</sup>

This article discusses the effect of common vacuum system and laboratory contaminants on Ga LMIS operation. The ion sources were submerged in liquid contaminants or exposed to a contaminant gas and the resulting changes in the stability of the direct current (dc) and pulsed LMIS operation were recorded. Ions emitted from contaminated LMISs were analyzed by time-of-flight (TOF) mass spectroscopy.

## II. EXPERIMENTAL APPARATUS

The Ga LMISs used in these experiments were fabricated by dc etching a tungsten wire (0.508 mm diameter) to a sharp point in a solution of 4 M NaOH at  $\sim 2.5$  V. A hot, saturated solution of 50% NaOH and 50%  $K_3(CN)_6$  was used to roughen the end of the wire in order to assist the Ga in fully wetting the tapered point of the emitter.<sup>15</sup> A Ga reservoir was formed near the tip apex by wrapping  $\sim 5$  turns of molybdenum wire (0.254 mm diameter) around the shank of the W wire and spot welding it in place. A Ga LMIS, after being thermally cleaned and wetted with Ga in a vacuum of  $< 10^{-6}$  Torr, is shown in Fig. 1.

After fabrication, each Ga LMIS was heated to a temperature between 300 and 800 °C for  $\sim 2-3$  s in a vacuum of less than  $5 \times 10^{-7}$  Torr to ensure that the Ga had fully wetted the tip surface. The Ga LMIS was then operated by applying a positive dc voltage to the ion source to ensure stable ion emission. The ion sources demonstrated a very low drift ( $< 3\%$ ) in the total ion current over time periods as long as 12 h and the expected linear current-voltage characteristics.<sup>14,20</sup>

It has been shown that the combination of bias voltage, pulse height, and pulse length are all important parameters that need to be optimized in order to obtain stable pulsed LMIS emission.<sup>18,21,22</sup> Pulsed emission was achieved in these experiments by adjusting the emitter voltage ( $V_{bias}$ ) to a value slightly less than both  $V_{th}$  and  $V_{ex}$  and capacitively coupling a short, positive voltage pulse ( $V_{pulse}$ ) onto the applied dc bias. The single shot square voltage pulses were generated with a cable discharge pulser approximately every 10 s. The width and rise time of the pulses were 26 ns and less than 2 ns, respectively. It was observed that for this

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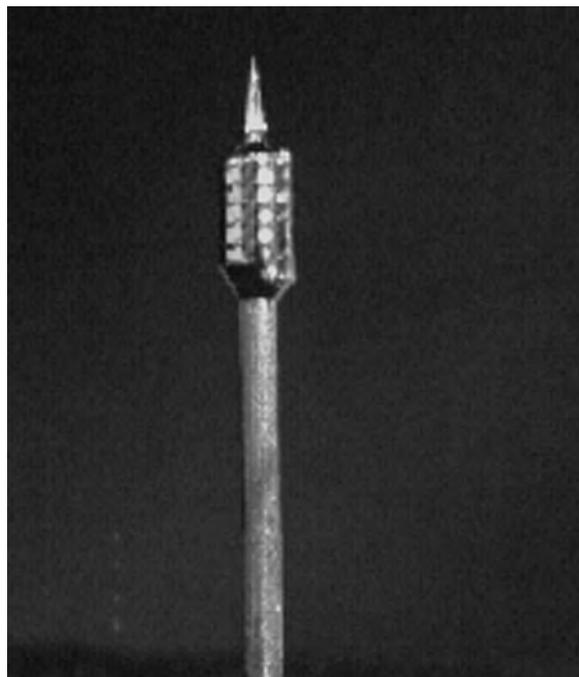


FIG. 1. Photograph of a typical LMIS that shows the etched W tip and Mo reservoir fully wetted with Ga.

pulse length a minimum pulse voltage of 250–500 V above  $V_{th}$  is typically needed to initiate stable pulsed ion emission.

The experimental apparatus is shown schematically in Fig. 2. The LMIS was mounted in the vacuum chamber by inserting the shank of the tungsten wire into a molybdenum heating coil. The apex of the LMIS was positioned  $\sim 5$  mm behind a 0.635 mm diameter hole in a stainless steel extraction electrode. This electrode was held at ground potential and confined the electric field to the region between the LMIS and the extraction electrode. Emitted ions, accelerated through the hole in the extraction electrode, entered a field free drift region before striking the ion detector.

The ion detector consisted of a 75 mm channel electron multiplier array (CEMA), a cathodoluminescent screen, and a Radio Corporation of America 4516 photomultiplier (PMT). After crossing the field free drift region, the ions strike the front surface of the CEMA and initiate a secondary electron avalanche in the individual channels of the CEMA. The secondary electrons are then accelerated through a potential of 3 kV onto the cathodoluminescent screen and the PMT detects the emitted light. The PMT provided a second-

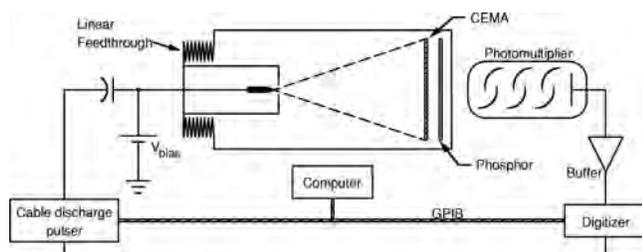


FIG. 2. Schematic of the experimental setup.

ary gain stage to increase the sensitivity of the ion detector and it optically decoupled the detected ion signal from the electromagnetic interference created by pulsing the LMIS.

The cathodoluminescent screen consisted of a 50/50 mixture of P1 and P47 phosphor. The P1 phosphor was used because the peak emission wavelength of  $\sim 525$  nm and the long decay time of  $\sim 40$  ms allowed the dc and pulsed operation of a LMIS to easily be observed by eye.<sup>23</sup> The P47 phosphor was used because it has a rise time of several nanoseconds and a decay time of  $\sim 80$  ns. Therefore, its temporal response was sufficient to detect the arrival of short ion pulses emitted from the LMIS. The spectral response of the PMT photocathode was shown to be very insensitive to light emission from the P1 phosphor and, as a result, it was unnecessary to filter the light before it reached the PMT.

A  $50 \Omega$  current viewing resistor was connected to the output of the PMT and the signal line was fed directly into a high speed voltage buffer.<sup>24</sup> The buffer was required to keep the rise time of the ion detection system  $\sim 5$  ns by driving the coaxial cable that leads to a Tektronix RTD 720 transient digitizer. The digitizer was triggered by the desorption pulse and recorded the arrival time of ions from the pulsed LMISs. The entire data acquisition process was computer controlled with LabVIEW<sup>25</sup> software and typically 50 digitizer wave forms were averaged in order to improve the signal-to-noise ratio.

### III. EXPERIMENT AND RESULTS

#### A. Operation of contaminated LMISs

Stable dc ion emission has been observed from Ga LMISs even when operated in high vacuum environments ( $\sim 10^{-6}$  Torr).<sup>14</sup> This indicates that Ga LMISs are relatively insensitive to common gas phase contaminants in the vacuum environment and prompted the testing of more highly contaminated ion sources.

Baseline operating characteristics of each LMIS were obtained under dc and pulsed conditions prior to contamination. The ion sources were cycled on and off several times to determine the values of  $V_{th}$  and  $V_{ex}$  and a single, stable emission spot on the phosphor screen was observed to verify that ion emission was occurring from a single Taylor cone. The ion pulse shape and amplitude were also measured to ensure repeatable pulsed LMIS operation.

Once these operating characteristics were determined for each ion source, the LMIS was exposed to liquid contamination. The LMIS was removed from the vacuum system and the entire source, including the Ga reservoir, was dipped into a contaminant liquid for 2–3 s. The liquid contaminants were heated to  $\sim 40$  °C prior to submersion to ensure that the Ga remained in liquid form. Although this is not a contamination mechanism encountered in most experimental situations, it does subject the LMIS an extreme exposure test. The ion source was then reinstalled in the vacuum system and, without heating the source, it was operated in a dc and pulsed mode of operation.

TABLE I. Effects of common laboratory and vacuum contaminants on the dc and pulsed operation of a Ga LMIS.

	Before contamination		After contamination				
	$V_{th}$	$V_{ex}$	Initial $V_{th}$	$V_{th}$	$V_{ex}$	dc operation	Pulsed operation
Water	2500	2460	3100	2530	2490	yes	yes
Ethanol	3560	3540	4975	3660	3640	yes	yes
Acetone	4100	4000	5000	4100	4000	yes	yes
Toluene	2640	2570	4370	2260	2220	yes	yes
CMP-19 pump oil	3500	3380	4350	2870	2810	yes	yes
Invoil 705 silicone diffusion pump oil	2850	2830	5450	3290	3210	yes	yes

The results of submersing a Ga LMIS in water, ethanol, acetone, toluene, CMP-19 mechanical pump oil, and Invoil 705 silicone diffusion pump oil are summarized in Table I. With the exception of an initially larger value of  $V_{th}$ , there was very little change in the operational characteristics of the ion sources. Since these experiments were performed in vacuum of  $10^{-7}$ – $10^{-8}$  Torr, these contaminants, with the possible exception of the diffusion pump oil (vapor pressure of  $2.4 \times 10^{-9}$  Torr at 25 °C), would have mostly evaporated from the surface of the Ga prior to testing.

Additional gas phase contaminant experiments were performed by regulating the pressure of laboratory air, argon (Ar), and carbon tetrachloride ( $CCl_4$ ) in the vacuum system with a variable leak valve. The pressure was varied for each contaminant gas between  $4 \times 10^{-8}$  and  $4 \times 10^{-5}$  Torr. There was no change in the pulsed or dc operating characteristics for either the Ar or  $CCl_4$  gas. However, when laboratory air was introduced to the vacuum system the LMIS ceased to operate after several minutes at pressures  $> 4 \times 10^{-6}$  Torr. The ion source could be restarted either by increasing the pulse voltage or raising the bias voltage to initiate dc ion emission, but it never exhibited stable pulsed operation at these pressures. The presence of oxygen at the surface has previously been associated with unstable Ga LMIS operation at elevated operating pressures.<sup>7</sup>

## B. TOF mass spectroscopy of contaminated LMISs

The experiments discussed earlier indicate that Ga LMIS operation is not significantly affected by exposure to common liquid and gas phase contaminants. However, since the composition of the ion beam is important for many LMIS applications, the field evaporated ion species were identified by atom-probe field ion mass spectroscopy.<sup>26</sup> In this TOF mass spectroscopy technique, the identity of an ion is determined by measuring its travel time,  $T$ , across a field-free drift region of length  $L$ . Since the ion potential, and hence, its energy, is defined by  $V_{bias} + V_{pulse}$  the mass-to-charge ratio,  $m/n$ , can be determined from the following equation:

$$\frac{m}{n} = 2e(V_{bias} + V_{pulse}) \left( \frac{T}{L} \right)^2,$$

where  $e$  is the electronic charge and  $n$  is the charge state of the ion. To achieve the best possible mass-to-charge resolu-

tion, it is important to minimize the rise time, and if possible the decay time, of the measured ion pulses. Since the decay time with this apparatus was fixed by the exponential decay of the P47 phosphor, only the risetime could be experimentally adjusted. It was observed that lower pulse voltages resulted in a shorter rise time of the Ga ion signal. Therefore, the pulse voltages used for obtaining TOF mass spectra were adjusted to be as low as possible while still producing an easily detectable ion signal.

Figure 3 shows a typical Ga LMIS TOF mass spectra acquired before exposure to a contaminant. For the purpose of calibrating the mass/charge spectra the  $Ga^+$  peak was placed at 69 amu. The spectrometer resolution for masses less than  $\sim 100$  amu was judged to be greater than 2–3 amu since  $^{69}Ga^+$  and  $^{71}Ga^+$  were not separated.

The LMIS TOF mass spectra revealed that in addition to the large  $Ga^+$  peak there are also peaks commonly observed at approximately 17, 30, and 44 amu. Since these species do not correspond to any charge state of Ga, GaO, or  $Ga_2O_3$  ions, it is suspected that these peaks are caused by ionized residual gas in the vacuum system. Residual gas analyzer analysis of the unbaked vacuum system confirmed that peaks at 18, 28, and 44 amu are the dominant residual gas species.

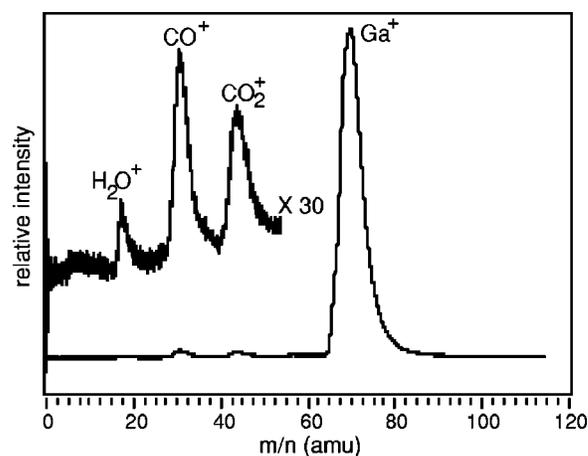


FIG. 3. Typical TOF mass spectrum of a Ga LMIS before exposure to a contaminant. The peaks located at  $\sim 17$ , 30, and 44 amu are attributed to  $H_2O^+$ ,  $CO^+$ , and  $CO_2^+$ , respectively. The spectrum was averaged 50 times with  $V_{bias}=2850$ ,  $V_{th}=3020$  V, and  $t_{pulse}=26$  ns.

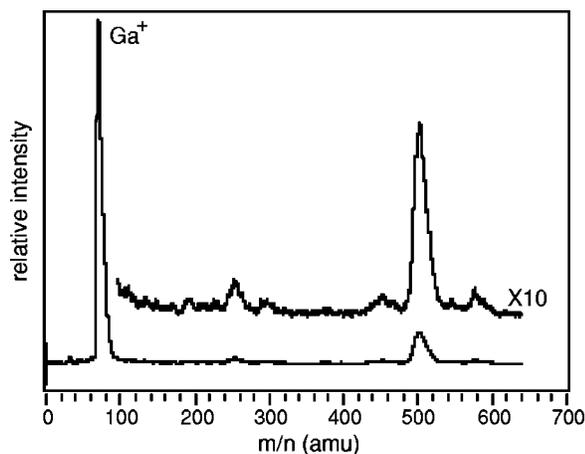


FIG. 4. TOF mass spectrum for a Ga LMIS after being dipped in Invoil 705 silicone diffusion pump oil (molecular weight=546 amu). The spectrum was averaged 50 times with  $V_{\text{bias}}=3100$ ,  $V_{\text{th}}=3290$  V, and  $t_{\text{pulse}}=26$  ns.

These peaks are commonly attributed to water, carbon monoxide, and carbon dioxide, respectively.

Two experiments were performed to determine if these ions are generated by gas phase ionization or field evaporation from the surface of the Ga. First, while regulating the pressure of laboratory air in the vacuum system, TOF mass spectra were obtained at pressures up to  $4 \times 10^{-5}$  Torr. No change in the height of the peaks at 17, 30, and 44 amu were observed, indicating that the peaks are not caused by gas phase ionization. Second, the TOF mass spectra confirm that the amplitude of the 17, 30, and 44 amu peaks do not diminish by repetitively pulsing a LMIS once a second at a pressure of  $10^{-8}$  Torr. We speculate that this is because unlike field evaporation from a conventional emitter, where the number of adsorbed gas ions emitted the tip apex depends upon the time between the pulses and the pressure in the vacuum system, a LMIS form will have a new emission surface at the apex of the Taylor cone during each voltage pulse. If this occurs, then it is expected that each pulse would field desorb a layer of adsorbed gas with the Ga substrate.

Exposure of the Ga LMIS to Ar and  $\text{CCl}_4$  gas phase contaminants showed no change to the TOF mass spectra even in partial pressures above  $10^{-5}$  Torr. This also confirms that if gas phase ionization occurs it is below the detection threshold of our measurement system. It also indicates that there is no significant component of the total ion current that is due to ionization of contaminant species from the gas phase.

The TOF mass spectra of the Ga LMISs exposed to water, ethanol, acetone, toluene, or mechanical pump oil show no indication of contaminant ions in the ion beam. However, the TOF mass spectra from the LMIS exposed to the silicone diffusion pump oil contained several additional mass peaks as is shown in Fig. 4. This result verifies that a contaminant remaining on the surface of a Ga LMIS can constitute a significant portion of the total emitted ion current. It also suggests that the quantity of remaining material in a chemisorbed layer of high vapor pressure contaminants such as

ethanol, acetone, etc. is below the detection threshold of the measurement system. Regardless, the results indicate that high vapor pressure materials do not significantly contribute to the total ion current.

#### IV. SUMMARY

Ga LMIS operation has been shown to be insensitive to common laboratory and vacuum system contaminants. Direct exposure to liquid contaminants does not significantly effect either the dc or pulsed operation of the source, even if a contaminant is adsorbed on the surface of the Ga. In addition, the introduction of Ar and  $\text{CCl}_4$  do not affect the source operation at pressures in excess of  $10^{-5}$  Torr. However, the Ga LMIS was found to cease pulsed operation after several minutes if the pressure of laboratory air in the system exceeded  $4 \times 10^{-6}$  Torr. This can be attributed to the presence of oxygen on the surface of the LMIS.<sup>7</sup>

TOF mass analysis of the ions emitted from a Ga LMIS has shown that contaminant species are primarily field evaporated with the Ga substrate rather than ionized from the gas phase. In addition, low vapor pressure contaminants have been observed to constitute a significant portion of the total emitted ion current.

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