Preparation of GaN Nanostructures by Laser Ablation of Ga Metal

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- **GaN semiconductors in bulk are used as blue emitters and are already used in DVD systems and other microelectronic equipments on commercial scale.**

- **Two methods in which we applied laser ablation technique on gallium metal, under two different gas environment and catalysts**

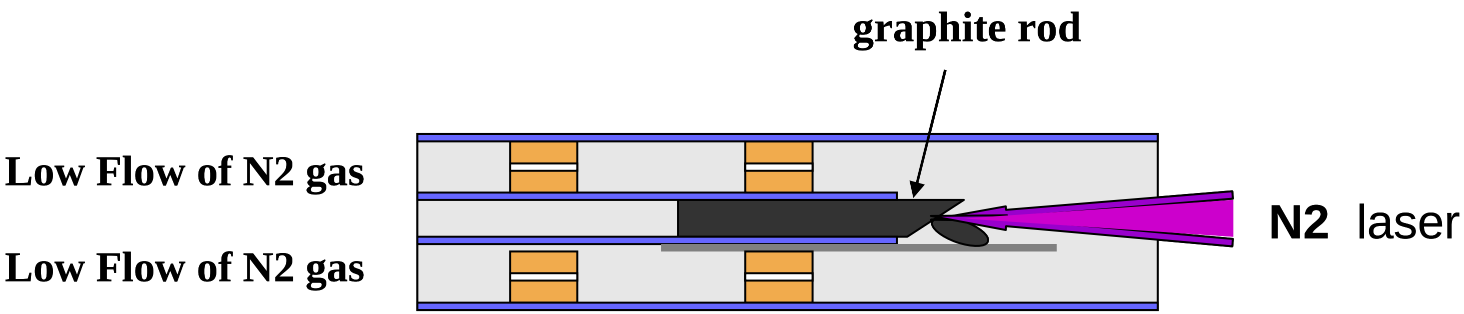
Experimental

- The laser ablation process was performed using N_2 laser with $\lambda=337 \pm 2$ nm, $\tau=15 \pm 1$ ns and energy per pulse of 15 ± 1 m J, for up to a total focused laser power 200-500 GW/cm^2 on the target.

- The plasma plumes produced during the two methods; ambient flowing N_2 gas only or with ammonia gas jet, were each allowed to deposit directly on cleaned stainless steel (Fe 91 %,Ni 4.5 %,Cr 4.5 %) substrates.

THE FIRST METHOD:

Gallium metal was introduced in the 10 mm long 3 mm diameter graphite rod. Carbon from graphite plays the role of the catalyst. N_2 gas flow was flushing the target set up during the ablation process to provide the N_2 needed as vapor and to prevent the formation of GaO, when in contact with air oxygen.



THE SECOND METHOD:

- **Gallium metal was mixed with $NaNo_2$ in 1:1 ratio by % weight and then introduced in the central pore of the graphite target.**

- **Ammonia gas jet was combined on the spot during laser irradiation using the low rate flow of NaOH solution dropping from a separating cone on solid NH_3Cl.**

- **The rate of ammonia gas jet flow on the target surface was adjusted to flow regularly during the experiment as shown in figure 1.**

- **The nitrogen gas flow through the target set up was also kept the same as in the first method.**

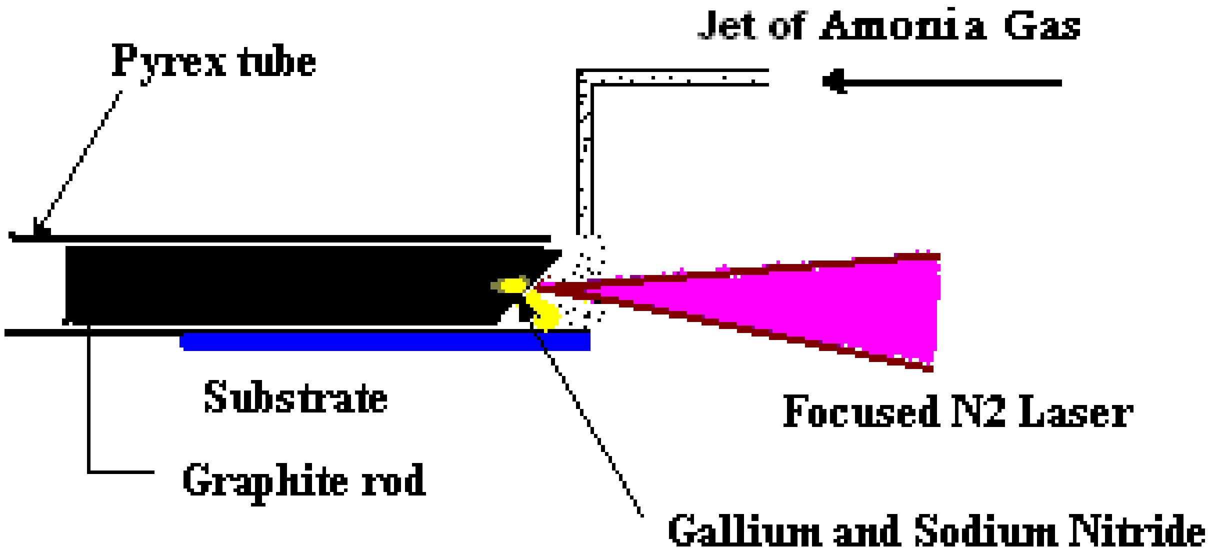


Figure 2. Experimental Set Up

RESULTS AND DISCUSSION

THE FIRST METHOD:

- A typical SEM image in which appears a central 1.45 µm average diameter GaN condensed droplet on the surface of the stainless steel substrate.

- The solidified droplet is surrounded by dots of average diameter 40 nm and short rods average diameter 80 nm scattered in a way that might suggest that they originated from the imposed laser ablated plume on the substrate surface (Fig. 2a).

- This micrograph has been obtained from the samples prepared by the first method for total accumulated laser power density of $\approx$ 500 GW/ Cm^2.

- **A high density of parallel grown nanowires can be recognized in figure having average length varying between 5 µm to 15 µm and average diameter of 300 nm and average density of 6.6 x 107 cm^{-2} by laser power density of 250 GW/ cm^2 (Fig. 2b)**

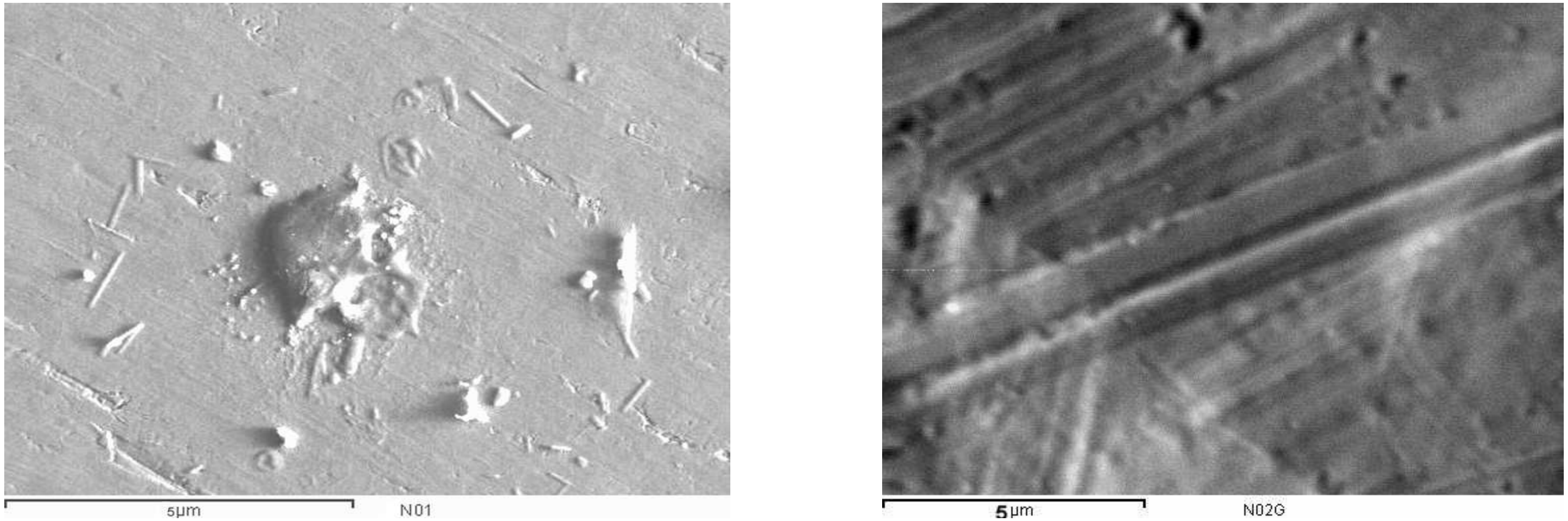


Figure 2: SEM image of GaN deposited on SS substrate, and prepared by first method

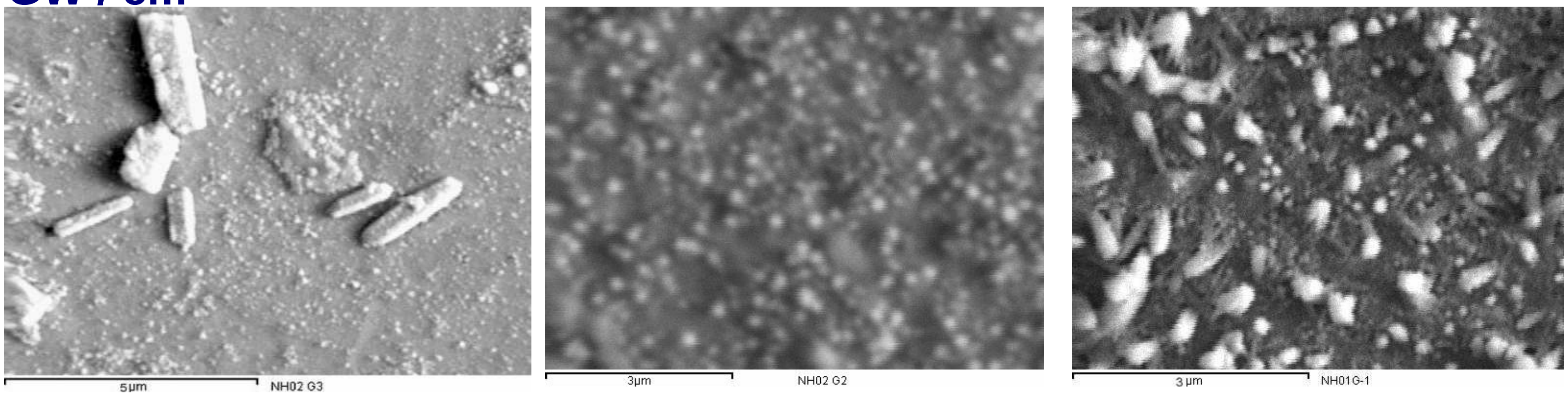
(a) GaN droplets ablated By laser power density of 500 GW/ cm^2

(b) GaN wires ablated by laser power density of 250 GW/ cm^2

THE SECOND METHOD

- Considering the GaN grown by the second method in pre sence of ammonia gas the growth of nanodots exceeded any other structure as clear from figure 3a.

- The morphology revealed the existence of both nanodots and nanowires, the average diameter of the dots 82 ± 20 nm, the rods have interesting wurzite crystal shapes and are confirmed to have the GaN structure from the measured XRD pattern. The average width of the top surface is 160 ± 40 nm and the average length is 1.77 ± 0.5 µm by laser power density of 500 GW / cm^2



(a) (b) (c)

Fig. 3: SEM image of GaN deposited on SS substrate, and prepared by second method (a) GaN nanodots and nanowires ablated by laser power density of 500 GW / cm2 (b) GaN nanodots and nanowires ablated by laser power density of 200 GW/ cm2, (c) GaN nanodots and nanowires ablated by laser power density of 400 GW/ cm2.

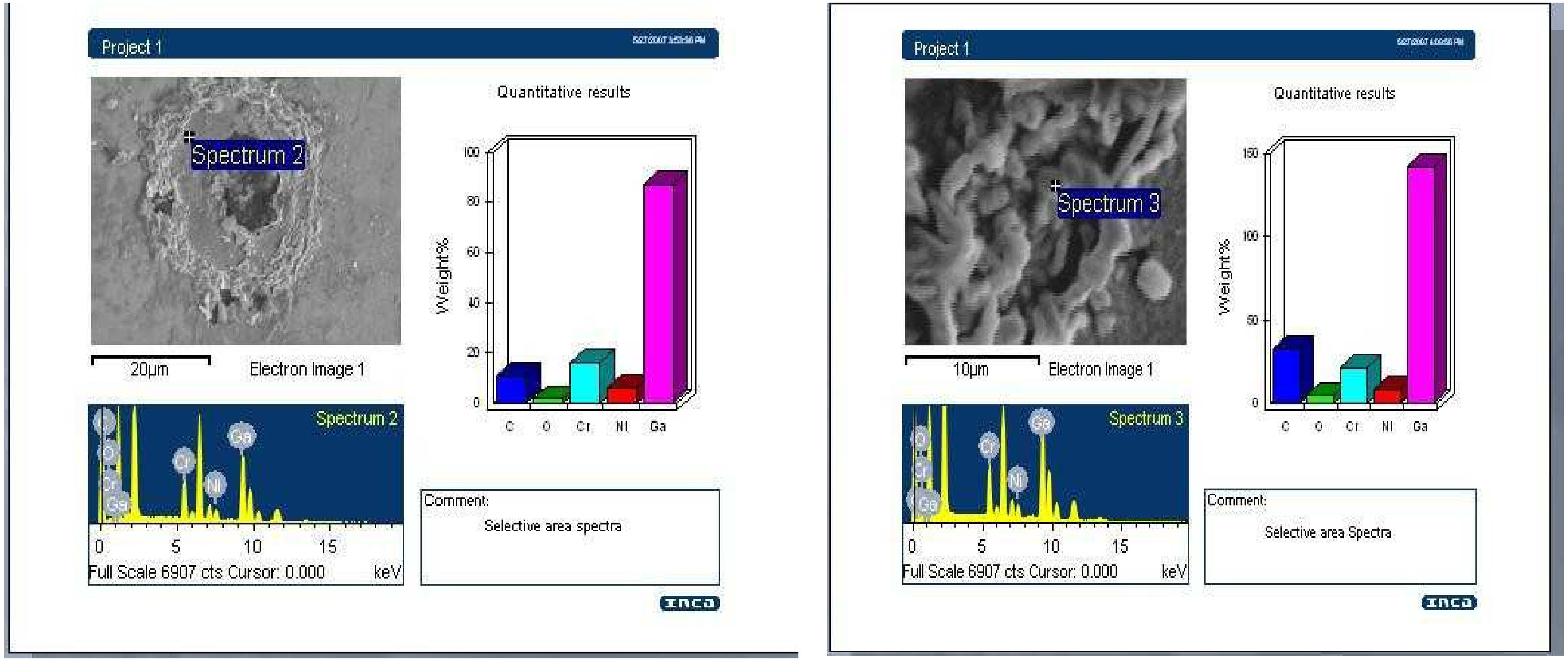
- **From Fig. 3b, the size of nanodots confirming the average diameter mentioned above and confirming the high density of the formation of the nanodots than the rods being 7.93 ±108 cm^{-2}.**

- **The micrograph is obtained by accumulated power 200 GW /cm^{2} laser power density in ablation of Ga metal mixture with Sodium Nitride $NaNO_2$ in presence of graphite and both N_2 and NH_3 gas, for the deposited plum.**

- **In the following micrograph, the GaN nanodots and nanowires are formed in scattered orientations under the same conditions but applying higher accumulated laser power density reaching up to 400 GW/ cm^{2}.**

- **Selective area SEM and EDX measurements are shown in Fig. 4. The spectrum shows the presence of GaN with peaks of Ga L_α and K_α lines.**

- **The unlabeled peaks correspond to the Fe Kα line from the substrate and other low intensity constituents**



(a) **(b)**

Fig. 4: Selective area spectra of SEM and EDX measurements. Both (a) and (b) are different areas of the same sample. The Lα (M→L**) and Kα** (L→K) **lines of Ga are clear, and Ka of N lines at low energy overlaps with C and O, and percentage by weight is 90% for (a) and 150% for (b).**

- **The reactants existing in the plume and deposited on the substrate**

$$\text{reactants} \quad Ga_{\text{liquid}} + C_{\text{solid}} + N_{2\text{gas}} \rightarrow GaN_{\text{solid}} + CN_{\text{gas}}$$

- **The CN gas can continuously be dissolved in the liquid Ga metal forming rolling droplets such as:**

$$\text{Proucts(1)} \quad CN_{\text{gas}} + Ga_{\text{liquid}} \rightarrow GaN_{\text{solid}} + C_{\text{solid}}$$

In case of the second method of growth of GaN the reactants in the ablated plume deposited on the substrate could be represented as forming tiny droplets of GaN.

$$\text{Reactants } 2Ga_{\text{liquid}} + NH_{3\text{gas}} + NaNO_{2\text{solid}} \rightarrow 2GaN_{\text{solid}} + NaOH_{\text{vapor}} + H_2O_{\text{vapor}}$$

- **While quite dense formations of droplets are formed during method 2. The absence of sodium lines in the EDX spectrum indicates that the formed sodium hydroxide vaporizes away from the substrate. The sodium nitride could be considered as a catalyst helping to provide more products of GaN as a clear from reaction 3.**

CONCLUSION

- One might state that GaN nanodots and nanorods were successfully sensitized through laser ablation of Ga metal as liquid phase (having low melting point) in the presence of nitrogen rich gases or solid catalysts.

- SEM micrographs showed morphology of 0D as well as 1D GaN nano-structures as well as GaN crystallites in wurzite state

CONCLUSION

• One may conclude that using Nile Blue as a dopant to Alq3, thin film layers could lead to an effective way to inject electrons and holes into an organic semicon-ductor device having suitable electrodes of well known ionization potential.

• Injection of charge carriers with high densities is expected to be feasible using lower applied voltages due to the decrease of the estimated energy gaps. Potential differences across the suggested design devices would be within the highest value of Eg - 3.6 V.

• The decrease of the cavity thickness would also help narrowing the emission spectra.

• It is worthwhile to carry out further studies of the suggested designs in order to create a p-n junction in situ forming emissive state of (Alq3)* which could be enhanced leading to high density photon emission.

Optical Properties of GaO Nanostructures

- **Nano meter size develops quantum one dimensional domain that provides special physical properties different from those of bulk materials.**

- **Ga_2O_3 has interesting optical and electrical properties, it has been prepared by carbothermal reduction from gallium oxide powder on silicon substrate.**

- **Growing Ga_2O_3 nanostructures using the silica assisted thermal process to investigate the effect of growth mechanism on the properties of the obtained nanostructures.**

Experimental

- The gallium metal and carbon powder were mixed thoroughly and homogenized in a porcelain morter for 1 hour.

- The mixture was then placed in a small porcelain crucible, topped by SiO_2 plate and covered by the crucible porcelain cover. It was then mounted into high temperature small compartment furnace.

- The temperature was raised to 950 ^{o}C during 45 minutes in low flow of atmospheric air. When the temperature reached 750 ^{o}C, the SiO_2 plates melted, at lower temperature than expected (SiO_2 Mp=1610 ^{o}C).

- The melt mixture of gallium metals + carbon powder in presence of silica melt was formed.

- The melts were allowed to cool down slowly reaching room temperature after approximately 4 hours. The grayish white crust on the crucible cover and walls, were then collected as fine powder and prepared for imaging by transmission electron microscopy and for spectral measurements.

- The samples of the crust powder to be spectroscopically examined were mixed in a test tube with micelle in DMF solution and homogenized in ultrasound basin.

- The emission spectrum was measured by Perkin Elmer LS55 applying excitation line at 330 nm. The products left overnight in the crucibles developed an extraordinary hard ingot, sticking to the crucible bottom.

- The ingots were crushed in a marble mortar and used for measuring the X-ray diffraction applying a Phillips X-ray diffractometer with Co K_α line

Results and discussion

The X-ray diffraction pattern as shown in Fig. 1 can be indexed in peak position to Ga_2O_3 although the relative intensities of the peaks are not consistent with that of bulk Ga_2O_3. Amorphous structure is proved to exist in addition to crystalline structure formation. Absence of metal gallium structure is noticed .

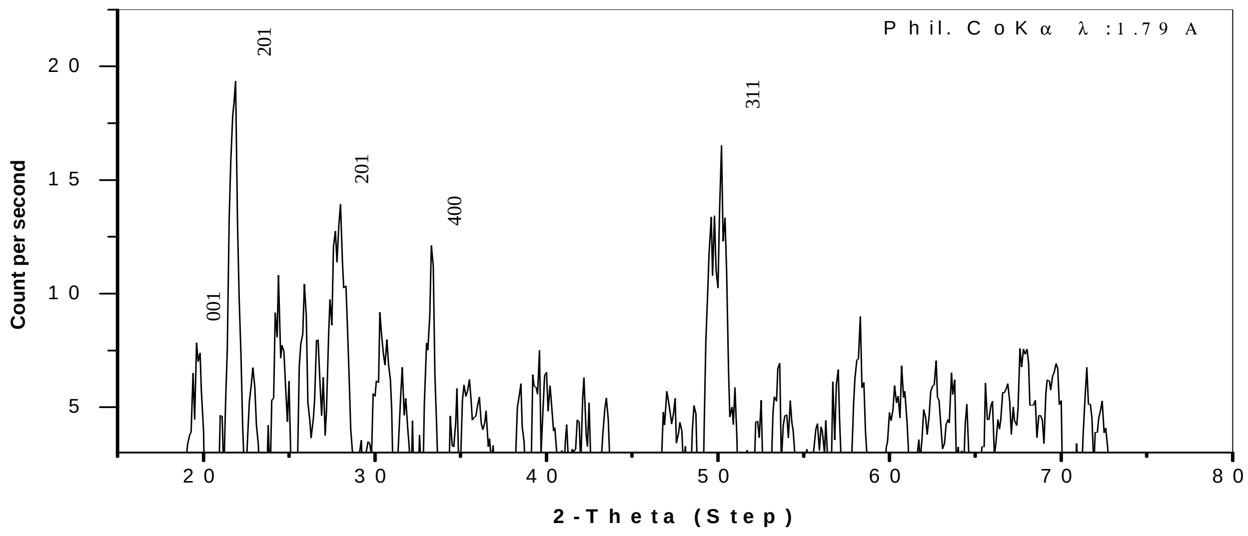


Fig. 1. X-ray diffreaction patterns of Ga_2O_3 nanodots

•The TEM image (Fig. 2) revealing the growth of only nanodots Ga_2O_3 of average diameter 200 ±2 nm and average density of 1.77x108 cm^{-2}

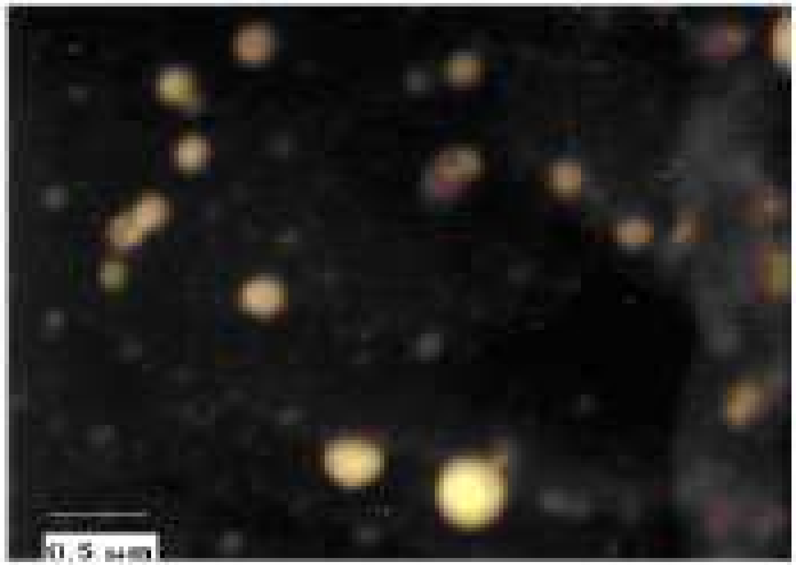


Fig. 2 TEM micrograph of Ga2O3 nanodots

•The absorption spectrum indicates that gallium oxide nanodots can absorb at 329.9 nm (3.76 eV) and 338.6 nm (3.67 eV) as shown in Figure 3.

•The emission spectrum proves that gallium oxide nanodots luminesces at 410.3 ± 3.28 nm (3.02 ± 0.03 eV) in the blue region. This is very near to the PL peak position 2.85 eV of β- Ga_2O_3 single crystal as shown in Fig.4.

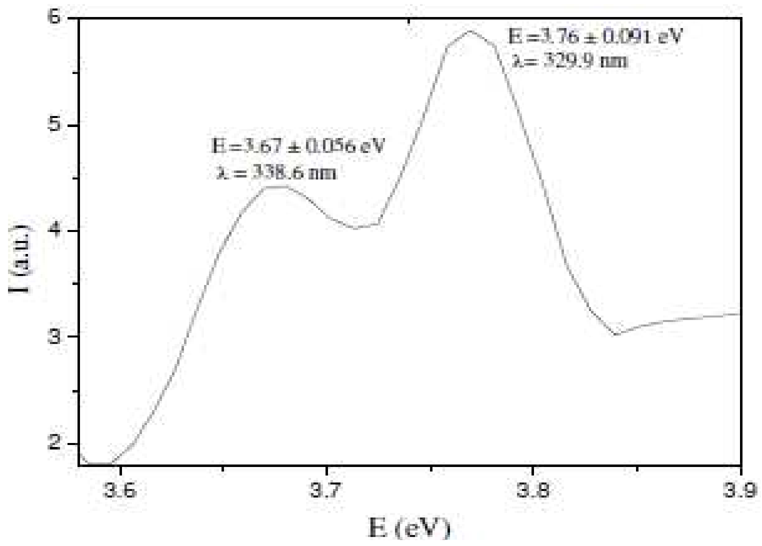


Fig. 3. The absorption spectrum of Ga2O3 suspension in DMF solution

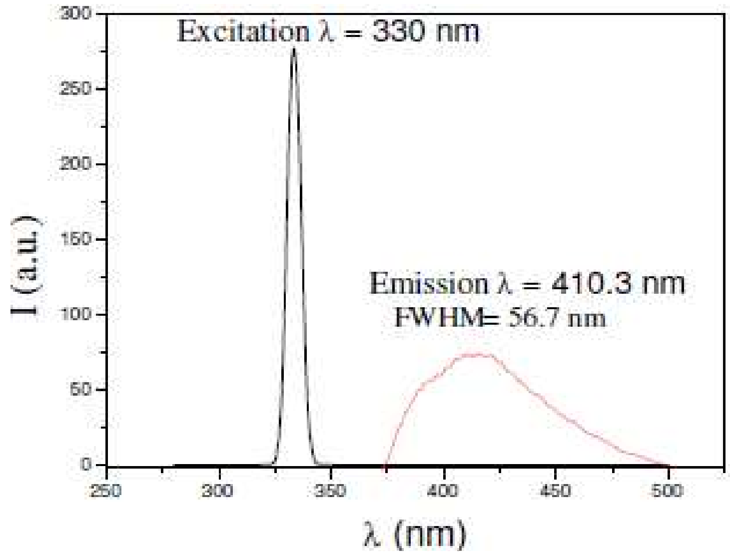


Fig. 4. Emission spectrum of Ga2O3 under excitation with λ= 330 nm

In order to investigate the growth mechanism one might easily consider that the original reactants to be:

1- Ga metal liquid at room temperature since it has a low melting point,

2- carbon solid in the graphite powder,

3- SiO_2 solid as the reaction started,
4- O_2 as a gas in the air flowing in the furnace.

- Then one may suggest that, during the process of heating in the oven the following reactions most probably occur according to the following processes:

REACTANTS	PRODUCTS
4 Ga (liquid) + C (solid) + 2 O_2 (gas)	2 Ga_2O (gas) + CO_2 (gas)
4 Ga (liquid) + SiO_2 (solid)	2 Ga_2O (gas) + Si (solid)

The expected reactions between the products in 1 and 2

$2Ga_2O$ + $2CO_2$ Products (1)	$2GaO_3$ + 2C
C + Si Products (2) &(3)	Si C tiny droplets

- The products of the reaction (3) super saturates when cooling takes place and solidify in the tiny droplets of SiC products of reaction (4).

• **Such tiny droplets of SiC enhance the further formation of the nanodots of Ga_2O_3.**

• **The image of two samples from the solid ingot which were removed from the crucible bottom when illumination by UV light and blue light respectively. It is clear that they luminece and emit visible light in agreement with the results of the emission spectra of Ga_2O_3**

Conclusions

- **Gallium oxide nanodots can be prepared by silica assisted thermal vaporization, of the mixture of metal, solid carbon and SiO2 as clear from the above reactions.**

- **The SiO2 has an important role in the catalytic growth of the metal oxide Nanoparticle. The SiC tiny droplets formed in reaction (4) enhances the formation of Ga2O3 during the super saturation stage.**

- **The final products in the gas phases Ga2O and Co2 gases supersaturate in the SiC tiny dots when cooling takes place providing Nanodots of the higher stage metal oxide Ga2O3. Accordingly the absence of nanowires could easily be explained**

Thank you