Ge nanocrystal formation versus Ge diffusion in Ge/SiO_2 multilayers

Magdalena Lidia Ciurea,
Ana-Maria Lepadatu, Ionel Stavarache, Toma Stoica, Valentin Serban Teodorescu

Outline

- Motivation/advantages
- Ge/SiO_2 multilayer structures
  - Transmission electron microscopy
  - Raman spectroscopy
  - Photoluminescence
- $Ge\text{-}SiO_2$ films
  - Transmission electron microscopy
- Conclusions

Motivation/advantages

Aim: **to develop engineered materials** for application in

- non-volatile memory (NVM) devices:
  - MOS-like devices with Ge NCs (2D film) embedded in gate oxide at tunnelable distance in respect to Si.
- solar cells:
  - ensure light absorption over almost the complete sunlight spectrum 0.4 – 2 μm;
  - reduce the thermalization loss of energetic excitons.
- photodetectors

Motivation:

- tailored formation of Ge NCs for both NVM devices and photovoltaic applications;
- using multilayers/superlattices ➔ reliable tool to control Ge NCs size after segregation ➔ charge transport via direct tunneling;
- using thin films Ge ➔ NCs with different diameters ⇔ absorption in a larger wavelength range.

1. Ge/SiO_2 multilayer structures

Preparation of structures

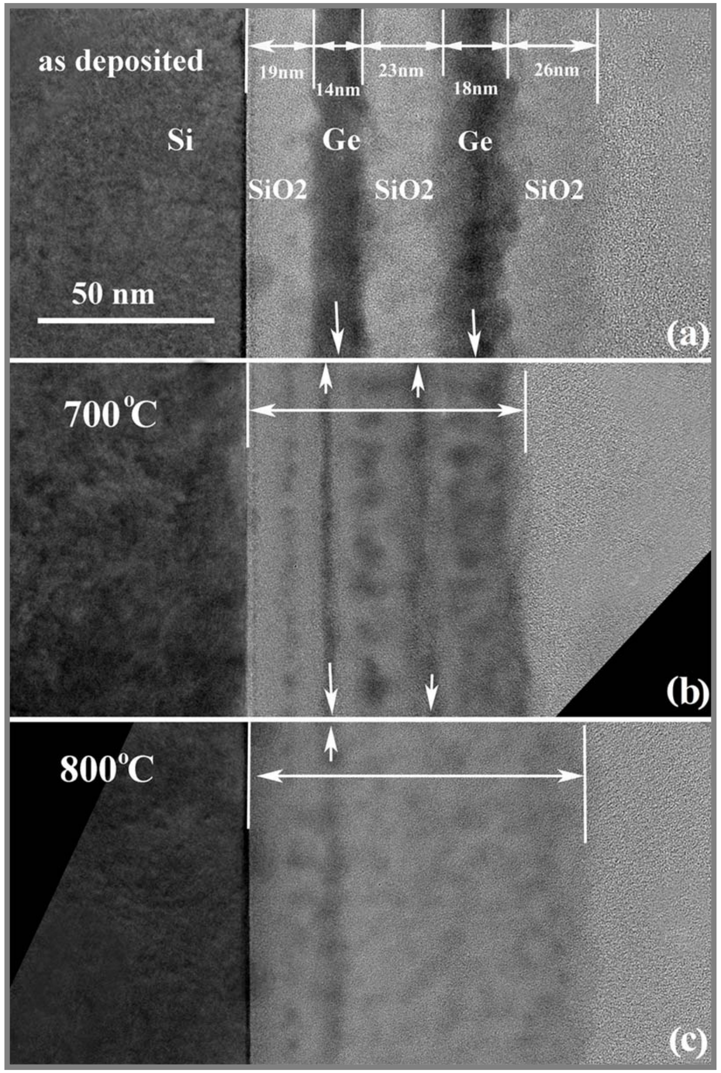
- (100) Si substrates **cleaned** using Piranha solution + dip in diluted HF

- **Preparation** by magnetron sputtering of $SiO_2/2x(Ge/SiO_2)/Si$ structures:
  - ⇨ SiO_2 layers : RF sputtering SiO_2 target at 100 W, 10 min;
  - ⇨ Ge layers : DC sputtering Ge target at 5 W, 25 min – first layer and 30 min - second layer.

- **Annealing** in N_2 at 650, 700 and 800 ^oC:
  - − conventional tube furnace 1 h
  - − RTA equipment 10 min

Transmission electron microscopy

Annealed structures in furnace



<u>As deposited structure:</u>

− thickness ~ 100 nm

<u>After annealing at 700 °C:</u>

− thickness ~ 85 nm;

− diffusion of Ge to the middle of SiO_2 layers ⇨ formation of Ge NPs.

<u>Annealing at 800 °C:</u>

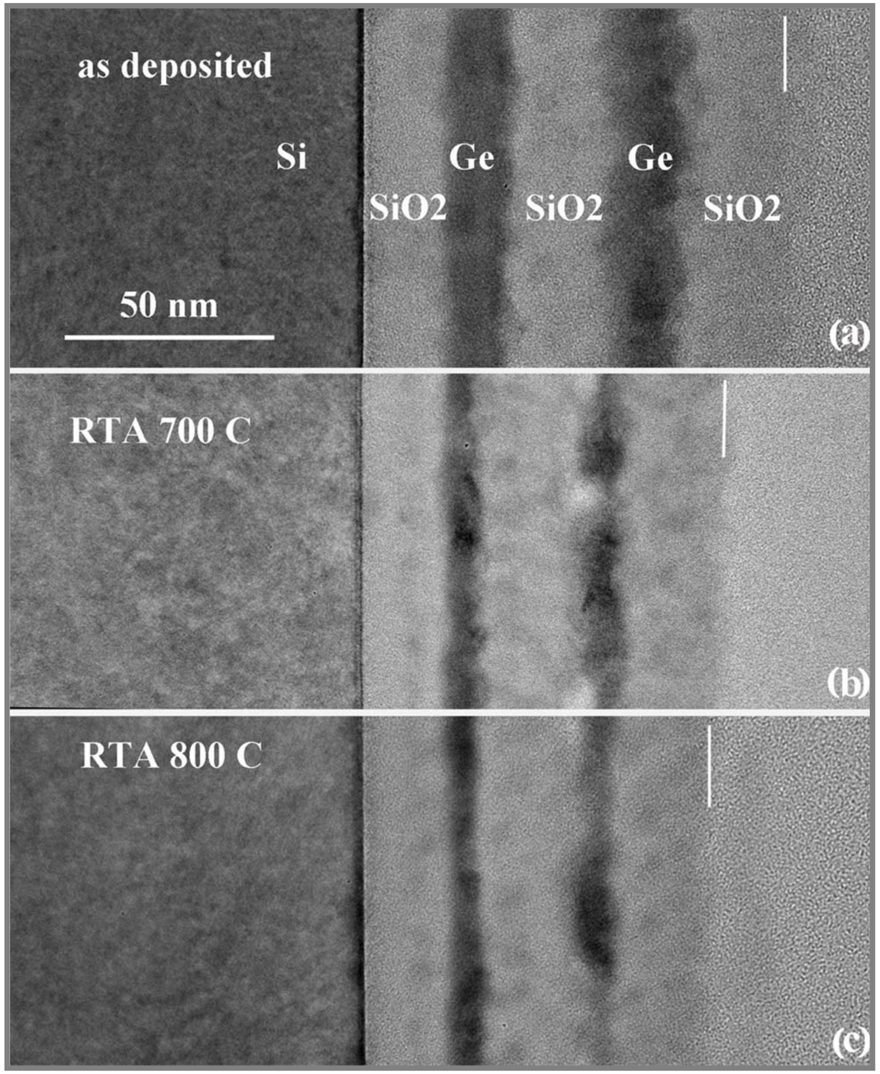
− thickness ~ 100 nm;

− diffusion of Ge more pronounced ⇨ upper Ge layer transformed in clusters distributed in oxide;

− Ge diffusion close to the structure surface > diffusion close to the substrate.

Lepadatu et al. *J Nanopart Res*, 2013

Annealed structures in RTA equipment



As deposited structure:

− thickness ~ 100 nm.

After annealing at 700 ^{o}C:

− thickness ~ 85 nm;

− diffusion of Ge into SiO_2 much reduced.

Annealing at 800 ^{o}C:

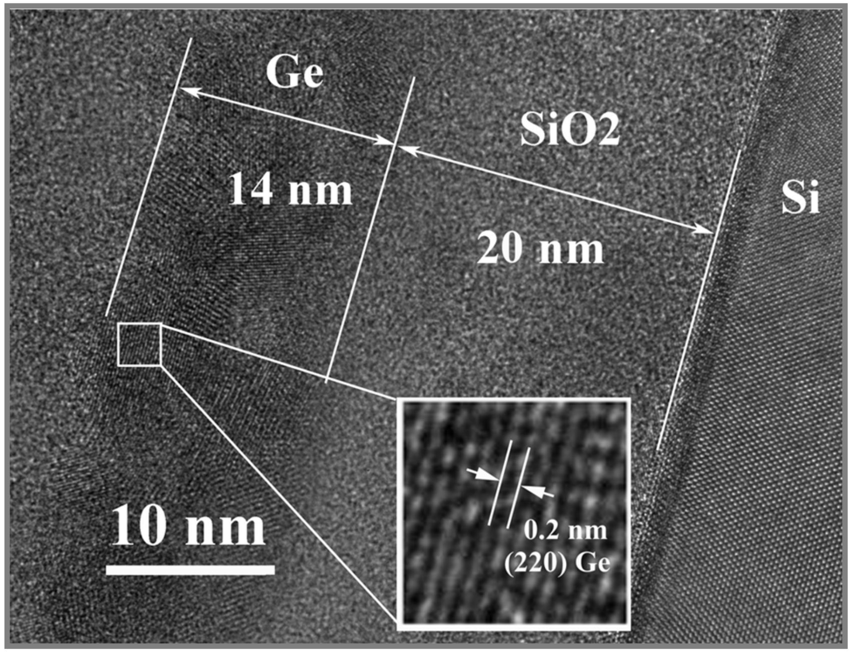
− thickness ~ 85 nm;

− diffusion of Ge into SiO_2 much reduced.

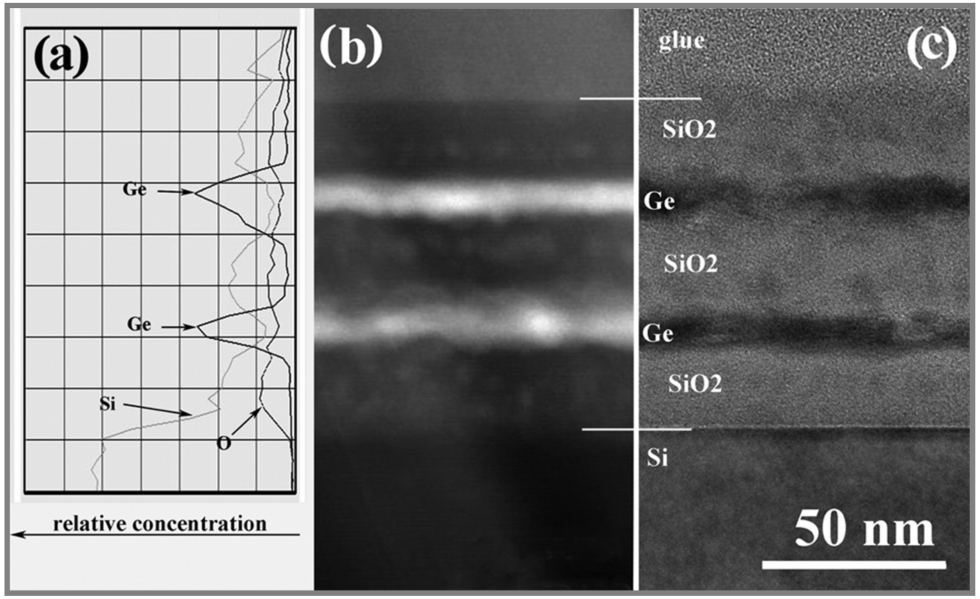
Annealed structures in RTA equipment

After annealing at 700 °C

HRTEM



EDX ADF-STEM HRTEM

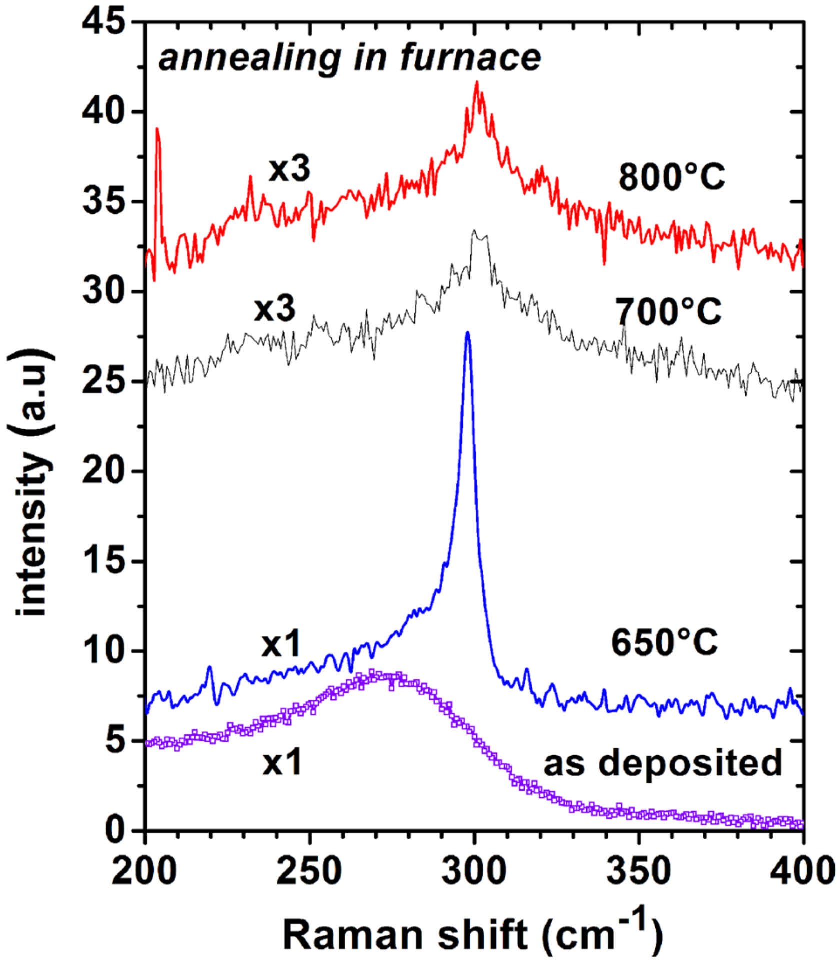


Ge cubic NCs: not uniformly distributed, random crystallographic orientation, 5 – 7 nm size.

Initial location of the (undiffused) Ge layers: maxima of Ge concentration & minimum O and Si concentrations ➔ crystallized Ge remains in the as deposited positions ➔ **Crystallization precedes the diffusion.**

Raman spectroscopy

Annealing in furnace



As deposited structure:

− amorphous Ge layers: broad asymmetric peak at about 274 cm^{-1}.

Annealing:

650 °C:

− Ge NCs peak ⇔ TO phonon mode;

− long tail (low energy) ⇔ amorphous Ge or/and Ge clusters in SiO_2.

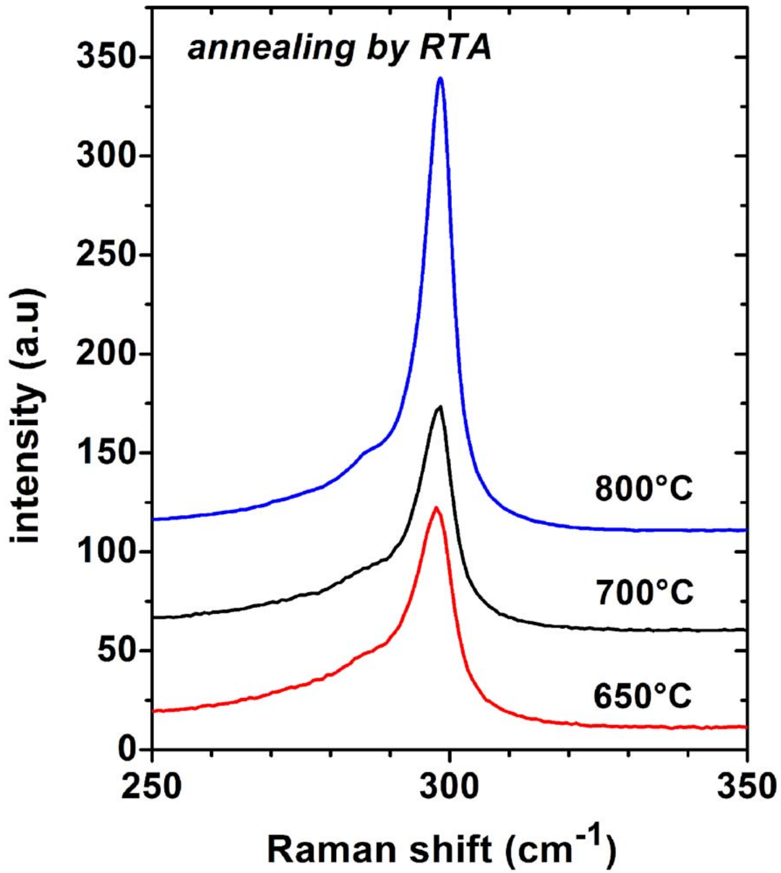
higher temperatures, 700 and 800 °C:

− strong diffusion and spreading of Ge in SiO_2 ⇨ Ge scattering mode drastically diminished; practically not detected (covered by the second order Raman scattering at 300 cm^{-1} in Si substrate);

− Ge loss by oxides.

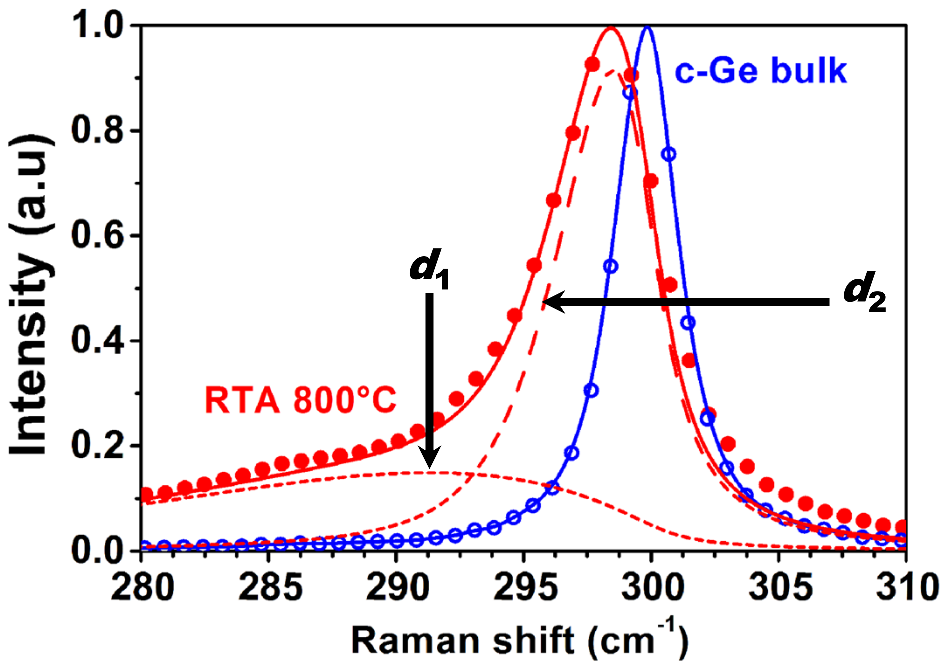
Rodríguez et al. *J Electron Mater* (2010); Pinto et al. *Nanoscale Res Lett* (2011); Lepadatu et al. *J Nanopart Res* (2013)

RTA annealing



- Ge NCs peak (297.7 – 298.4 cm^{-1}) red shifted than bulk c-Ge (299.8 cm^{-1}) ⇔ TO phonon mode and/or tensile strain;
- asymmetry and broadening of peak ⇔ phonon confinement in Ge NCs.

Phonon quantum confinement model (Richter model)



$$I(\omega) \propto \int_0^1 e^{-\frac{q^2 \times (d/a)^2}{4}} \times \frac{4\pi q^2}{(\omega - \omega(q))^2 + (\Gamma_c/2)^2} dq$$

$$\omega(q) = \sqrt{\omega_c^2 - \frac{43565 q^2}{q + 0.5766}}$$

$\vec{q} \neq 0$ - phonon wave vector (in $2\pi/a$ units)

a - Ge lattice constant (0.566 nm)

d - nanocrystal diameter

Γ_c - bulk c-Ge FWHM

$\omega(q)$ - phonon dispersion

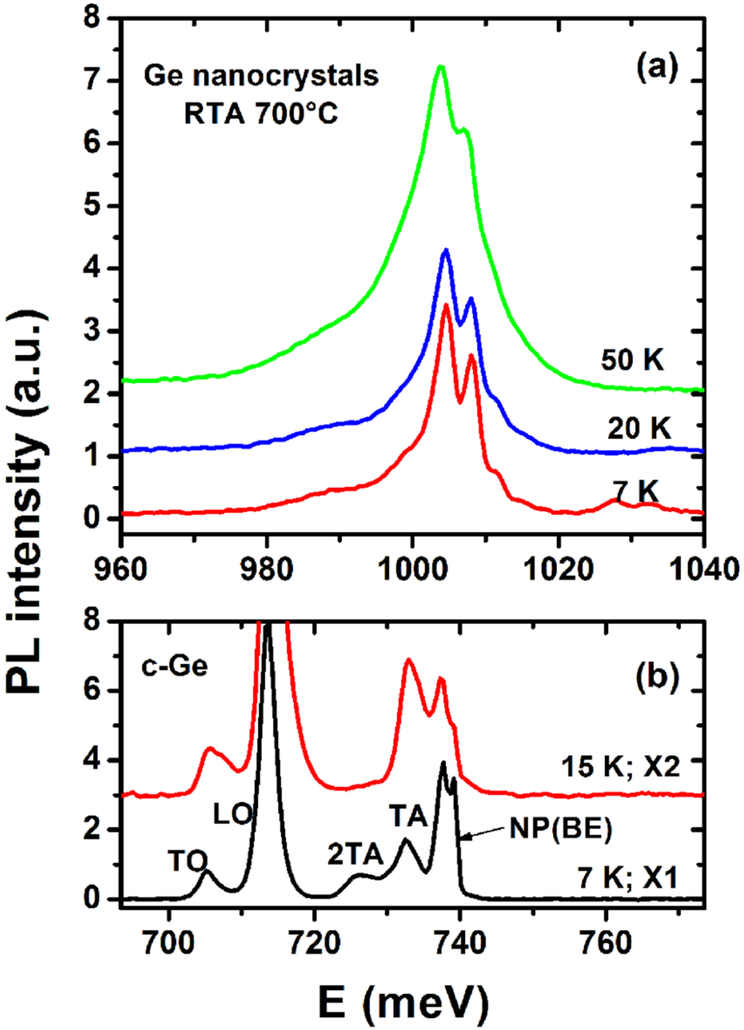
ω_c - position of bulk c-Ge peak

➔ **d_2 = 9.5 nm & d_1 = 3 nm**

❖ RTA at 650 °C => d_2 = 8 nm, at 700 °C => d_2 = 8.5 nm & d_1 = 3 nm

Richter et al. *Solid State Commun* (1981); Lepadatu et al. *J Nanopart Res* (2013)

Photoluminescence



- 2 main sharp peaks at 1004 and 1008 meV, FWHM = 2 meV;
- 2 additional broad peaks at 991 meV (FWHM = 20 meV) and 1004 meV (FWHM = 11 meV) – deconvolution;
- IR PL emission bands - recombination of excitons in two step transitions involving surface states located at the Ge nanocrystal surface.

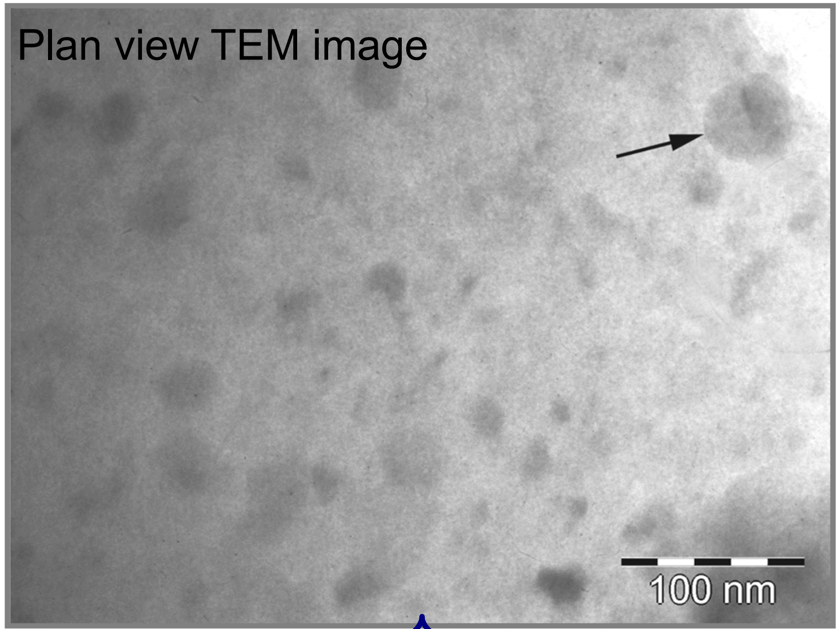
Lepadatu et al. *J Nanopart Res* (2013)

2. Ge-SiO_2 films

Preparation of films

- co-sputtering of Ge and SiO_2: 40 % Ge & 60 % SiO_2
- annealing in H_2, 2 atm.

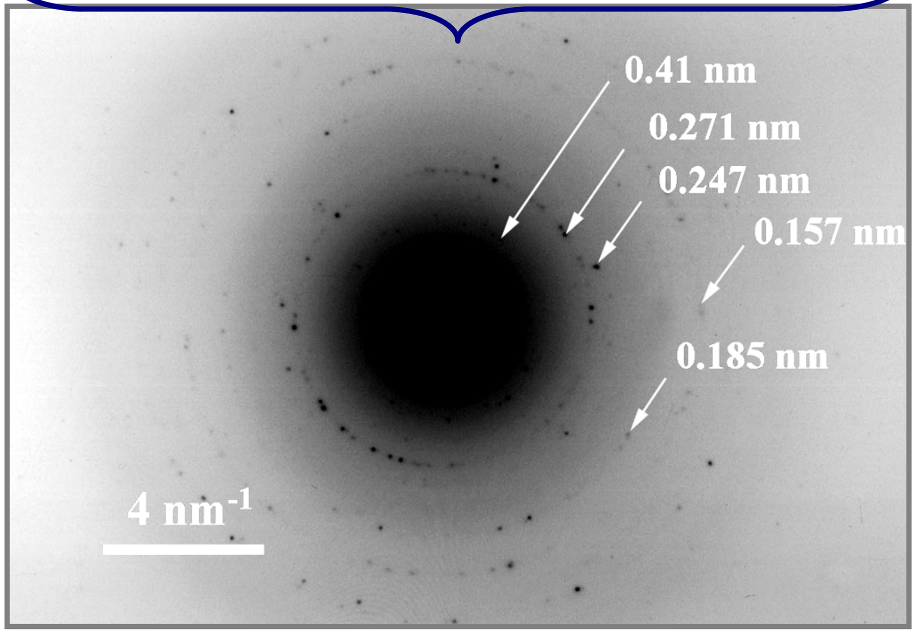
Transmission electron microscopy



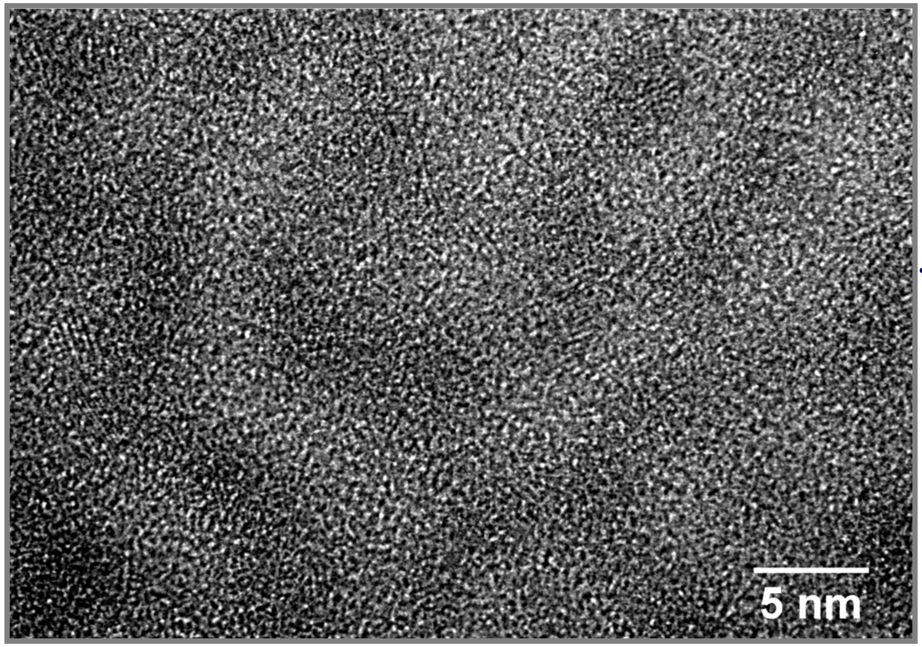
- **low density of big NPs**;
- **high density of small amorphous NPs**, **uniformly distributed**.

SAED pattern : Strong diffraction spots - clear ring (lattice distance: 0.271 nm).

➔ Main contribution - **tetragonal big NPs** (20 – 50 nm).



Stavarache et al. *J Nanopart Res* (2011)



HRTEM image of **dark contrast NPs network**:

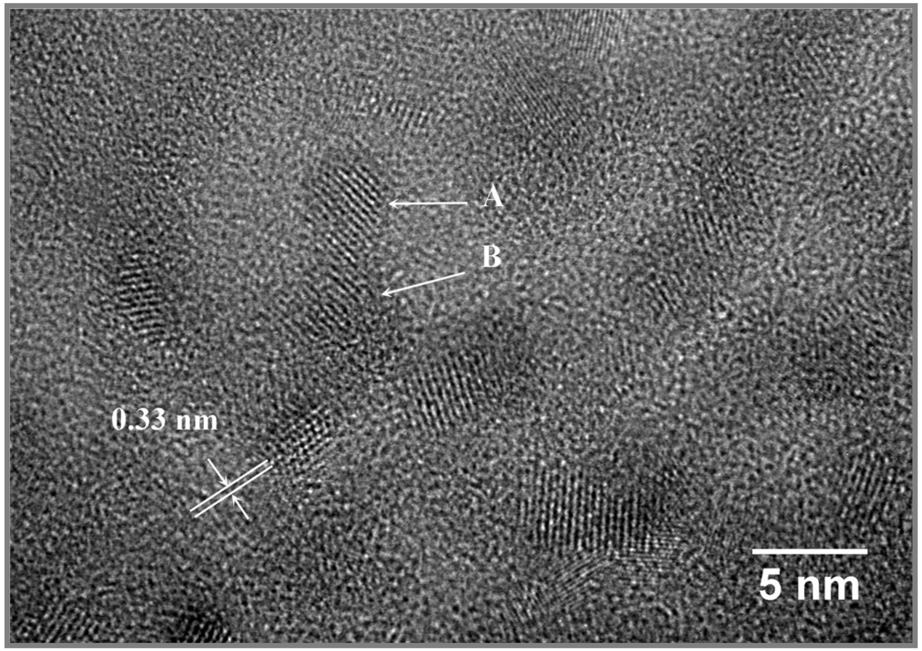
⇒ **Amorphous globe-shaped NPs:**

- **5 nm average size;**
- **separation - similar distance or less.**

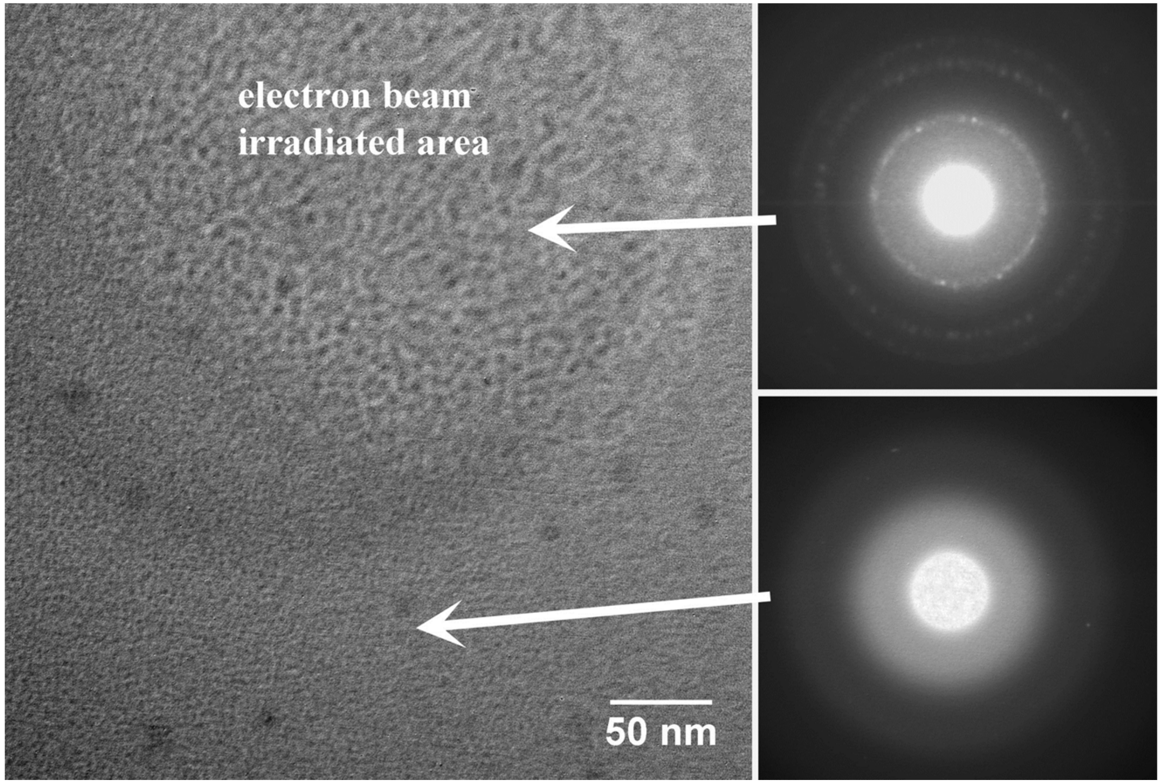
Crystallization of dark contrast NPs **under the electron irradiation** during the HRTEM observations:

⇒ **Ge nanocrystallites with cubic structure.**

⇒ NPs A and B show the same crystalline orientation ⇨ **Initial amorphous Ge NPs were connected.**



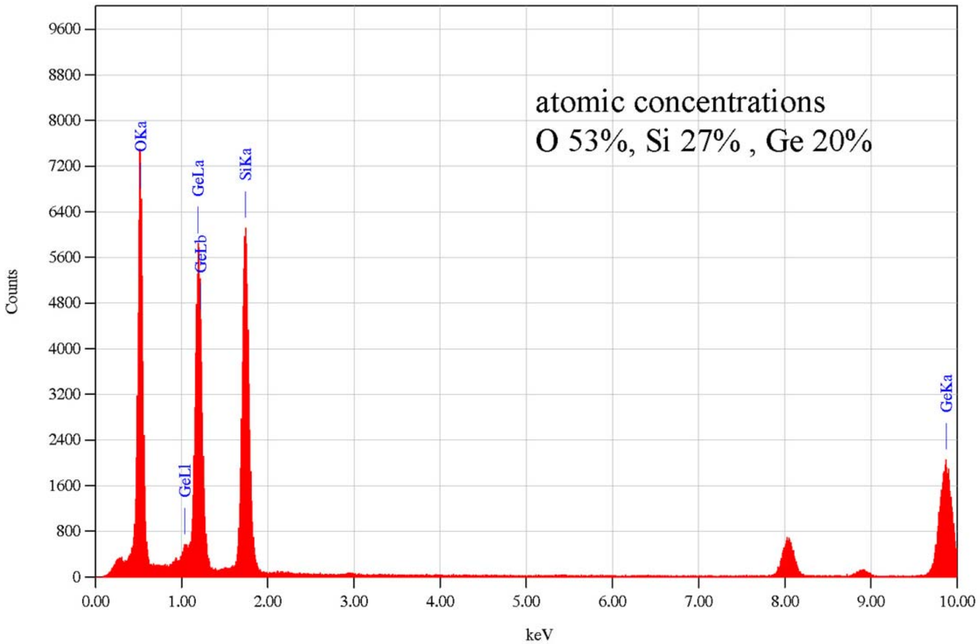
Stavarache et al. *J Nanopart Res* (2012)



Irradiated area after several minutes of HRTEM observation:

⇒ **Crystallization of the amorphous NPs**

Non irradiated area

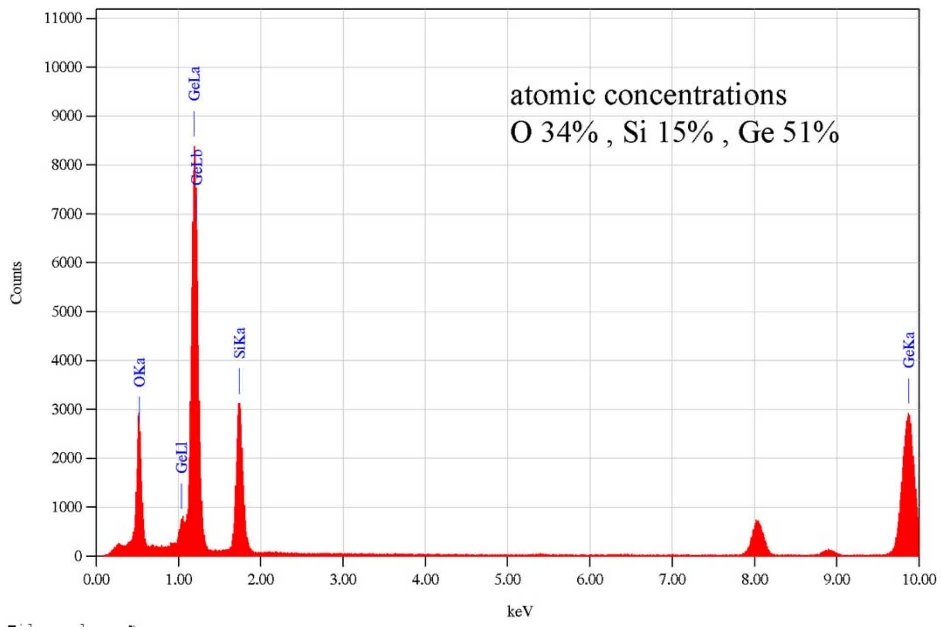


EDX spectrum obtained from a large area (300 nm diameter):

⇒ **Ge/Si atomic ratio of ~ 0.73**

EDX spectrum obtained with a probe diameter of 3 nm centered in the middle of a dark contrast NP:

⇒ **Ge amorphous NPs**



Conclusions

- **SiO_2/2x(Ge/SiO_2)/Si multilayer structures annealed in furnace or by RTA in N_2**
  - ❖ The faster crystallization of Ge in RTA process is favored by its reduced diffusion; Ge diffusion from crystalline phase in amorphous SiO_2 is low compared to Ge diffusion from amorphous phase.
    - ➔ faster Ge NCs formation has a positive feedback in reducing the Ge diffusion ➔ Ge NCs layers located closer to the position of the as deposited samples.
  - ❖ Raman: good theoretical fit of spectra by superposition of light scattering on big (8 – 9.5 nm) and small NCs (3 nm) & amorphous Ge clusters in SiO_2 (tails).
  - ❖ IR PL: strong emission at low T, with two main sharp peaks close to 1000 meV; energy separation ≈ 4 meV; ← recombination of excitons in two step transitions involving surface states located at the Ge NC surface.

- **Ge-SiO_2 films annealed in H_2**
  - ❖ Two kinds of features: low density of big tetragonal Ge NCs and high density of small amorphous Ge NPs embedded in SiO_2.

- **Formation of Ge NCs/NPs in amorphous SiO_2 matrix strongly depends on annealing conditions.**

Thank you for your attention!