

## **New type of metal ion source: Surface diffusion Li<sup>+</sup> ion source**

V. K. Medvedev, Yu. Suchorski and J. H. Block

Citation: *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures Processing, Measurement, and Phenomena* **13**, 621 (1995); doi: 10.1116/1.587927

View online: <https://doi.org/10.1116/1.587927>

View Table of Contents: <https://avs.scitation.org/toc/jvn/13/2>

Published by the [American Institute of Physics](#)

---

### **ARTICLES YOU MAY BE INTERESTED IN**

[Lithium ion beams from liquid metal alloy ion sources](#)

*Journal of Vacuum Science & Technology B* **37**, 021802 (2019); <https://doi.org/10.1116/1.5086271>

[Dual scanning tunneling microscope mode of the surface diffusion metal ion source: Li transfer and scanning](#)

*Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures Processing, Measurement, and Phenomena* **15**, 491 (1997); <https://doi.org/10.1116/1.589606>

[Helium ion microscopy](#)

*Journal of Vacuum Science & Technology B* **32**, 020801 (2014); <https://doi.org/10.1116/1.4863676>

---

# New type of metal ion source: Surface diffusion Li<sup>+</sup> ion source

V. K. Medvedev,<sup>a)</sup> Yu. Suchorski,<sup>b)</sup> and J. H. Block

*Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany*

(Received 7 July 1994; accepted 16 November 1994)

A surface diffusion metal ion source, a new type of metal ion source, is explored. In this device a field desorption process is used to achieve an almost monoenergetic continuous flux of Li<sup>+</sup> ions from a [111]-oriented W field emitter. Earlier difficulties with the continuous supply of adatoms, required to produce measurable desorption rates, were overcome by making use of solid state surface diffusion from the Li multilayer reservoir at the shank of the field emitter. The high density of the ion beam (an ion current of 10<sup>-12</sup> A was achieved from a W trimer), the extremely narrow energy distribution (full width at half-maximum of 0.25 eV) and the stable geometric form of the emitter itself during the operation are advantages of the new ion source which may be important in different areas of nanotechnology. © 1995 American Vacuum Society.

## I. INTRODUCTION

Narrowing the energy distribution of ions emitted from gas field ion sources (GFIS) and liquid metal ion sources (LMIS) is a long-standing unresolved problem in vacuum microelectronics. The values of the full width at half-maximum (FWHM) of the energy distribution of ions emitted from known field ion sources (about 1 eV for GFIS and 4.5 eV for LMIS, respectively<sup>1</sup>) still do not meet the prerequisites of modern ion beam technology.<sup>2</sup> The achieved values cannot be essentially improved due to the physical peculiarities of the field ionization mechanism itself employed in these sources.<sup>3</sup> To squeeze remarkably the energy spread of emitted ions, one should search for an alternative, more localized mechanism of field ion formation.

Since field desorption can be considered as a field emission of positive ions that originate from a bound state on a metal surface,<sup>4</sup> it is challenging to use the field-desorption process for the construction of a metal field ion source useful in electronic devices. For this purpose a continuous flux of field desorbed ions is necessary which in turn demands a controlled continuous supply of adatoms to the tip apex. The difficulties in creating such efficient supply were an essential shortcoming in the development of the field-desorption ion sources until now. In this article we report a novel procedure which allows a well-controlled continuous surface-diffusion feeding of the field-desorption zone on the apex of a field emitter tip with alkali (Li) adatoms, providing in this way the continuous desorption flux of Li<sup>+</sup> ions.

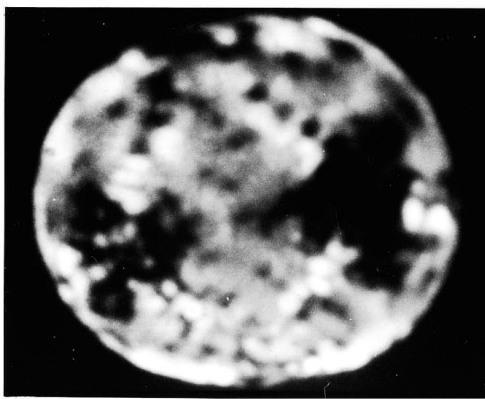
## II. LITHIUM FIELD-DESORPTION MICROSCOPE AS A PREDECESSOR OF THE LI SURFACE DIFFUSION METAL ION SOURCE

The idea of using the field-assisted surface diffusion supply for creating a continuous flux of field-desorbed Li<sup>+</sup> ions is based on the early work of Gavrilyuk and Medvedev<sup>5</sup> in which this experimental procedure was proposed for imaging of the surface of the field emitter by field-desorbed Li<sup>+</sup> ions. In developing these preliminary attempts to image a metal

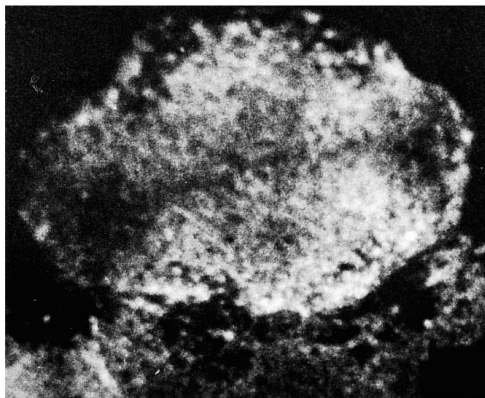
surface with field-desorbed Li<sup>+</sup> ions, a new lithium field-desorption microscope (Li FDM) was recently constructed.<sup>6</sup> In this device Li atoms diffuse from the shank of a field emitter towards its apex. Li<sup>+</sup> ions field-desorbed from the top of the tip form a FDM image on a fluorescent screen. The Li<sup>+</sup> ion desorption rate under these conditions is sufficient for the visualization of the surface in the continuous mode of imaging. In this mode of imaging the protruding (imaged) surface atoms operate as atomic-size sources for the strong emission of Li<sup>+</sup> ions producing bright images of selected surface sites in the same way as Ne<sup>+</sup> or He<sup>+</sup> ions do in the field ion microscope (FIM). The Li FDM, however, operates at essentially lower applied electrostatic fields and, in contrast to FIM, is able to provide high resolution at elevated temperatures (up to 450 K). The achieved brightness of the spots on the screen is comparable with that in the field ion microscope with Ne or He as imaging gases, indicating the high density of the Li<sup>+</sup> ion flux. This device was recently successfully employed for the imaging of clean and adsorbate-covered metal surfaces, and even fast dynamic processes on the surface such as the catalytic CO-oxidation reaction<sup>7</sup> on Pt. Figures 1(a) and 1(b) show the clean and CO-covered surface of a [110]-oriented Pt tip imaged by Li<sup>+</sup> ions which were field desorbed from the imaged surface area after arriving there via surface diffusion from the shank of the tip. The detailed investigation of different field emitters in Li FDM imaging mode, in which the spatial distribution of emitted Li<sup>+</sup> ions can be estimated from the projection on the screen, led to the conclusion that a [111]-oriented W tip is favourable for creating a high density Li<sup>+</sup> ion flux [Fig.1(c)]. The particular atomic geometry of the apex plane of such a tip causes highly inhomogeneous local field distributions above individual surface atoms of the W(111) plane.<sup>8-10</sup> This leads to a very high degree of localization of the field ionization process for noble gases ionized above such surface atoms.<sup>9</sup> Therefore a high degree of the localization of the Li<sup>+</sup> field ion formation process for the W(111) is expected and, as a result, an extremely narrow energy distribution of the Li<sup>+</sup> ions originated from the surface sites on W(111) may also be anticipated. Thus, it is tempting to use the working

<sup>a)</sup>On leave from Institute of Physics, National Academy of Sciences, Kiev, Ukraine.

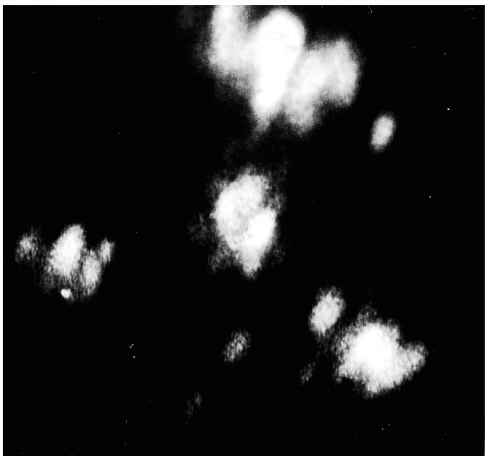
<sup>b)</sup>On leave from Technical University Lviv, Lviv, Ukraine.



(a)



(b)



(c)

FIG. 1. (a) Clean field evaporated surface of the [110]-oriented Pt tip imaged by  $\text{Li}^+$  ions in the Li FDM at 446 K, (b) the same surface but covered with carbon monoxide at 417 K, (c) the image of the [111]-oriented W tip created by  $\text{Li}^+$  ions in the continuous mode of imaging in the Li FDM at 352 K and 7.9 V/nm. The  $\text{Li}^+$  ions originated from the bright area in the central part of the image [(111) plane] were analyzed in the probe hole experiment.

mechanism of the Li FDM as a base for creation of a new type of the metal ion sources: surface diffusion metal ion source (SDMIS).

### III. OPERATION CHARACTERISTICS OF THE Li SDMIS

To create a continuously working Li SDMIS using the idea of the field stimulated surface transport of Li atoms to

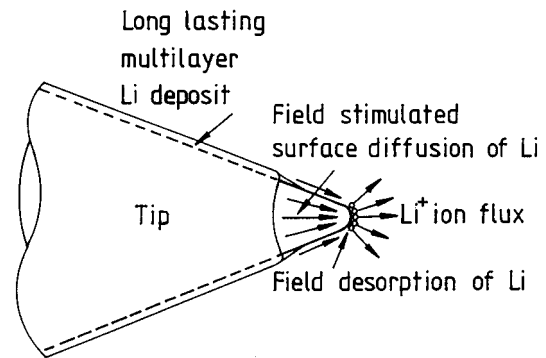


FIG. 2. Principle of operation of the surface diffusion  $\text{Li}^+$  ion source.

the top of a field emitter, where they could be field-desorbed as positive ions, one needs a sufficient Li reservoir. This problem was successfully solved by depositing a Li multilayer on the shank of a field emitter tip by *in situ* evaporation of Li from a commercial SAES getters Li source. If the shank is a cone with length  $L$  and base diameter  $d_0$  and the top is a hemisphere of radius  $r$ , then the ratio of the areas of the shank and the top is  $d_0L/4r^2$ . With typical values  $L=1$  mm,  $d_0=0.1$  mm, and  $r=500$  Å this ratio equals  $10^7$ , i.e., one monolayer of Li on the shank can provide  $10^7$  monolayers of Li to the top of the tip. The estimation of the rates of Li surface diffusion, based on Fick's equation and experimental data,<sup>6,7</sup> shows that surface diffusion of Li can transport about  $10^2$ – $10^3$  monolayers of Li per second to the top of the tip in the temperature range of 300–400 K (diffusion coefficient equals  $10^{-8}$ – $10^{-7}$   $\text{cm}^2 \text{s}^{-1}$ ). It should be stressed that under present experimental conditions Li surface diffusion proceeds in the *solid state*. This was checked by the investigation of Li surface diffusion, performed in the pulse mode of imaging in the Li FDM (Ref. 7) and is in detail discussed in Refs. 6, 7, and 11. Another process affecting the working characteristics of Li SDMIS is concerned with the thermal evaporation of Li at the operating conditions. From the known vapor pressure<sup>12</sup> of Li ( $10^{-10}$  Torr at 450 K) it can be estimated that at this temperature the multilayer reservoir would last for several hours.

The principle of operation of the Li SDMIS is illustrated in Fig. 2. Li atoms diffuse from the multilayer Li deposit on the shank of the tip towards its apex.  $\text{Li}^+$  ions, field-desorbed from the top of the tip, form a flux of  $\text{Li}^+$  ions directed to the counter electrode. It is to be noted that field desorption of Li occurs at essentially lower fields than field ionization of noble gases: for instance, Li can be desorbed from the W surface by externally applied field in the range of 0.5–1 V/even at 78 K (Fig. 3).<sup>13</sup> The desorbing field will further decrease if the temperature of the emitter increases, in accord with the known trend in field desorption of metals. On account of these properties a surface diffusion  $\text{Li}^+$  ion source was created, applying the above described procedure to the [111]-oriented tungsten tip. It is to be noted that at the present conditions  $\text{Li}^+$  ions originate from the second Li layer on the W surface, as follows from the analysis<sup>6,7</sup> of the imaging mechanism in the Li FDM. Using the known prepa-

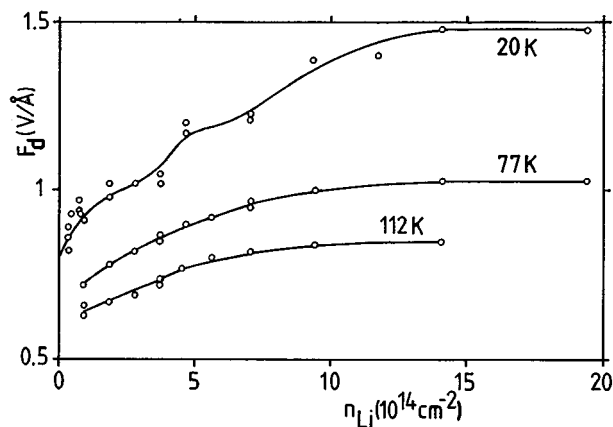


FIG. 3. Dependence of the desorbing field,  $F_d$ , for (110) plane of a [110]-oriented W tip on the surface density of lithium,  $n_{Li}$ , at different tip temperatures (Ref. 13).

ration techniques,<sup>14,15</sup> one can restrict the emitting area to the few surface sites of the central (111) plane of the tip. We were able to create a three-atom terrace on the top of the tip and to achieve a stable  $Li^+$  ion current of  $10^{-12}$  A from this Li covered tungsten trimer. No influence of Li on the stability of the emitting region was observed for any geometric configuration of the tip apex. A total  $Li^+$  ion current of  $10^{-10}$  A was routinely achieved from the whole W tip. Similar experiences were made with Rh and Pt tips.

#### IV. ENERGY DISTRIBUTION OF $Li^+$ IONS EMITTED FROM Li SDMIS

To check our expectations concerning the energy distribution of SDMIS-generated ions, a retarding potential analysis of  $Li^+$  ions emitted from the Li SDMIS was performed. Combining the new Li SDMIS with the recently developed retarding potential technique,<sup>8</sup> the energy distribution of  $Li^+$  ions emitted from the Li SDMIS can be obtained. Choosing the selected surface sites of the [111]-oriented W tip imaged by Li FDM [Fig. 1(c)], one can analyse the  $Li^+$  ions emitted from these sites in the probe-hole experiment. In the experiment, kinetic energies of  $Li^+$  ions, field-desorbed from a few surface sites of the apex plane of a [111]-oriented W tip and mass-to-charge resolved in a magnetic sector field,<sup>3</sup> were measured with the five-electrode electrostatic retarding potential analyser.<sup>16</sup> Using a secondary electron multiplier detector,  $Li^+$  ion counting rates,  $N$ , were acquired as a function of a voltage,  $\delta$ , applied between the retarding gold meshes and the emitter tip.  $Li^+$  ion retardation curves,  $N(\delta)$ , were then differentiated for obtaining the energy distribution,  $dN(\delta)/d\delta$ , of  $Li^+$  ions emitted from the Li SDMIS. Figure 4 shows results of the retarder potential analysis of  $Li^+$  ions originated from the bright area in the central part of the Li FDM image of the [111]-oriented W tip [Fig. 1(c)]. Both the locally measured  $Li^+$  ion retardation curve  $N(\delta)$  and the differentiated curve  $dN/d\delta$  are shown. It is to be noted that the energy distribution presented in Fig. 4 is still convoluted with the transmission function of the apparatus.

Even this non-deconvoluted energy distribution of  $Li^+$  ions for the present  $Li^+$  ion source has a full width at half-

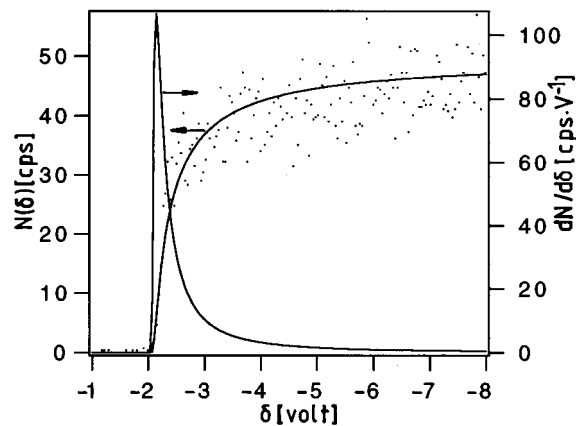


FIG. 4.  $Li^+$  ion retardation curve,  $N(\delta)$ , locally measured from W(111) sites at 352 K and at 7.9 V/nm and the differentiated curve,  $dN/d\delta$ , FWHM = 0.25 eV.

maximum (FWHM) of 0.25 eV. This is by a factor of almost 20 smaller than the best achieved value of FWHM of the ion energy distribution (of about 4.5 eV) for the liquid metal ion sources (LMIS).<sup>1</sup> The value of FWHM of the present  $Li^+$  ion energy distribution is even smaller than in the case of localized ionization of noble gases at 79 K.<sup>3,17</sup> The account of the transmission function of the spectrometer would further diminish the FWHM.<sup>17</sup> Thus, it is possible to realize a nearly mono-energetic  $Li^+$  ion source.

#### V. POSSIBLE APPLICATIONS OF THE SDMIS

The possible application of the present Li SDMIS is not limited by the cone formation at the instant of switching on the ion current as it is the case of LMIS (i.e., no geometric changes take place near the surface of the SDMIS up to a distance close to the diameter of a Li atom). Therefore, SDMIS may be highly suitable for the use in the scanning tunneling mode of operation for direct deposition of nanometer-size structures. The absence of a reservoir with liquid metal and therefore the absence of any dimension limitation as well as the essentially lower temperature of the source itself are further advantages if compared to corresponding LMIS. The lack of emission of neutral Li atoms, the very narrow (nearly mono-energetic) energy distribution and the small mass of  $Li^+$  ions indicate the usefulness of the presented  $Li^+$  ion source also for the scanning transmission ion microscopy (STIM).<sup>18</sup>

#### VI. CONCLUSIONS

A novel type of metal ion source is presented: the surface diffusion metal ion source, in which metal ions are generated directly on a metal surface via field desorption from the chemisorbed state. Due to the physics of the field desorption process itself this allows one to produce an almost mono-energetic ion flux and to keep constant the geometric dimensions of the source during operation. The transport of the working substance proceeds by surface diffusion in the solid

state from a multilayer deposited on the shank of a field emitter providing in this way a long-lasting operation of the device.

## ACKNOWLEDGMENTS

The authors thank Dr. W. A. Schmidt for the advice in performing the energy distribution measurements. They also thank Professor A.G. Naumovets for critical reading of the manuscript and profitable discussions. A fellowship of the Max-Planck-Gesellschaft for two of the authors (V.K.M. and Yu.S.) and the technical assistance of M. Naschitzki are gratefully acknowledged.

<sup>1</sup>A. E. Bell, K. Rao, G. A. Schwind and L.W. Swanson, *J. Vac. Sci. Technol. B* **6**, 927 (1988).

<sup>2</sup>J. Melngailis, *J. Vac. Sci. Technol. B* **5**, 469 (1987).

<sup>3</sup>W. A. Schmidt, Yu. Suchorski, and J. H. Block, *Surf. Sci.* **301**, 52 (1994).

<sup>4</sup>E. W. Müller and T. T. Tsong, *Field Ion Microscopy, Field Ionization and Field Evaporation*, Progress in Surface Science, Vol. 4, Part 1, edited by S. G. Davidson (Pergamon, Oxford, 1973).

<sup>5</sup>V. M. Gavriilyuk and V. K. Medvedev, *Sov. Phys. Tech. Phys.* **11**, 1282 (1966).

<sup>6</sup>V. K. Medvedev, Yu. Suchorski, and J. H. Block, *Ultramicroscopy* **53**, 27 (1994).

<sup>7</sup>V. K. Medvedev, Yu. Suchorski, and J. H. Block, *Appl. Surf. Sci.* **76/77**, 136 (1994).

<sup>8</sup>W. A. Schmidt, N. Ernst, and Yu. Suchorski, *Appl. Surf. Sci.* **67**, 101 (1993).

<sup>9</sup>Yu. Suchorski, W. A. Schmidt, J. H. Block, and H. J. Kreuzer, *Vacuum* **45**, 259 (1994).

<sup>10</sup>Yu. Suchorski, W. A. Schmidt, N. Ernst, J. H. Block, and H. J. Kreuzer, *Prog. Surf. Sci.* (to be published).

<sup>11</sup>V. K. Medvedev, Yu. Suchorski, and J. H. Block, *Vacuum* (to be published).

<sup>12</sup>*Gmelins Handbuch der Anorganischen Chemie, Lithium, System-Nr 20* (Verlag Chemie, Weinheim, 1960), p. 171.

<sup>13</sup>V. K. Medvedev, *Bull. Acad. Sci. USSR Phys. Ser.* **33**, 489 (1969).

<sup>14</sup>H. W. Fink, *IBM J. Res. Develop.* **30**, 460 (1986).

<sup>15</sup>H. W. Fink, *Phys. Scr.* **38**, 260 (1988).

<sup>16</sup>T. T. Tsong, W. A. Schmidt, and O. Frank, *Surf. Sci.* **65**, 106 (1977).

<sup>17</sup>N. Ernst, G. Bozdech, H. Schmidt, W. A. Schmidt, and G. L. Larkins, *Appl. Surf. Sci.* **67**, 111 (1993).

<sup>18</sup>G. Bench, A. Saint, M. N. Cholewa, G. J. F. Legge, D. L. Weirup, and A. E. Pontau, *Nucl. Instrum. Methods B* **68**, 481 (1992).