



# Investigation of Nanoskin Peculiarities Formed During Oxidation of Liquid Gallium Surface

Giorgi Kvinikadze\*, Elguja Kutelia

Republic Center for Structure Researches, Georgian Technical University, Tbilisi, Georgia

## Email address:

giorgikvinikadze89@gmail.com (G. Kvinikadze)

\*Corresponding author

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**Abstract:** In the given work, the formation mechanism and kinetics of nano skin obtained on the super-pure ( $6N - 7N^+$ ) gallium melts surface during oxidation in air at temperature range  $20 - 100^\circ\text{C}$  is studied by methods of TG, SEM-EDX and AES. It is shown that, as a result of penetration of oxygen atoms (released by dissociative adsorption) in the layered subsurface with 5 – 6 atomic diameter thickness, transforms to amorphous gallium oxide elastic skin, such as continuous nanoshell of equal thickness ( $\sim 15 \text{ \AA}$ ) on the whole surface of the melt. The growth of the mentioned oxide skin thickness formed in the first seconds, obeys more retarded linear kinetics up to  $100^\circ\text{C}$ , and after few hours its thickness reaches  $\sim 50 \text{ nm}$ . Further oxidation process in the atmospheric condition at room temperature practically stops.

**Keywords:** Liquid Gallium (L-Ga), Super-Pure Gallium, Oxidation, Nanoskin, SEM-EDX, TG, AES

## 1. Introduction

In accordance with the existing representations, that is based on the both theoretical and experimental data, formation of oxide films on the surfaces of metals is complicated multistage process, which nucleation and grow on the surface of metal being in a crystalline (solid) state depends on many factors. Most of these factors are conditioned by nature of the metal and its surface; in particular: surface crystallographic orientation, existence of surface impurities, phase composition, existence of chemically and electronically active centers, origins of different channels of oxygen atoms facilitated diffusion into metal depth located on a surface and others. Exclusion most of the mentioned factors is possible in the case of conducting oxidation process on the liquid metal surface maximally cleaned from impurities; however, in this case, existence of surface tension force of melt will become as an additional factor.

Surface delamination effect caused by electron density oscillation, which for its part is induced by surface tension of liquid metal, is experimentally well studied for metals having low melting temperature as are Hg, Ga and In [1 – 4]; there is shown that electron density profiles are significantly different

for each of these metals and form at ion of oxide layer on the surfaces of their melts happens with different mechanisms; in particular, during oxidation, homogeneous oxide layer of equal thickness forms on the surface of liquid gallium [5 – 7], while oxide film on the surface of indium melt forms like macroscopic islands [2]. However, it should be noted that formation mechanisms of adsorbed and oxide films on the surfaces of liquid metals in connection with structure of melt's subsurface layers practically are not studied. Therefore, for studying of melt's structure, its crystallization processes, melt's surface conditions and fundamental issues about liquid metal surface interaction with environment based on the modern imaginations, it is necessary to conduct experiments on the objects maximally purified from impurities. From this standpoint the high purity gallium melt attracts a great interest since it is a fascinating object in several aspects due to its low  $L \leftrightarrow S$  transition temperature, very high surface tension, maintaining in an overcooled liquid state for a long time and the possibility of reaching high purity level (up to  $8N$ ) in it.

Our development regarding the membrane technology of purification of liquid gallium from impurities [6, 7], ensuring quick production of over cooled  $7N^+ - 8N$  purity non-crystallizing L-Ga from commercially available  $5N - 6N$  purity gallium, gives us opportunity to receive the unique

model object for investigation of oxidation process of super-pure metal melt with atomically flat surface.

In relation with the above-noted, the aim of this work represents the complex study of formation kinetics and structure of nanoskin on the  $6N^+$  and  $7N^+$  purity gallium melts surface during oxidation in air at temperature range 20 – 100 °C by using modern analytical methods such as a thermogravimetric analysis (TG), an Auger electron spectroscopy (AES), an scanning electron microscopy (SEM) and an energy dispersive X-ray spectrometry (EDX).

## 2. Materials and Experiments

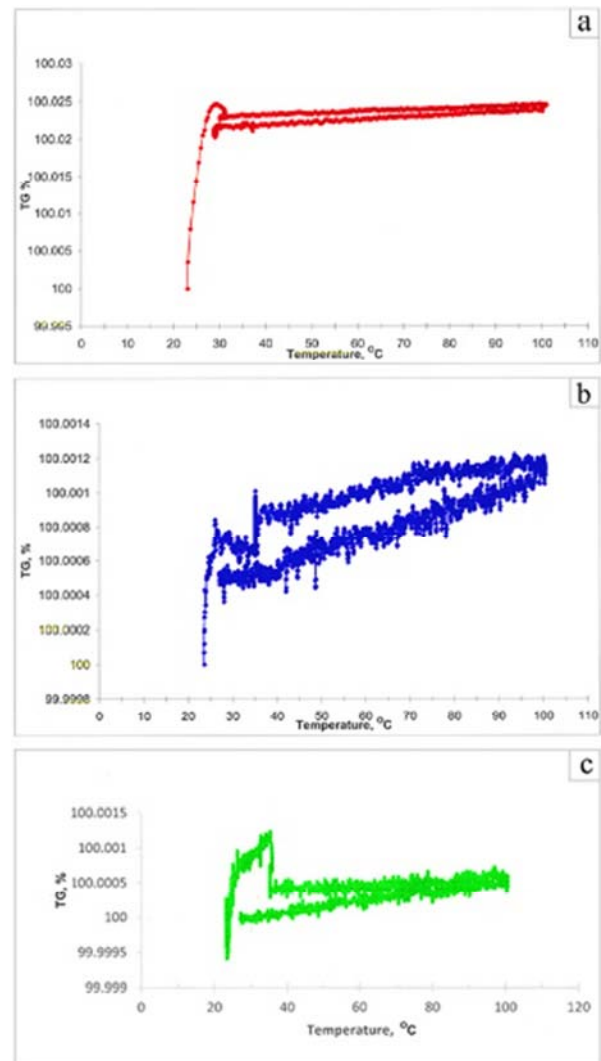
Preparation of overcooled super-pure (up to 8N) liquid gallium samples for TG analysis we were performing using method of membrane purification (MP) [6, 7] from commercially available 5N and 6N purity gallium, produced and certificated by company MaTeck GmbH (Germany). We were conducting control of certified data and achieved purity level for L-Ga samples obtained after MP by the method described in our previous work [8] using glow discharge mass spectrometric analysis (GDMS). The results of GDMS analysis for commercial gallium (according to the 16 elements defined by certificate) and for liquid gallium purified by membrane technology (according to 24 elements) showed us that commercial gallium really fits purity level specified by certificate, and after one-step membrane refinement of commercial 5N gallium ( $5N + MP$ ) we obtained  $6N^+$  purity gallium, after two-step membrane refinement ( $5N + MP + MP$ ) –  $7N$  purity gallium and after one-step membrane purification (refinement) of commercial 6N purity gallium – L-Ga with purity level very close to 8N. Obtaining of the super-pure ( $\geq 7N$ ) gallium melts of ~ 40 g encapsulated in a membrane bag and its remaining in an overcooled liquid state at room and lower temperatures ( $\leq +20^\circ\text{C}$ ) practically unlimited period of time was giving the opportunity of taking the assays ~ 2 g from volume of the melts using Teflon tube for TG analysis just before starting the experiment. The TG experiments were carried out via the device of STA449C Jupiter, Netzsch (Germany). Preparation of analytical assays was going on the same way for AES and SEM–EDX analysis. Investigations of the morphology and composition of nanoskin formed during oxidation of super-pure liquid gallium surface were conducted using Auger-electron-spectrometer LAS–2000 Riber (France) and scanning electron microscope DSM–960 Opton (Germany).

## 3. Results and Discussion

The thermogravimetric analysis was performed for the L-Ga samples in the temperature range 20 – 100 °C in the flowing environment of synthetic air (50 ml / min of  $N_2 / O_2 + 25$  ml / min of He) where the heating up and cooling down velocity was 1 °C / min. The TG experiments were initiated by the as-prepared overcooled L-Ga samples with starting temperature of 22 °C.

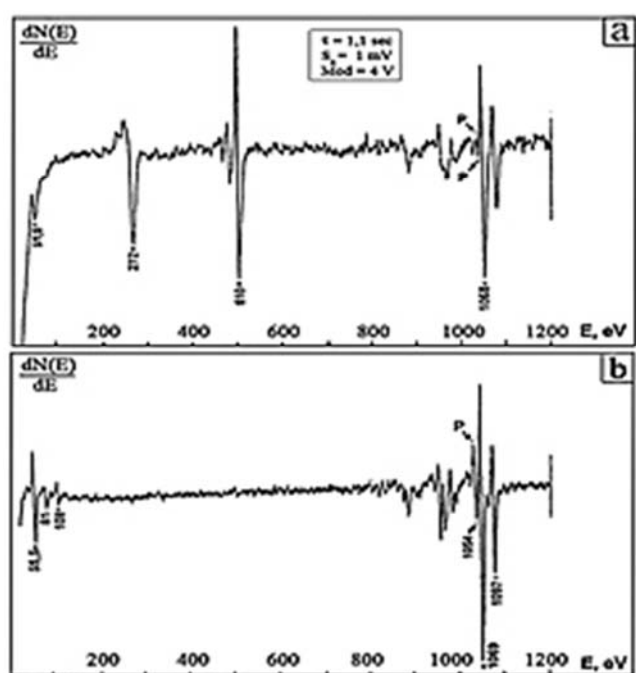
Figure 1 shows the results of the TG analysis performed

with the  $6N^+$  purity L-Ga obtained from the initial commercial 5N gallium using one-step membrane purification ( $5N + MP$ ) (Figure 1a), the 7N purity L-Ga obtained from the initial commercial 5N gallium using two-step membrane purification ( $5N + MP + MP$ ) (Figure 1b) and the  $7N^+$  purity L-Ga obtained from the initial commercial 6N gallium using one-step membrane purification ( $6N + MP$ ) (Figure 1c). The TG curves plotted for each of the three samples do indicate very fast weight change in the first minute from the start of heating and further very slow linear kinetics oxidation while increasing the heating temperature up to 100 °C. In addition, it is revealed that mass change rate decreases as on the initial stage of oxidation well as on the area of linear kinetics when purity level of L-Ga sample increases (compare Figure 1a and Figures 1b and 1c). Auger-spectroscopic analysis were conducted on the same samples in order to determine formation mechanism of oxide film and connection of above mentioned kinetic peculiarities of oxidation process with structure of gallium melt's subsurface layers revealed as a result of the TG experiments.



**Figure 1.** TG curves of as-prepared overcooled noncrystallizing liquid gallium samples: a)  $6N^+$  ( $5N + MP$ ) L-Ga; b) 7N ( $5N + MP + MP$ ) L-Ga; and c)  $7N^+$  ( $6N + MP$ ) L-Ga.

Auger-spectroscopic analyze was carried out directly on the surface of overcooled  $7N^+$  purity liquid gallium drop, which had contact with atmosphere during few minutes before recording Auger-spectrum. Recording of the Auger-spectra was going on the sample surface loaded in a spectrometer from the atmosphere (in the absence of adsorbed layer) and also after removal of the surface layer from the same sample (sputtered with the speed of  $2\text{ \AA} / \text{min}$ ) using argon ions bombarding. The Auger-spectrum of the liquid gallium drop's surface before etching by argon ions is given on the Figure 2a. The peaks of gallium, oxygen and adsorbed carbon are only visible on the spectrum. At the same time, it appears that oxygen is entered in to the chemical bond with gallium atoms in contrast to carbon, because the  $M_3M_{45}M_{45}$  transition Auger-peak of unoxidized gallium atom is shifted from 55.5 to 51.5 eV and also plasmon peak (P) at the energy of 1054 eV is disappeared. The ratio of intensities of oxygen and gallium atoms Auger-peaks shows that  $\text{Ga}_2\text{O}$  is the formula of the formed oxide. The Auger-spectrum of the same surface recorded after removal of surface layer  $\sim 20\text{ \AA}$  thickness by 3 keV energy argon ions bombardment (etching) during 10 min is shown on the Figure 2b. The received spectrum perfectly coincides to the theoretical Auger-spectrum corresponding to the gallium atoms; in particular, the red is appeared oxygen and carbon peaks, the  $M_3M_{45}M_{45}$  transition Auger-peak of gallium atom is disposed at 55.5 eV, and plasmon peak at 1054 eV is displayed with maximal intensity.



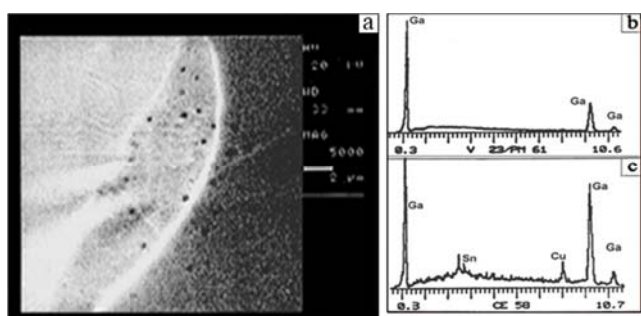
**Figure 2.** Auger-spectra obtained from the sample surface of overcooled super-pure  $7N^+$  gallium melt: a) spectrum recorded after  $\sim 3$  min soaking in air at room temperature; b) spectrum of the same surface area recorded after removal of surface layer  $\sim 20\text{ \AA}$  thickness by 3 keV energy argon ions etching.

Thereby, the experimentally determined (by us) fact, that  $\text{Ga}_2\text{O}$  oxide skin thickness ( $\sim 20\text{ \AA}$ ) formed during first minute contact with the atmosphere on the surface of overcooled

super-pure L-Ga practically coincides to the concentratedly delaminated subsurface layer  $\sim 15\text{ \AA}$  thickness (also experimentally determined [3 – 5]), induced by surface tension of liquid gallium, gives us reason to explain the above observed peculiarities on the TG curves and conclude that the initial stage of oxide formation on the overcooled super-pure liquid gallium surface upon contact with the atmosphere includes penetration of oxygen atoms generated from the dissociative adsorption of oxygen molecules into the concentratedly delaminated subsurface layer of  $\sim 15\text{ \AA}$  thickness and its transformation (practically instantly) into the same thickness skin of  $\text{Ga}_2\text{O}$  oxide. The further growth of the mentioned oxide skin thickness, such as continuous nanoshell of equal thickness on the whole surface of the melt, while raising the temperature up to  $100\text{ }^\circ\text{C}$  (or isothermal delaying on the room temperature during a long time) takes place too slowly with linear kinetics because of the barrier properties of the  $\text{Ga}_2\text{O}$  oxide skin formed during the initial stage toward the penetration of oxygen atoms into the following concentratedly delaminated subcutaneous (subskin) layers. It is obvious that oxidation process (thickness growth of oxide skin) will practically stop after some time by the joint action of the following two factors: first – by decrease of oxygen atoms penetration toward the separator border of oxide skin and melt along with oxide thickness growth and second – by decrease of the following layer thickness of subcutaneous concentrative delamination, conditioned by reduction of surface tension force, because of the primary ( $\sim 20\text{ \AA}$ ) oxide film formation, which is lyophilic toward the melt. The linear kinetic of the oxidation process using the described mechanism is so slow that continuous oxide film thickness generated over the entire surface of super-pure ( $\geq 6N^+$ ) gallium during few days delay on  $\sim 30\text{ }^\circ\text{C}$  temperature in the atmospheric conditions does not exceed  $\sim 50\text{ nm}$ . The fact that rolling of the certain spheroidal mass ( $\sim 20\text{ g}$ ) of gallium melt, encapsulated in the mentioned film, on a flat teflon surface did not cause oxide skin cracking (splitting), was indicating that the described oxide skin is elastic. Formation of a skin crack is possible by mechanical shear on the surface or melt shocking.

The SEM observation in the area of the oxide skin crack existing on melt surface enabled us to locally investigate in such areas chemical composition on the melt surface free from oxide and on the oxide surface close to the crack. For this, we were recording energy dispersive X-ray spectra (EDX) of secondary radiation from the both mentioned zone with locality  $\sim 4\text{ }\mu\text{m}^2$ . Results of this analysis are given on the Figure 3a, band c. The impurity concentration scattered in the gallium melt is out of the method sensitivity and only gallium peaks are observed on the relevant EDX spectrum (Figure 3b), whilst the number of impurities concentrated in the oxide film, which moved from melt, is clearly sensible and they appear in the corresponding EDX spectrum as distinctly identified peaks (Figure 3c). It should be noted that display of membrane properties of the analogous oxide formed on a liquid gallium surface during photostimulated oxidation process is described in our previous works [8, 9] and shown that oxide skin formed on a L-Ga surface, besides the movement of impurity atoms,

implements isotopic separation of the Ga too.



**Figure 3.** Surface zone of ~ 10 g “drop” of oxidized gallium melt in the oxide skin split (crack) area: a) SEM image; b) EDX spectra obtained from the melt (L-Ga) surface free from oxide (left section on the Figure 3a); c) EDX spectra recorded from the oxide surface (right section on the Figure 3a).

Therefore, in our opinion, consideration of the received results is necessary for anomalies of liquid gallium viscosity and surface tension [10], and for creation of a clear picture of oxide skin existence on a melt surface and the melt’s purity level impact on the skin.

## 4. Conclusions

The three important conclusions follow from the results of the above mentioned:

First – The initial stage of oxide formation on the overcooled super-pure liquid gallium surface upon contact with the atmosphere includes penetration of oxygen atoms generated from the dissociative adsorption of oxygen molecules into the concentratedly delaminated subsurface layer of ~ 15 Å thickness and its transformation (practically instantly) into the same thickness skin of  $\text{Ga}_2\text{O}$  oxide;

Second – The further growth of the mentioned  $\text{Ga}_2\text{O}$  oxide skin thickness while raising the oxidation temperature up to 100°C (or isothermal delaying on the room temperature during a long time) takes place too slowly with linear kinetics and the process practically stops after formation of skin thickness ~ 50 nm such as continuous elastic nanoshell of equal thickness on the whole surface of the melt; and

Third – Gallium melt of some mass (10 – 50 g) encapsulated in the given skin naturally generates system of module “melt–membrane–atmosphere”, in which extraction of impurity atoms from melt into the reactive membrane is ongoing.

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