Growth of Nanostructure of Metal Oxides by Laser Ablation and by SiO$_2$ Assisted Thermal Evaporation

Lotfia M. EL Nadi, Galila .Mehena, Mgdy M. Omar, Hussein A. Moneim, Fakiha$^1$ H. A. Taieb, **Farid M. Abdel Rahim**$^2$

$^1$Laser Physics Lab., Physics dept., Faculty of science, Cairo university, Giza, Egypt.
$^1$Chemistry dept., Faculty of science, Cairo university, Giza, Egypt
$^2$Physics Dept., Faculty of Science, Al-Azhar university,, Egypt.

Abstract We report the results of growing nanostructures of gallium oxide and indium oxide by two methods. In the first one we applied laser ablation in air of pure graphite rod filled with Gallium or Indium metals. The ablated plume then deposited on SS substrates in air. In the second method the oxides were synthesized by thermal heating of the Ga or In metals mixed with powder of graphite and covered with SiO$_2$ plates, supported by ceramic, in high temperature oven. The ablation method produced nanowires of Ga$_2$O$_3$ and nano particles of In$_2$O$_3$ developing in nanowires. The solid carbon ablated from the graphite rod existing in the ablated plume as fine solid particles mixed with metal Ga or In melt in contact with oxygen gas in air, produced the growth of the metal oxide nano structures by solid–liquid–gas mechanism.

The silica assisted catalytic growth oxides produce only nano particle of each metal. The reaction of the metals with SiO$_2$ melt and graphite produced Si and carbon. The then formed Si carbide can effectively initiate vapor–liquid–solid growth of nano structure metal oxide. It seems that SiO$_2$ in addition to the atmospheric oxygen provide the oxygen source for forming metal oxide nano dots.

INTRODUCTION

Material science and laser technology are introducing revolutionary discipline of nano technology. The advances of producing Nanoparticles or nanostructure for various material imposed many important questions of how to control the growth, how to identify the produced nano structure and how to assemble them into new devices. The extraordinary accomplishments of arranging them into circuits that perform logic operations amplifying signals invert current flows and even perform simple computing tasks, call for new methods for growing and identifying nanostructures [1-5]. Many methods are still developing for preparation of nano meter sized material. One important method vapor-liquid-solid growth either in oven or by laser evaporation or solution–liquid–solid growth at lower temperature, have been used for the synthesis of oxide, carbide and nitride nanostructures [6-9]. Other new growth method known as oxide–assisted nanowire growth, developed Si and Ge nanowires [10-11], during which the decomposition of vapor oxides at high temperature during thermal evaporation or laser ablation helped to grow nano wires. Nanowires of tungsten oxide growth as nano tree like structure has been synthesized by Zhaw et al [12]. By heating tungsten foil covered by SiO$_2$ plate or high temperature Gallium oxide, β-Ga$_2$O$_3$ being a wide band gap [4.9 eV] compound [16]. Has interesting conduction and optical properties therefore its nano structures may also have important applications the fabrication of nano wires of gallium oxide were achieved by physical evaporation [14]. Characterization of photoluminescence
properties of Gallium -oxide nanowires grown by carbothermal reduction from gallium oxide powder was reported by X.C. Wu et al [15]. Silica assisted catalytic growth of Ga\textsubscript{2}O\textsubscript{3}, GaN and AlN nano wire has been prepared and identified recently [16].

In this study a comparative study for synthesis of nanostructures of Ga\textsubscript{2}O\textsubscript{3} and In\textsubscript{2}O\textsubscript{3} was carried out using two methods in the first one, UV laser ablation of the Ga or In metals embedded in graphite was applied the ablated plumes in air were deposited on SS substrates. While the second method used was the silica assisted catalytic growth of the metal oxide at elevated temperature. Fine powder of graphite mixed with Ga or In metal were heated in atmosphere after covering with SiO\textsubscript{2} plate. It has been proved that the laser ablation method enhanced the growth Ga and In oxide nanowires while in the second method, Nanoparticles for both Ga and In oxides were observed.

**EXPERIMENT**

For the laser ablation method, the confined geometry of the target chamber used for nitrogen laser ablation of graphite described before for formation of the carbon nanowire was applied [17]. A modification has been introduced on the graphite rod in which an axially drilled hole of diameter 2 mm and length 5 mm in the rod was filled with gallium or indium metal as shown schematically in figure.1

![FIGURE 1: Experimental setup with modified graphite drilled rod](image)

The pulsed UV N\textsubscript{2} laser beam was focused on the center of the graphite filled metal rod by quartz crystal. The ablated plum consists of ablated carbon and metal at high temperature. The probability of forming the metal oxide during the ablation process is expected since the laser irradiation process took place in the vicinity of atmospheric air. The irradiance at the target was 25±5 MW/cm\textsuperscript{2} per one laser shot summing up to 25±GW/cm\textsuperscript{2} for one thousand laser shots. The ablated plumes were allowed to deposit on an area of 1 cm\textsuperscript{2} of stainless steel substrates (SS Fe 91%, Ni 4.5%, Co 4.5%) for 1000 laser shots or 2000 laser shots respectively. The substrates were examined by scanning electron microscope (Jeol JXA-840A SEM) provided by electron probe micro analyzer. In the second method of silica assisted catalytic growth of Ga or In oxide nanostructures, 99.99% graphite plays the role of the catalyst. The equal amounts of metal and fine carbon, from graphite, were mixed thoroughly and
homogenized in a porcelain mortar for 1 hour. The mixtures were then placed in small porcelain crucibles, each covered with SiO₂ Plate. They were then mounted into high temperature small compartment furnace. The temperature was raised to 950 °C during 45 minutes in low atmospheric air flow. When the temperature reached 750 °C, the SiO₂ plates melted, at lower temperature than expected (SiO₂ Mp=1610°C). The melt mixture of the metals (Ga or In) + SiO₂ in presence of solid carbon was formed. The melts were allowed to cool down slowly reaching room temperature during 4 hours. The grayish white crust on the walls of the porcelain crucible, were then collected as fine powder and prepared for imaging by transmission electron microscopy. The samples of the crust powder, dispersed in acetone were pipetted onto Cu grids covered with carbon thin films. The grids were examined by "TEM 10 Zeiss WW EM", and constituents were identified by EDX. The Products left overnight developed in extraordinary hard ingots, sticking to the crucible bottom and it was difficult to turn them in fine powder by conventional methods.

RESULTS AND DISCUSSION

The deposited plumes on each substrate were examined after the laser ablation experiments by SEM. Figure 2a shows the morphology of the plane substrate surface. In figure 2b the image of the deposited plum formed during 1000 laser shots, indicate the presence of Nanowires with few Nanodots of Ga oxide (bright) and few carbon Nanodots (black). The average diameter for gallium oxide nanowires (GaONW) were measured to be 380±20 nm with average length 160 ±9µm and average density \((1.2±0.4)×10^5\) wires/cm². The GaOND are of average diameter 330±30 nm and average density \((3±0.4)×10^4\) dots/cm².

![FIGURE 2](image-url) Morphology of the substrate surfaces examined by SEM for the deposits of Ga oxide on (a) plane SS substrate surface, (b) formed GaONW after 1000 laser shots, (b’) a spotted magnified area of (b) revealing Nanodots(bright) GaOND, and few carbon Nanodots (Black)(c) formed GaONW after 2000 laser shots and (C’) Spotted magnified area of (C)revealing the parallel nature of GaONW growth.
The deposits due to ablation with 2000 laser shots reveals an appreciable increase in the diameter of the GaONW reaching 420±40 nm while the average length is nearly unchanged as clear from figure 2c where GaOND and the CND nearly vanished. The morphology suggests that the nanowires grow due to accumulation of the GaOND along one axis forming parallel nanowires. Figure 2b’ and 2c’ are spotted magnified areas of figure 2b and figure 2c confirming the above mentioned suggestions.

Figure 3a represents the morphology of the deposits of indium oxide nanodots (bright) together with carbon Nanodots (black). The InONW seems to be in their early stage of growth for the case of ablation by 1000 laser shots. The SEM Images shown in figure 3b due to ablation with 2000 shots clearly indicate the growth of InONW (bright) in parallel close packing along an incomplete straight fiber like-structure. It is clear that InOND increased in density but the average diameter of 320±30 nm seems to be the same for 1000 or 2000 laser shots within the error limit. One notices that carbon Nanodots(black) increased in density in figure 3b than in figure 3a. An important symptom of the increase of carbon Nanodots noticed for the In case points to lower utilization of carbon with indium metal in the ablated plum.

![Image](image_url)

**FIGURE 3.** (a, b): the SEM images representing the morphology of InOND (bright) and CND(black). (a) the growth for the case of ablation of In by 1000 laser shots, (b) the growth for ablation of In by 2000 laser shots.

The characteristics GaONW and InONW formed from attached nanoparticles indicate that a solid-liquid-gas growth may be the most suitable mechanism for the formation of the metal oxide. The growth process could only be explained if there liquid phase existed that nucleated growth of droplets of the metal in contact with oxygen gas to form oxide wire like growth. Could then build up due to super saturation [18]. This condition could be achieved at higher number of laser shots. The carbon existing in the ablated plumes as solid fine particles as well as the low melting point (Mp) of the metals (Ga Mp=29.78 °C, In Mp=156 °C) support the solid-liquid-gas growth mechanism. The reactants existing in the plume and deposits on the substrate could be represented as

Reactant \[4\text{Ga} + 2\text{O}_2 + \text{C} \rightarrow 2\text{Ga}_2\text{O} + \text{CO}_2\]  \hspace{1cm} (1)

\text{Liquid} \hspace{0.5cm} \text{gas} \hspace{0.5cm} \text{solid} \hspace{0.5cm} \text{gas} \hspace{0.5cm} \text{gas}

The \(\text{Ga}_2\text{O}\) and \(\text{CO}_2\) gases can be dissolved continuously into the liquid Ga metal forming drops inside which the following reaction takes place:

Products of (1) \[\text{Ga}_2\text{O} + \text{CO}_2 \rightarrow \text{Ga}_2\text{O}_3 + \text{C}\]  \hspace{1cm} (2)

\text{gas} \hspace{0.5cm} \text{gas} \hspace{0.5cm} \text{solid} \hspace{0.5cm} \text{solid}
The solid products deposits on the substrates. When Ga$_2$O$_3$ saturates formation of nanowire increase accompanied with nanodots. For the case of indium metal, of higher melting point than Ga, it is suggested that the liquid phase contribution is lower than in the case of Ga. The saturation of the drops with In$_2$O$_3$ needs higher dissipation of laser power in order that INONW could grow.

The results of the silica –assisted catalytic growth of Ga and In oxides, are shown in figure 4(a,b) respectively. The TEM images do not indicate growth of nanowires, but only reveal GaOND of average diameter 200±20 nm and InOND of average diameter 320±20nm. The following reaction most probably occur during the heating process of the Ga or In metals with SiO$_2$ and the carbon from the fine graphite powder in presence of O$_2$ gas of air in the furnace:

\[
\begin{align*}
4Ga + SiO_2 & \rightarrow 2Ga_2O + Si \\
\text{(Liquid)} & \quad \text{(Solid)} & \quad \text{(Gas)} & \quad \text{(Solid)} & \quad \text{products 1}
\end{align*}
\]

The reactants

\[
\begin{align*}
4Ga + C + 2O_2 & \rightarrow 2Ga_2O + CO_2 \\
\text{(Liquid)} & \quad \text{(Solid)} & \quad \text{(Gas)} & \quad \text{(Gas)} & \quad \text{product 2}
\end{align*}
\]

The reactant

\[
\begin{align*}
C + Si \rightarrow SiC \\
\text{(Solid)} & \quad \text{Tiny Droplets}
\end{align*}
\]

The products from 1 and 2

\[
\begin{align*}
3Ga_2O + 2CO_2 & \rightarrow 2Ga_2O_2 + 2C \\
\text{(Gas)} & \quad \text{SiC} & \quad \text{final product 4}
\end{align*}
\]

The final products Ga$_3$O$_2$ +C supersaturates when cooling takes place and solidify in the droplets of SiC(products 3). Nanodots of the metal oxide are then probably formed the same occurs for the indium oxide.
CONCLUSION

The metal oxides of Ga and In as nanostructure can be synthesized by UV laser ablation of graphite with each metal in air. The deposited plume on stainless steel substrates forms nanowires of gallium oxide and nanodots. The Nanodots in case of In oxide could develop in Nanowire. The solid carbon with the metal liquid melt existing in the ablated plume in contact with oxygen gas of air, suggest that the growth was nucleated through solid-liquid – gas mechanism. In the metal oxides of Ga and In as nanoparticles or dots can also be prepared by silica assisted thermal vaporization, of the mixture of solid carbon. The SiO$_2$ has an important roles in the catalytic growth of the metal oxide Nanoparticle. It provide Si which forms SiC tiny droplets. The final products in the gas phase. Ga$_2$O and Co$_2$ gases supersaturates in the SiC when cooling takes place providing Nanodots of the metal oxide. The metal oxide Nanostructures could effectively grow through vapor (gas)-liquid –solid growth mechanism.

REFERENCES

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