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Lithium Ion Beams from Liquid Metal Alloy Ion Sources

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Abstract

In recent years Focused Ion Beam (FIB) processing has been developed into a well-established and promising technique in nearly all fields of nanotechnology for patterning and prototyping on the µm-scale and below. Liquid Metal Alloy Ion Sources (LMAIS) represent a promising alternative to expand the FIB application fields beside all other source concepts. The need of light elements like Li was investigated using various alloys. A promising candidate is a $Ga_{35}Bi_{60}Li_5$ based LMAIS which is introduced in more detail and operates stable for more than 1000 µAh. It enables high resolution imaging and patterning using Li and sample modification using Ga or heavy polyatomic Bi clusters, all coming from one ion source.

Keywords: Lithium ion beam, liquid metal alloy ion source, FIB, ion lithography

I. INTRODUCTION

Focused Ion Beam (FIB) devices are essential instruments in nano-technology for local surface modification, doping, prototyping as well as for ion beam analytics. A crucial part of a FIB system is the ion source [1]. The Ga liquid metal ion source (LMIS) dominates the instrumentation, but the requirement for other ion species for different nanoscale applications is still increasing [2]. An important element of interest is lithium, the lightest metal in the periodic table, suitable for application in LMIS with respect to high resolution imaging and ion beam processing. Light ions can transfer enough energy to a specimen to induce chemical reactions that result in etching or deposition down to 1 nm [2, 3]. The melting point of Li amounts to T_{melt} = 180.5°C with a vapor pressure of about 10^{-8} mbar, but increases strongly with temperature. This behavior requires a careful operation during preparation and operation of the Li LMIS. Lithium has two stable isotopes with a mass of 6 amu (7.4% natural abundance) and 7 amu (92.6% natural abundance). They can be easily separated by a Wien filter also known as velocity or ExB mass filter. The energy spread of a LMAIS depend on the emission current, the temperature and the ion mass to the power of 1/3 and should be for Li in the range of 2 eV [4] which guarantees a low chromatic aberration of the FIB. This could be experimentally confirmed to about 2 eV at 1 µA emission current from a $Ga_{35}Bi_{60}Li_5$ LMAIS [5]. The small energy spread is important to minimize chromatic aberrations. Highly focused ion beams on the nm-scale are very promising for ion lithography [6] as well as for ion beam analysis, for instance high resolution Rutherford

Backscattering Spectrometry (RBS) [7] or channeling [8]. In the last decades numerous efforts have been made to test high brightness Li ion sources on quiet different bases of pure lithium, of lithium containing alloys or lithium compounds. To overcome the difficulties of handling the chemical active lithium an *in-situ* rewetting of the needle by shifting it into the molten material was applied [8, 9]. Another approach was the permanent heating and cleaning of the emitter tip by electron bombardment [10] which was used for bimetallic cluster ion emission from liquid metals like Li-Na and Li-Mg [11]. A wide range of attempts for a Li LMAIS were carried out using certain compounds as source material. Among others $LiBO_2$ [12], $LiNO_3$ [13] and Li_2CrO_4 [14] were applied and tested. Unfortunately, only small extent about details of operation is published especially the source live time was never mentioned in these references. Although this contribution is focused mainly on Li LMAIS, other investigated source types should also be mentioned. A Cs sputter source for negative Li ions for tandem accelerators was reported [15]. Controlled continuous Li surface diffusion from a Li covered shank to the apex of a <111> W tip [16] was used to operate a field emitter like in a Helium Ion Microscope (HIM) [17]. An alternative and promising solution for Li-FIB application was presented using a Magneto-Optical Trap Ion Source (MOTIS) delivering nm-resolution from laser-cooled Li atoms [18].

II. EXPERIMENTAL

Standard hairpin emitters were fabricated from 250 µm metallic wires (see table 1) and spot welded on a filament. The tip was mechanically sharpened to a final radius of 3 – 5 µm. The emitters were cleaned by heating to 1200°C in UHV and then wetted in a crucible with the certain materials listed in table 1. Those materials were selected according to the phase diagrams of low temperature melting Li-alloys and stable other binary ones able to absorb a small amount of Li [19]. A first test of emission was then performed always in the same geometry. The slowly heating of the emitter is necessary to obtain a homogeneous temperature distribution in the source reservoir.

Table 1: Source materials, melting temperature, emitter tip material and emission behavior.

Source material	T_{melt} (°C)	Emitter	Useable Li beam
Li	180.5	Ta, Ti	-
$Ga_{35}Bi_{60}Li_5$	222	Ta, W	+
$In_{60}Bi_{30}Li_{10}$	230	Ta	+
$Ga_{60}In_{20}Sn_{10}$ + Li (Galinstan + Li)	200	Ta	+/-
$Sn_{95}Li_5$	222	Mo, Ni	+
Li_2CO_3 (Li-Carbonate)	720	Ta	-
Au_5Li_{95}	155	Ti	-
$Bi_{86}Li_{14}$	243	Ta	-
$Pb_{84}Li_{16}$	235	Ti	-

Successful working emitters (marked with a “+” in Tab. 1) were introduced in a cartridge and installed in an analytic test-FIB described in [20]. Measurements of the I-V characteristics, the mass spectrum, current stability, live time and the energy distribution for each ion species depending on the emission current were carried out.

III. RESULTS AND DISCUSSION

A: Li rich materials

As a first attempt pure Li was tested on different needle materials. Due to the high chemical affinity the handling in atmosphere as well as the exposure to the residual gas in the high vacuum chamber (<10^{-6} mbar) is problematic. The wetting of the needle tip resulted in a very fragmentary film. The Li became a porous structure, possibly induced by outgassing. The aim was to keep the temperature at all time below 250°C, since an increase in temperature leads to evaporation of the Li material. Preparation and storing under Ar atmosphere could not overcome the difficulties. Similar behavior was found for Li_2CO_3 (Li-Carbonate), Au_5Li_{95}, $Bi_{86}Li_{14}$ and $Pb_{84}Li_{16}$ which were not wettable or could only be operated for a short time due to chemical disintegration of the source material or the needle tip. Another approach was to solve about 5 at% Li in $Ga_{60}In_{20}Sn_{10}$ (Galinstan) which has a melting point of only -11°C. Galinstan is liquid at room temperature which can be a problem during transportation. The source was operated at 200°C, above the melting point of Li, but over time high melting components formed on the tip limiting live time of the ion source. Alloys such as $Ge_{50}Li_{50}$ or $Au_{77}Si_{18}Li_5$ were also considered but rejected due to the high melting point of 528°C and about 400°C, respectively. The high temperatures would possibly lead to Li outdiffusion. Likewise $Ag_{10}Li_{90}$ (T_m = 145°C) or Ga_3Li_{97} (T_{melt} = 180°C) as high content Li materials behaved like pure Li and therefore could not be established in a LMIS (marked with "-" in Tab.1).

B: $Ga_{35}Bi_{60}Li_5$ and $In_{60}Bi_{30}Li_{10}$

The characterization and investigation of a $Ga_{35}Bi_{60}Li_5$ LMAIS, prepared by adding of Li to the stable binary alloy, was described earlier [5]. It should be mentioned that in all working Li containing sources no double-charged Li ions could be found. Whereas the first ionization energy of Li is 5.4 eV, the second is already as high as 75.6 eV [21] prohibiting the emission of Li^{2+} ions. The ion source was operated stable over more than 1000 µAh in a VELION FIB-SEM (Scanning Electron Microscope) system (Raith GmbH) [22]. The stability measurements showed fluctuations below 1% over 3 hours (Fig. 1a). All ion species can be clearly mass separated as demonstrated in Fig. 1b with a Li ion beam of up to 100 pA.

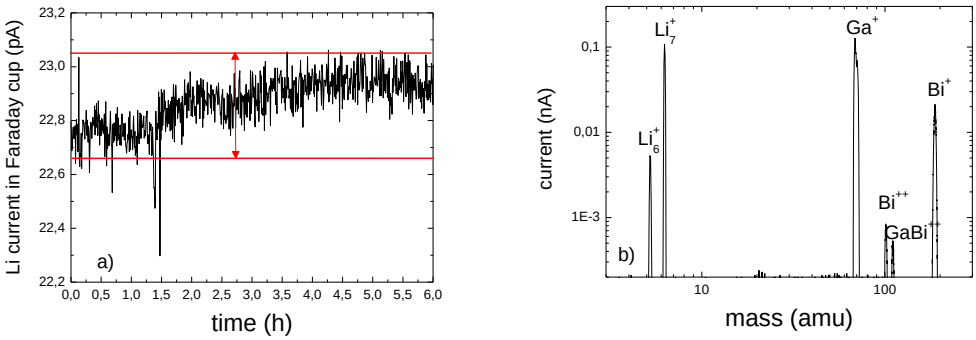

Fig.1: Stability of ^{7}Li probe current from GaBiLi LMAIS over 6 h at 35 keV (a) and the corresponding mass spectrum of the GaBiLi LMAIS in the VELION system (b).

The Li-FIB performance was investigated by imaging and milling of circular holes (d = 125 nm) into 1x1 µm² gold squares on a silicon bulk sample (chessy target from Plano GmbH). The thickness of the gold structure is 100 nm. The secondary electron (SE) image of the gold structure obtained by scanning the focused Li^{+} ion beam is shown in Fig. 2. The beam diameter is about 4 to 8 nm corresponding to 1 – 2 pixel shown in the inset of Fig. 2a. Also this beam can be applied to fabricate features with resolution as small as about 10 nm in width. The milling of 7 circles with a ^{7}Li ion beam at an energy of 35 keV and a current of 3 pA is presented in Fig. 2b. The patterning took 40 s and results in a sputtering coefficient of about 0.5 for Li in Au. At the given parameter set the SRIM code provides a coefficient of 0.4 [23].

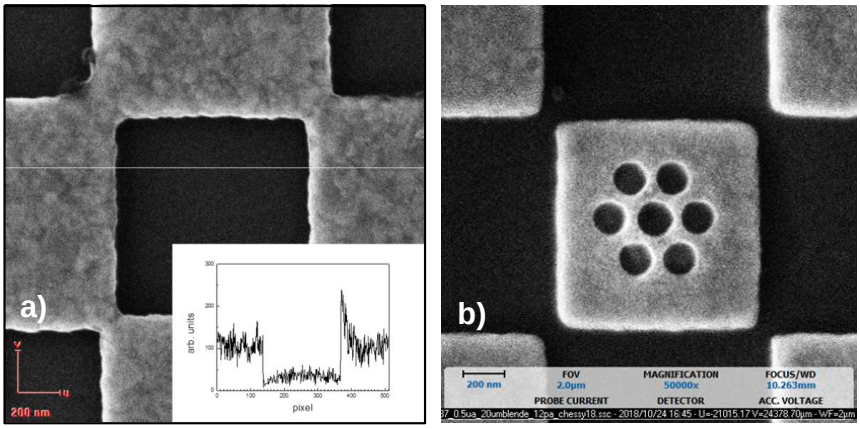

Fig. 2: FIB-SE image of a gold structures using a 35 keV ^{7}Li beam. The inset in (a) shows a line profile revealing a resolution of 4 – 8 nm. 7 milled circles with a diameter of 125 nm in a 100 nm Au film (b).

The $In_{60}Bi_{30}Li_{10}$ LMAIS was derived from the experience of a stable working $Ga_{35}Bi_{60}Li_5$ source taking additionally the In-Bi phase diagram into account. The mass spectrum of this source is shown in Fig. 3 measured with the test FIB [20]. The $^{7}Li^{+}$ intensity is about 0.5% of the $^{115}In^{+}$ peak. The separation of the $^{115}In^{+}$ and the $^{104}Bi^{++}$ species could be a problem in FIB columns with low mass separation capability. The behavior of this source due to the Li beam was comparable to the GaBiLi LMAIS.

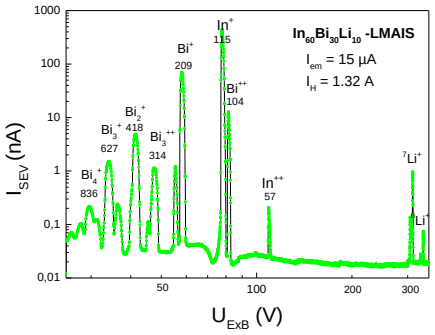

Fig.3: Mass spectrum of an $In_{60}Bi_{30}Li_{10}$ LMAIS. The current I_{SEV} in the test FIB was measured with a secondary electron multiplier.

C: $Sn_{95}Li_5$

All investigated low melting and low Li containing binary alloys were studied by the phase diagram [19]. Among them, $Sn_{95}Li_5$ is a promising candidate. In the eutectic point at 222°C the Li concentration is only 5% (Fig. 4a). The corresponding mass spectrum of the $Sn_{95}Li_5$ LMAIS is shown in Fig. 4b. The intensity of the Li ions is comparable to that of the Sn^{++} peak. The Na^{+} peak is revealed to be a residue from the production of pure Li material, in which Ni is dissolved material from the used emitter needle. The I-V characteristic of a $Sn_{95}Li_5$ LMAIS (not shown) has a typical behavior for a LMIS. The up and down measured curve is nearly congruent with a slope of 0.041 µA/V. The source could be operated in the test-FIB in a very stable manner but the source life time was limited to lower than 10 µAh. Additional work is required to increase the lifetime of the source. The energy spread for the $^{6}Li^{+}$ isotope at 1 µA emission current could be determined to 3 eV using a retarding field analyzer [20]. The increase of the energy spread with increasing emission current is also quite flat compared to the well-known Ga-LMIS [2, 5] which is advantageous for a stable source operation working with higher emission currents due to lower chromatic aberration.

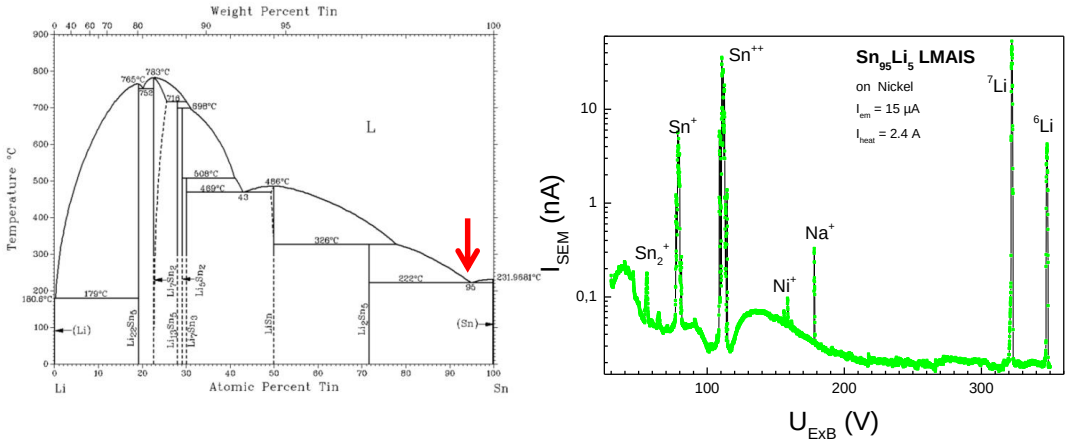

Fig. 4: Phase diagram of a Li – Sn alloy [19] (a) and mass spectrum of a $Sn_{95}Li_5$ LMAIS obtained in the test-FIB (b).

IV. SUMMARY AND CONCLUSIONS

The investigation of Li containing alloys with the aim to fabricate a long lasting and stable Li LMAIS results in three feasible solutions namely $Ga_{35}Bi_{60}Li_5$, $In_{60}Bi_{30}Li_{10}$ and $Sn_{95}Li_5$. The first one was tested under real practical conditions in a VELION FIB-SEM system (Raith). The source life time was longer than 1000 µAh and a first application showed a beam spot of 4 - 8 nm so far. This LMAIS has several applications in mass-filtered FIB like implantation, high rate sputtering, surface patterning, ion lithography or as primary ion for SIMS. The fast switching between the certain ion species from Li – very light to Ga – medium and finally to Bi – quite heavy, leads to remarkable expansion of the application spectrum of FIB technology.

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