In Situ Catalytic Growth of GaN Nanowires

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Introduction

- Group III nitride large band gap semiconductors have attracted special interest for applications in optoelectronics devices[1] (Fig. 1)
- Lattice mismatches between the III nitrides multi-layer epitaxial structures and their substrates result in a high density of dislocations → reduction in device efficiency (Fig. 2)[2]
- One possible solution for this problem is to substitute semiconductor nanowires for epitaxial films. Nanowires often have stress-free surfaces and similar or even better electrical and optical properties[3] (Fig. 3)
- Vapor-liquid-solid (VLS) catalytic growth is one of the most common methods used to synthesize 1-D nanostructures[4] (Fig. 4)
- Although ex-situ catalytic growth of gallium nitride (GaN) nanowires has been achieved[5,6], there is not a complete understanding of the role of the catalyst, the growth mechanisms, and the interface dynamics involved in this process
- **This work presents dynamic observations of the nucleation and growth of GaN nanowires (GaNnws) which were formed by direct reaction of ammonia (NH_3) with gold (Au) – gallium (Ga) alloy droplets**

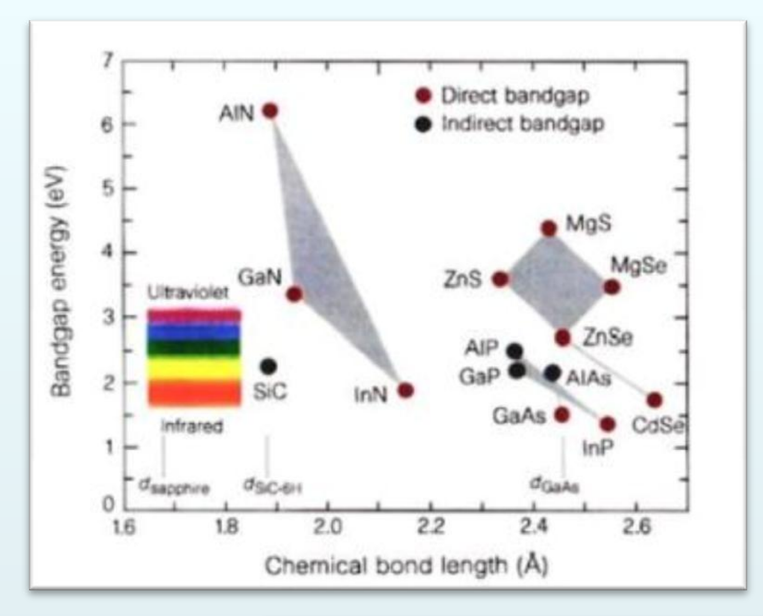

Fig. 1

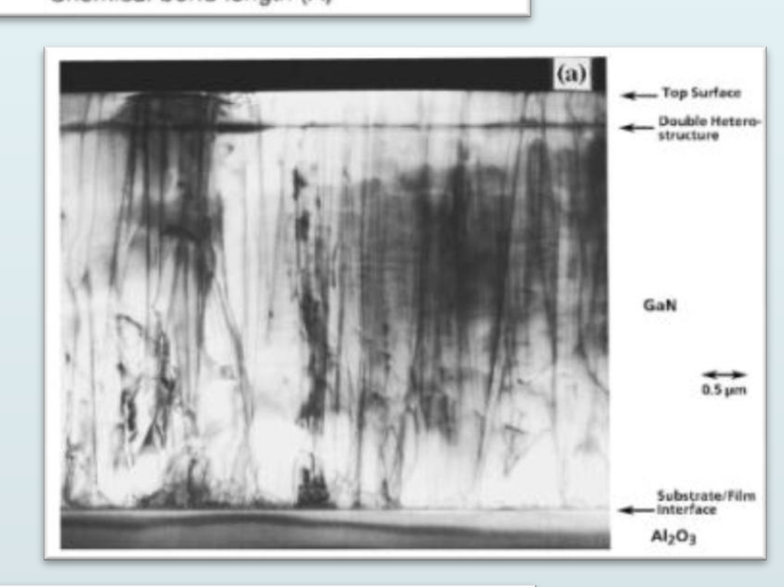

Fig. 2

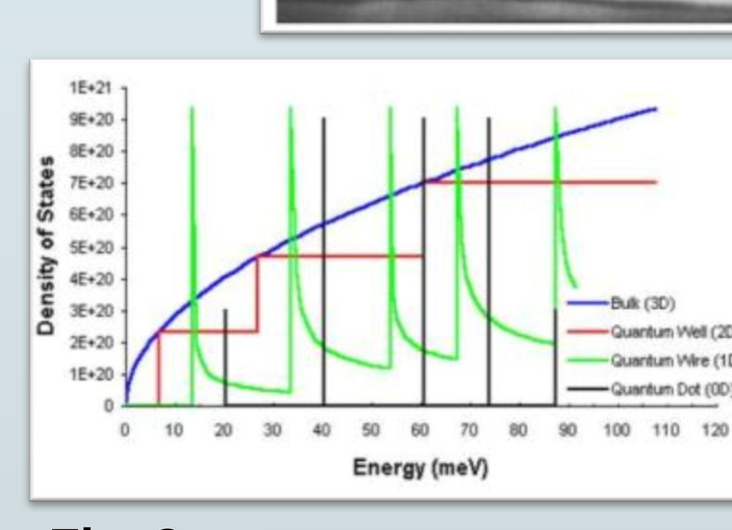

Fig. 3

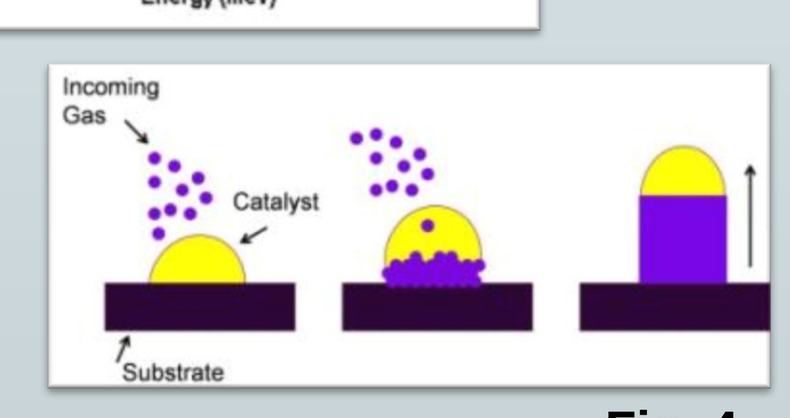

Fig. 4

Materials and Method

- For in situ observations we used a modified environmental scanning/transmission electron microscope (**E(S)TEM**), **Tecnai F20** (Fig. 5A), equipped with a differential pumping system (Fig. 5B) and a Gatan imaging filter[7]. P_{max} ~ 10mbar and specific information limit ~ 0.14nm
- Temperatures refer to thermocouple readings on the single tilt TEM holder mini furnace (Fig. 5C)
- Low and high magnification images and digital videos (15fps) were recorded using Gatan Orius 600SC camera
- Au particles were deposited onto SPI perforated SiOx membranes TEM ready grids (Fig. 5D) by sputtering
- JEOL 2010F TEM/STEM was used for ex-situ imaging and chemical analysis

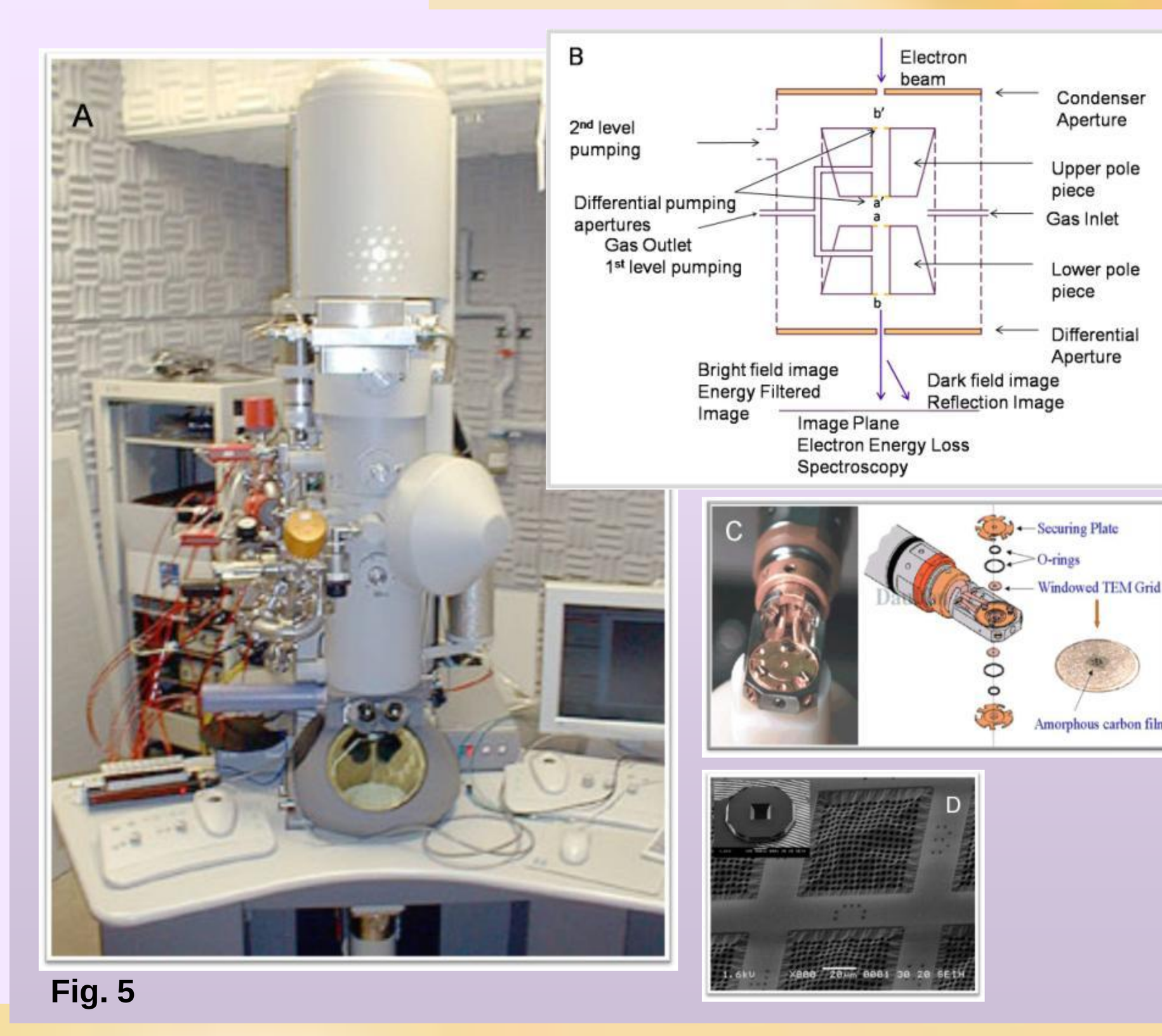

Fig. 5

Experimental procedure

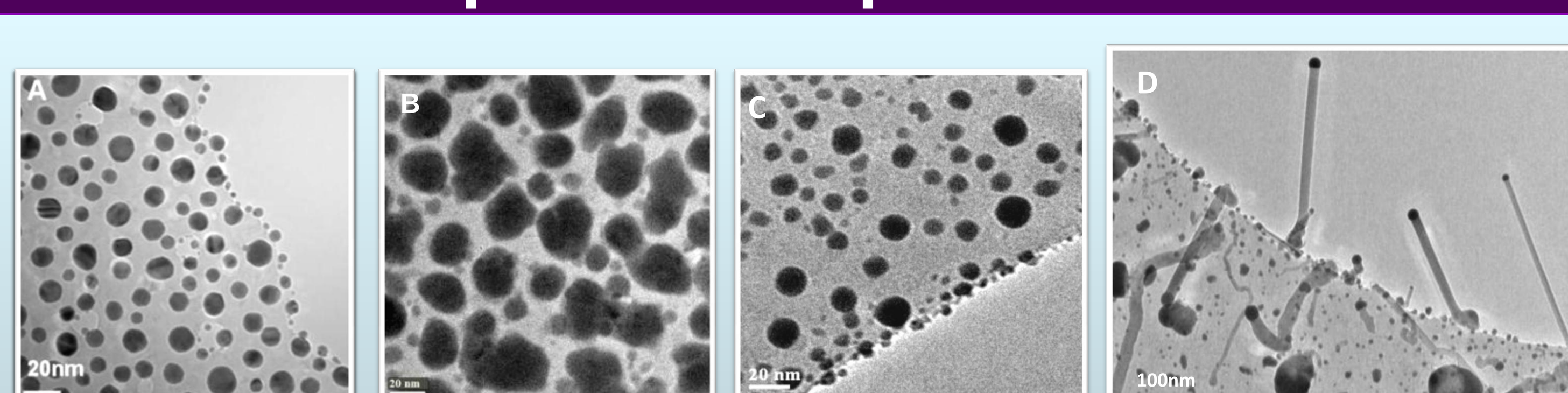

Fig. 6

Au particles with diameters between 5 and 10nm were deposited onto SiO_x membranes by sputtering.

The sample was introduced into the E(S)TEM column and heated up to 400C

60 mTorr of trimethylgallium (TMGa) was leaked into the column

The sample temperature was increased to 800C

In the process some evaporation of Ga occurred

Right after reaching a temperature of 800C, 40-70 mTorr of NH3 was leaked into the E(S)TEM column and GaNnws were grown

Results

- GaNnws grew at 800 ˚C after 40 mTorr of NH_3 was introduced
- Several nanowires with different length, diameter, and growth direction were observed over the whole substrate → no growth due to electron beam effect (Fig. 7)
- Figure 8 shows a sequence of frames extracted from digital video during nucleation and growth of GaNnws at 795 – 800 ˚C and 0.1 - 40 mTorr of NH_3
- Times and diameters of Au-Ga droplets are plotted and shown in Fig. 9. The liquid-solid interface forms after an incubation time, and the Au-Ga droplet sits on it with a wetting angle of ~150˚ (Fig. 7B)

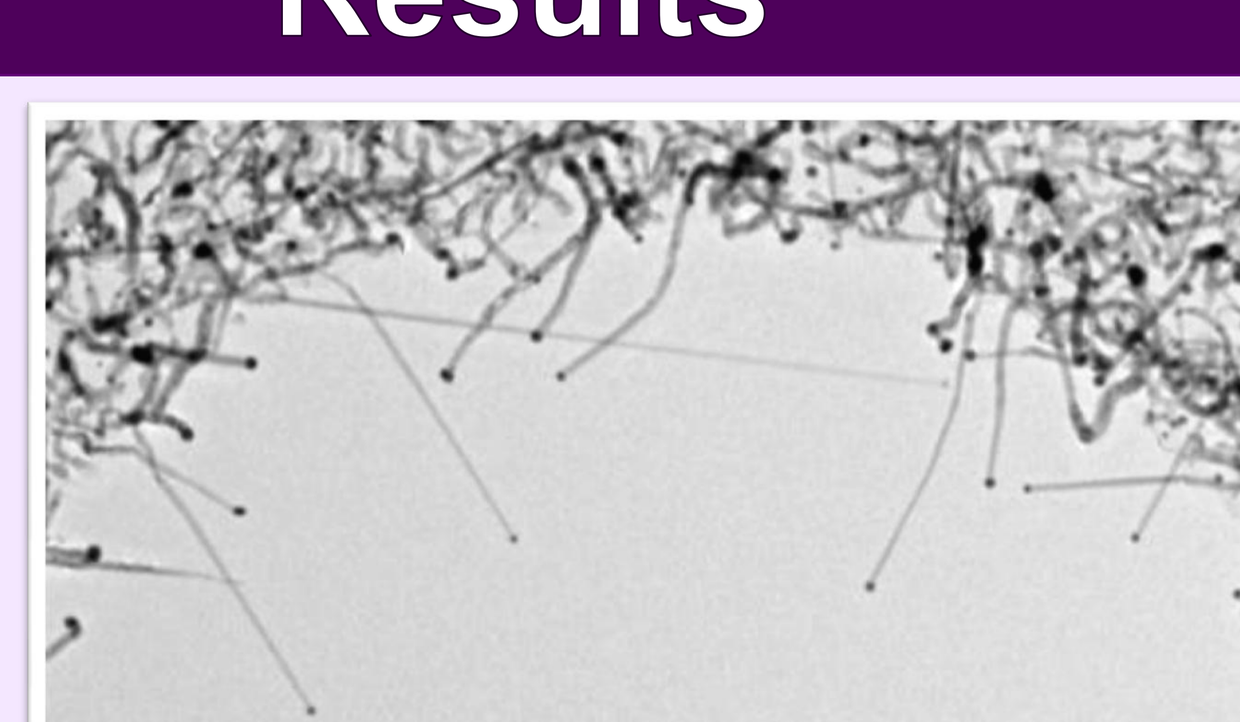

Fig. 7

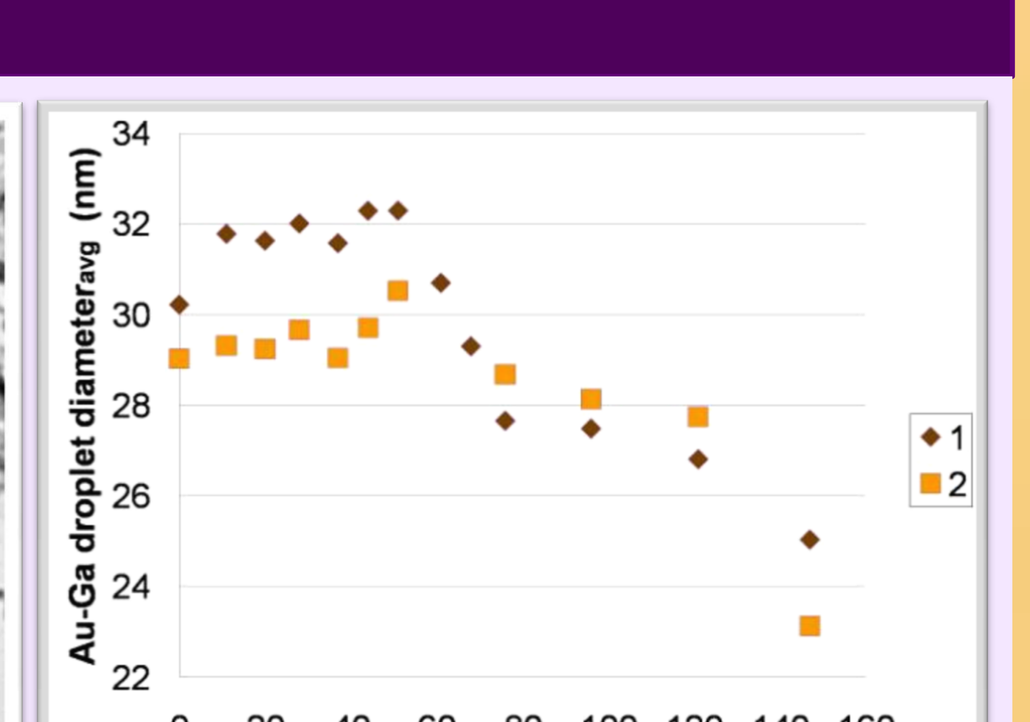

Fig. 9

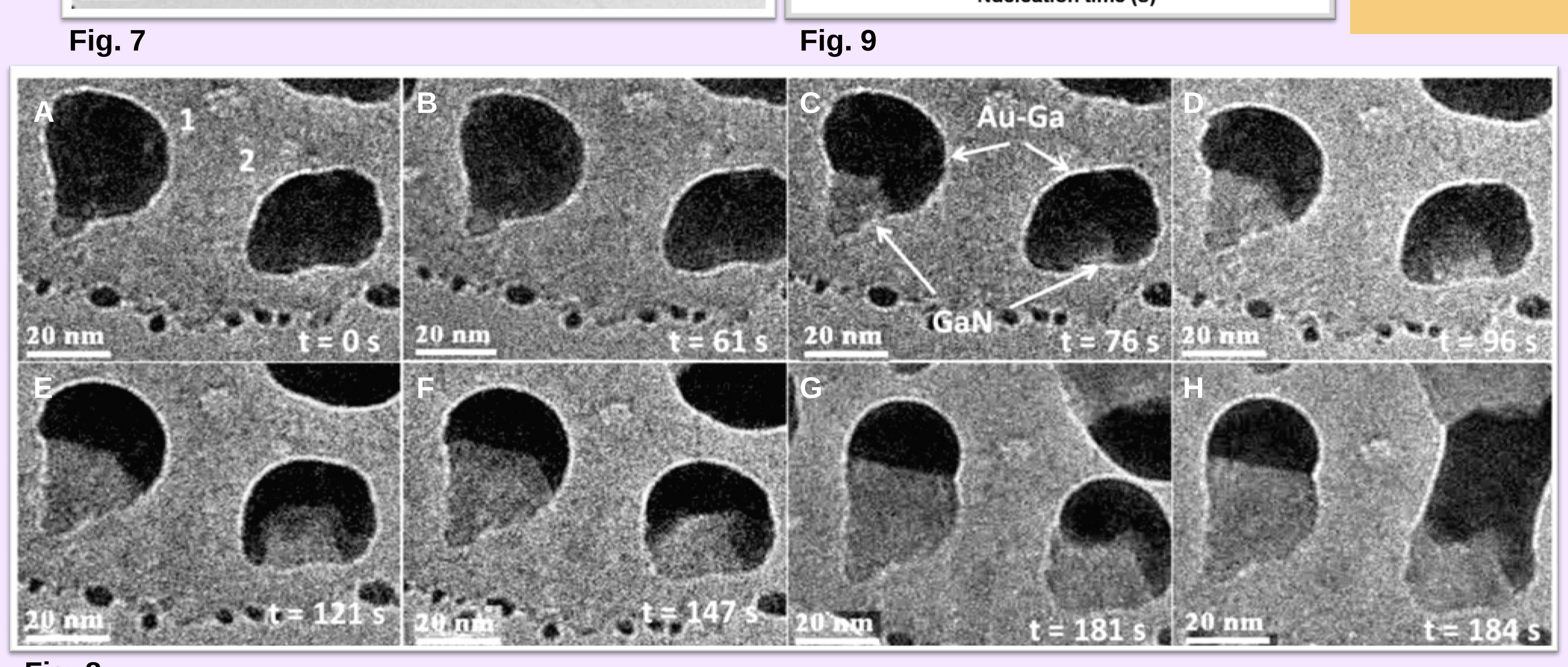

Fig. 8

Results

- Figure 10 shows a growth sequence under 70 mTorr of NH_3 and 810 ˚C. Growth rates were calculated to range between 3 and 10 nm/s depending on the diameter of the wire

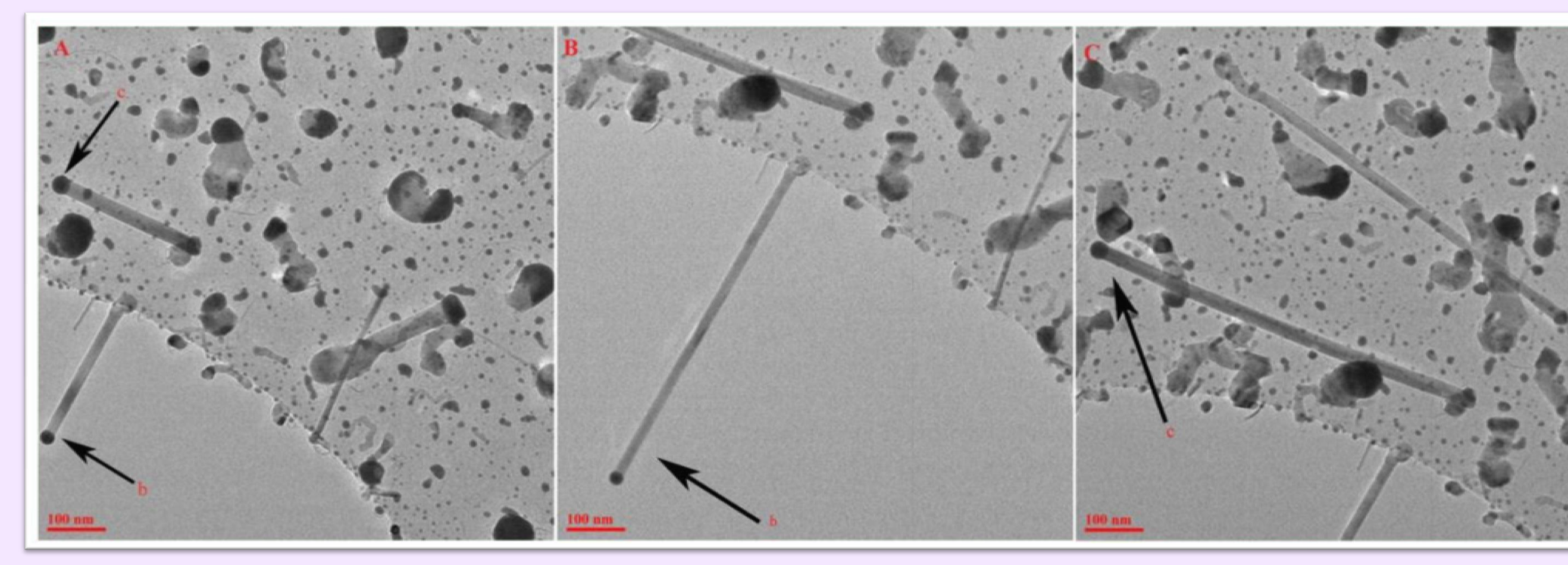

Fig. 10

- Analytical analysis on GaNnws confirms the presence of Ga and N. Fig. 11 shows an electron loss energy spectrum (EELS) performed after growth in the E(S)TEM and Fig. 12 shows an energy dispersive X-ray spectrum (EDS) with a respective STEM image.

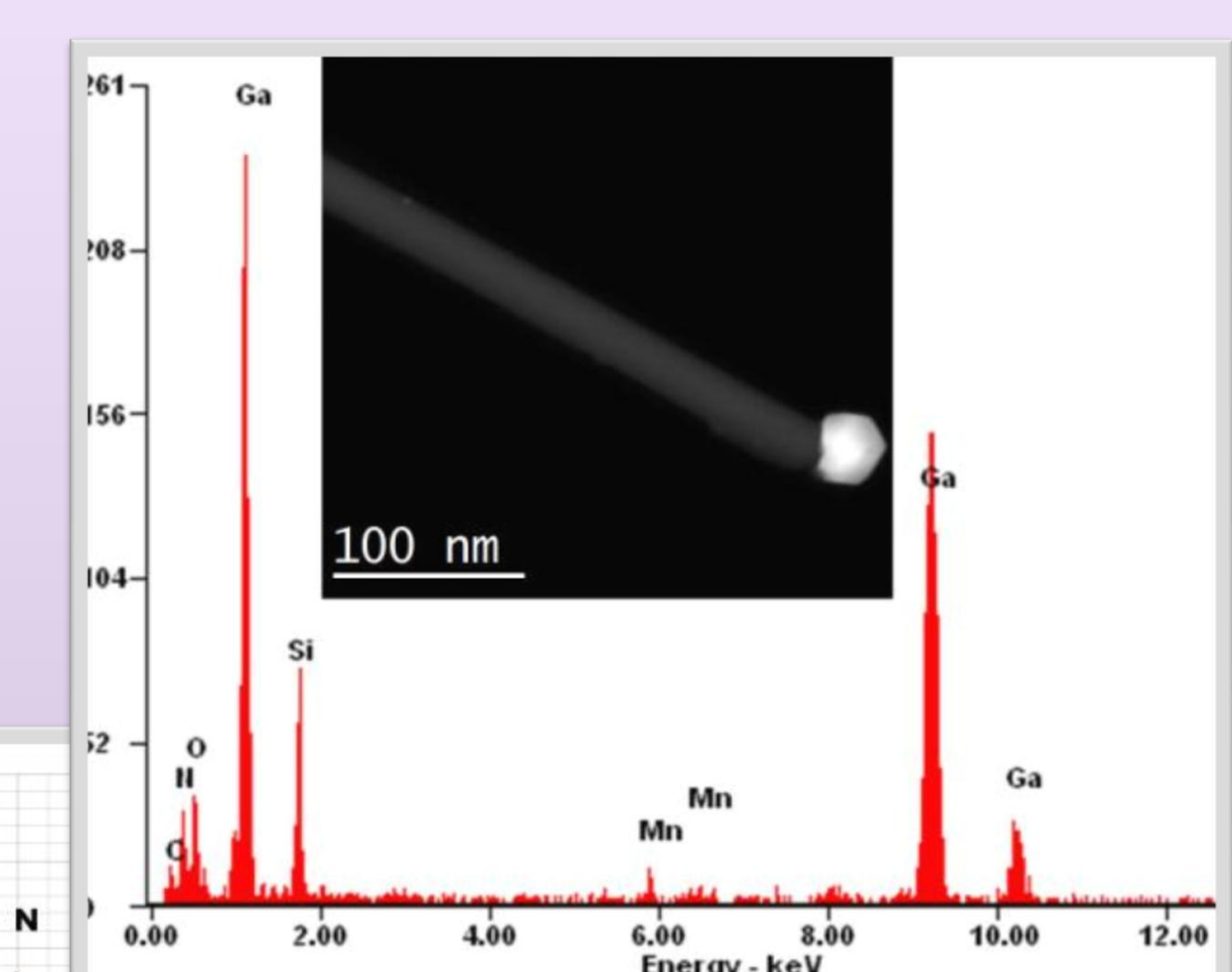

Fig. 12

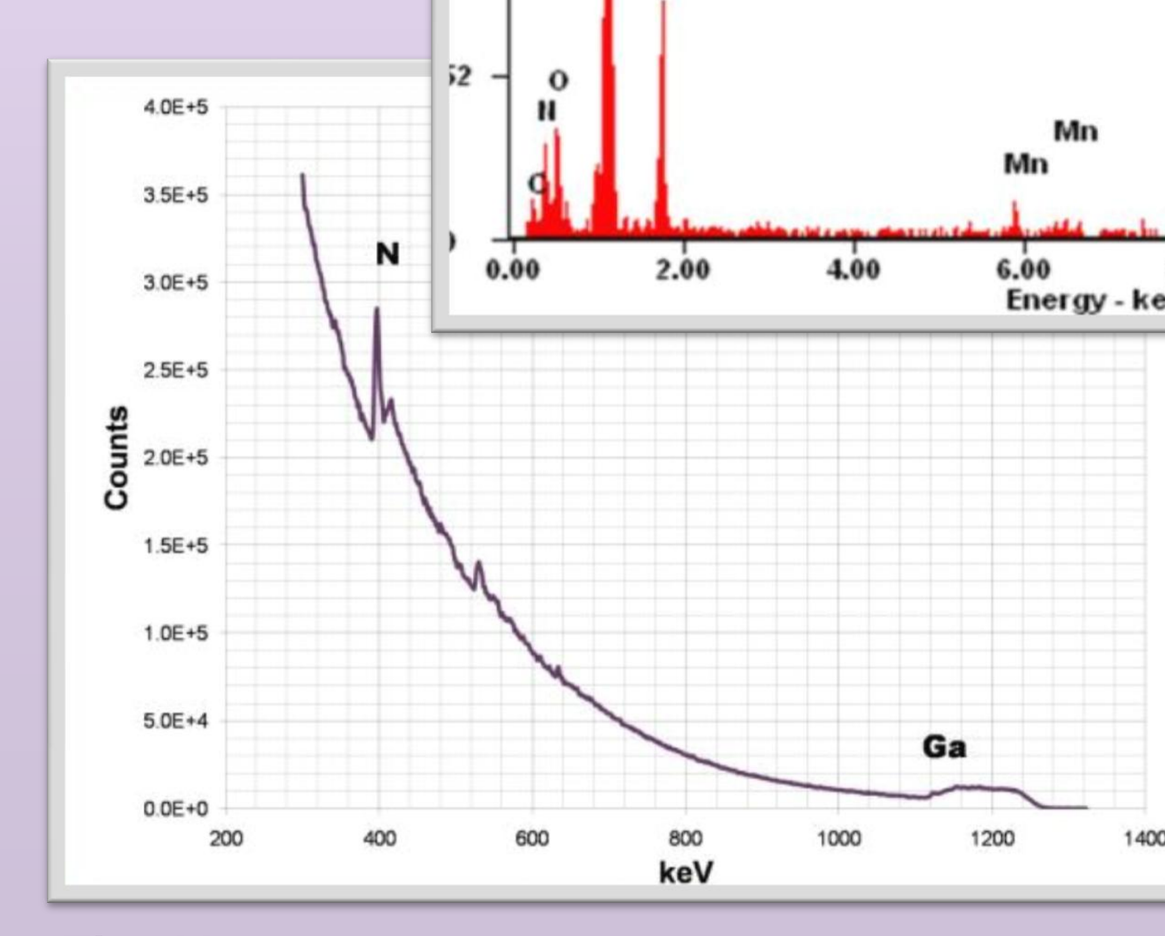

Fig. 11

- Lattice resolve HRTEM images (Fig. 13 A, B) show the wurzite GaN structure. Insets are the indexed FFT showing the plane zone axis [001] (A) and [100] (B)

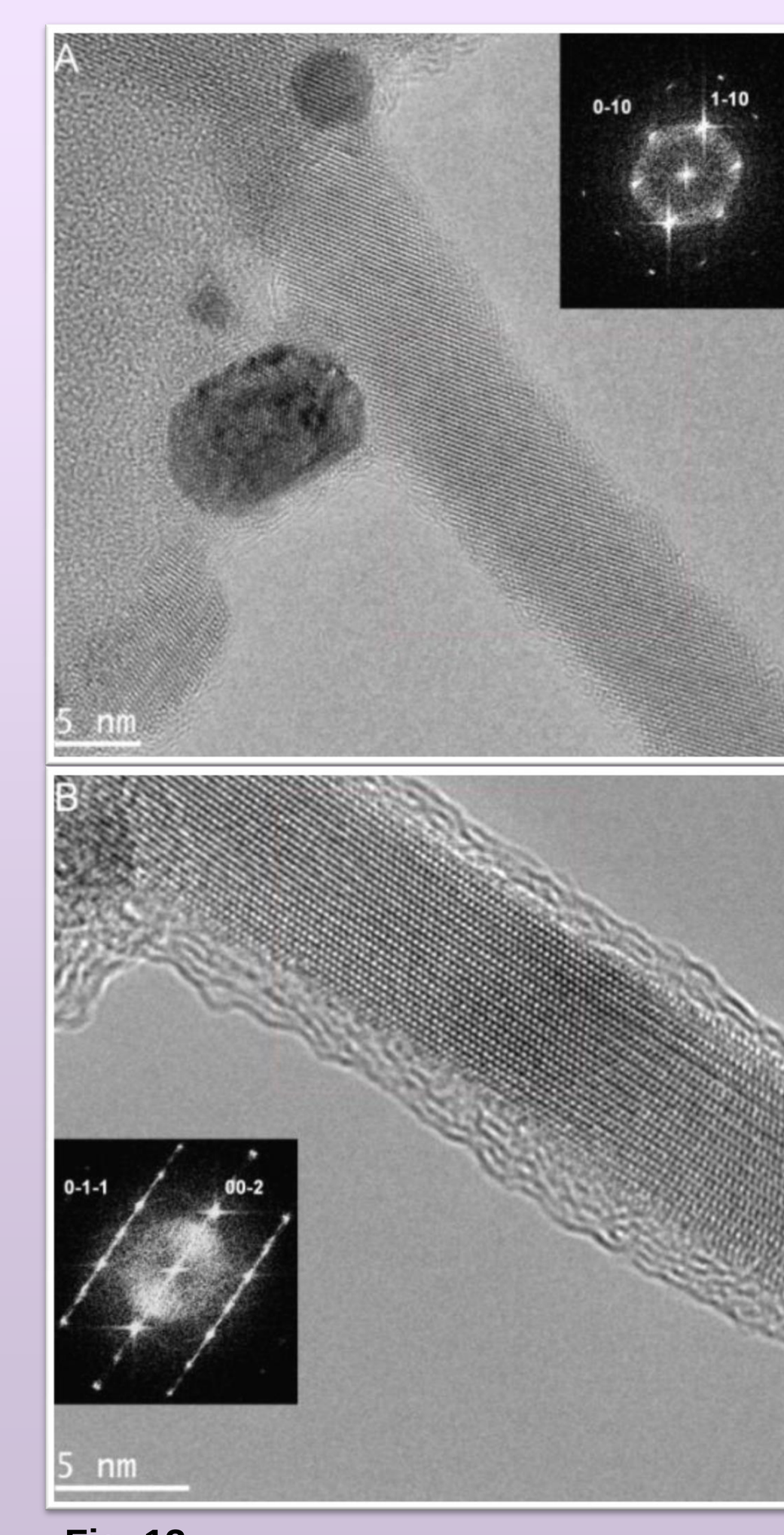

Fig. 13

Conclusions

- GaNnw nucleation occurs after an incubation time (Fig. 9), in which the diameter of Au-Ga alloy droplets increases due to N inclusion
- Once the droplet becomes supersaturated with N, the sol-liq interface appears and the Au-Ga droplet diameter decreases due to Ga consumption (Fig. 9) and diffusion of Au through the GaNnw
- Secondary nucleation is suppressed, so each catalyst particle has only one growth front. If two droplets find each other they undergo significant reshaping and redirect itself to a different direction of growth. There is no dissolution of GaN back into the catalytic droplet (Fig. 14)
- Direct observations revealed that after initial nucleation, growth continued a decreased rate when temperature and/or NH_3 pressure where lowered
- Diameters of the GaNnws are found to be dependent on the size of the Au-Ga alloy droplet (Fig. 15, 16) and GaNnw lengths are limited by the Au/Ga ratio in the droplet, temperature, and NH3 pressure

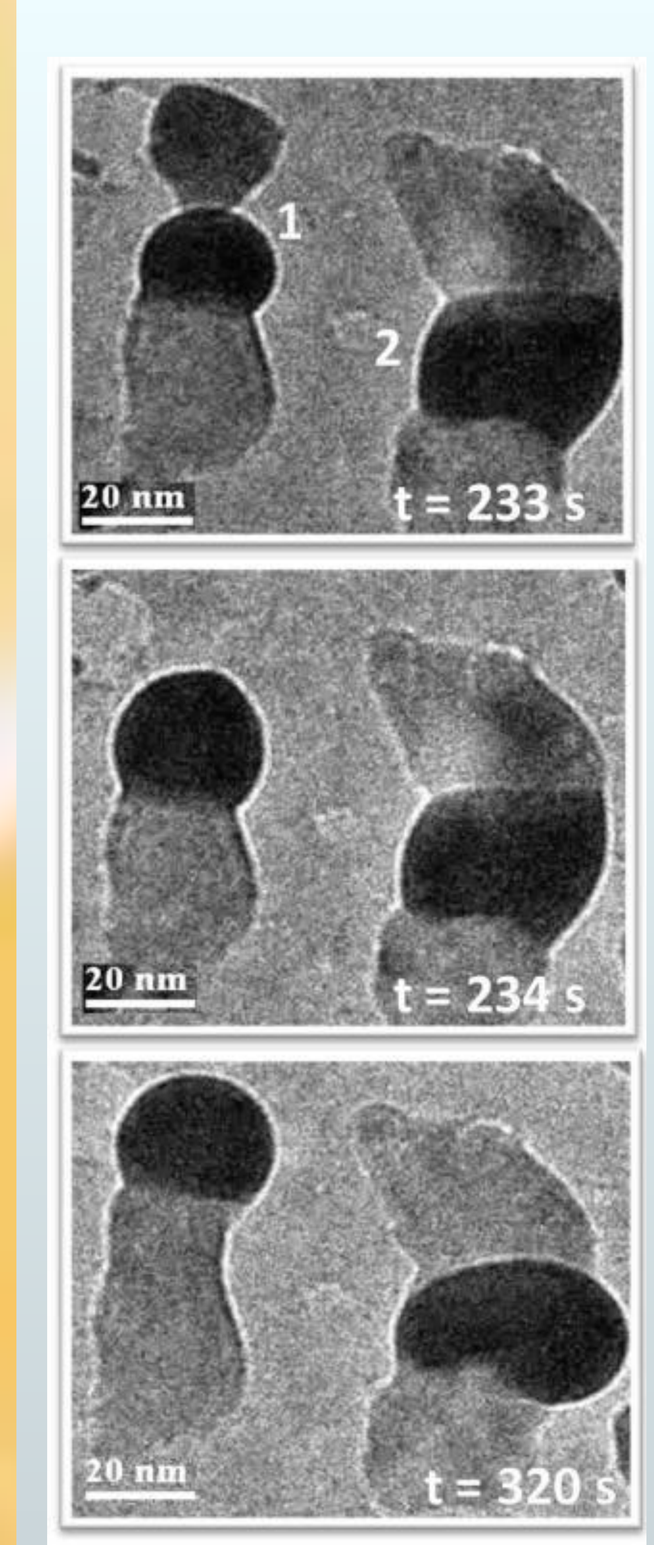

Fig. 14

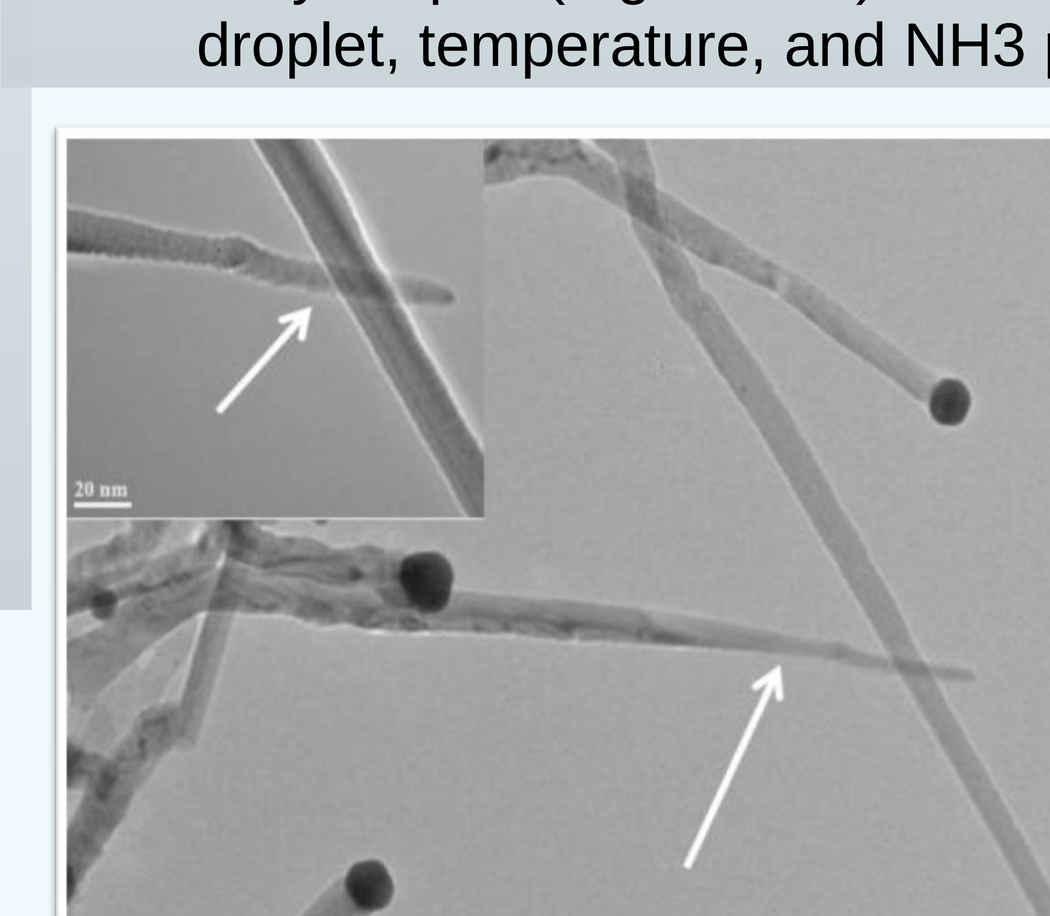

Fig. 15

- Two different cases for the VLS growth mechanism were observed:
  - i. Ga is consumed and droplet became Au-rich → droplet solidifies (Fig. 17) and growth stops (wire 2 and 3 in Fig. 16)
  - ii. Ga is consumed and Au diffuses through the GaNnw keeping the droplet in the liquid phase (wire 4 in Fig 15 and wire 1 in Fig. 16)

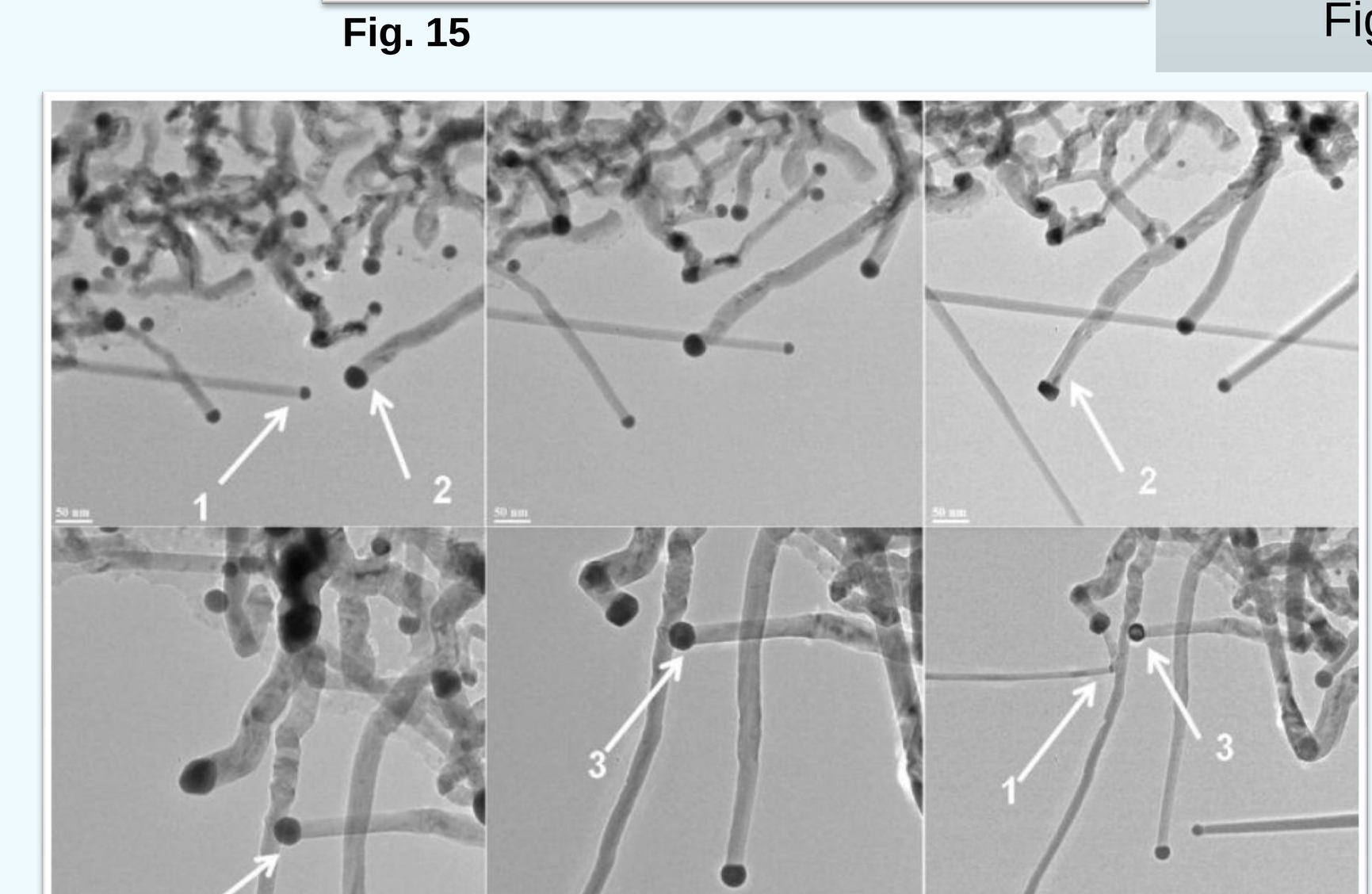

Fig. 16

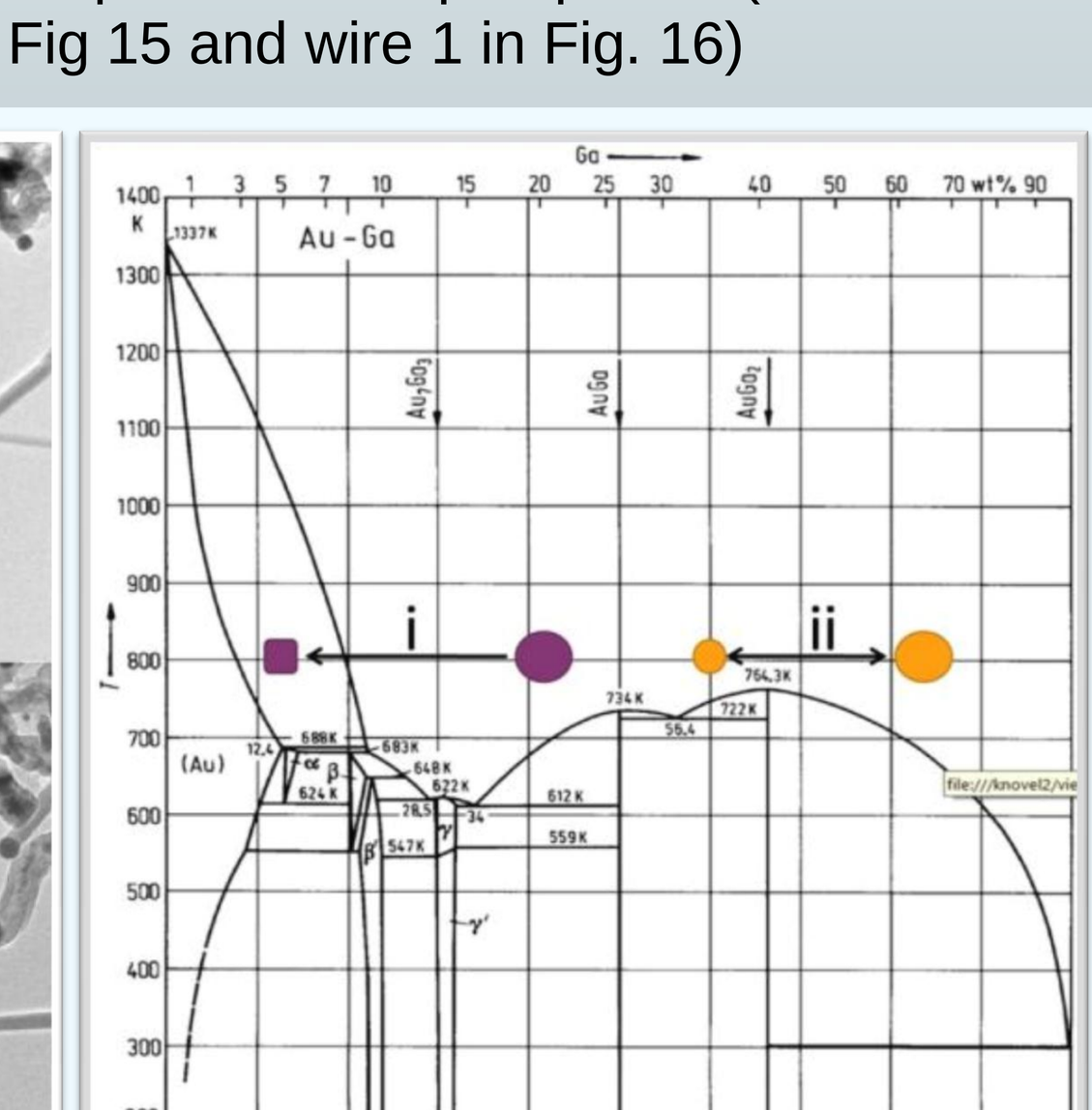

Fig. 17

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