

Estimation of Ge nanocrystals size by Raman, X-rays, and HRTEM techniques

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Ge NCs have attracted considerable attention because of their potential applications in nonvolatile memory and integrated optoelectronics. A number of groups have already proposed integrate flash memories based on Ge NCs embedded SiO₂ matrix [1]. Since Al₂O₃ presents a high dielectric constant comparatively to SiO₂, it is a good candidate to replace silica in flash memory systems, and therefore improve their performances [2]. Moreover, Al₂O₃ presents good mechanical properties, and supports high temperature, which leads it to be an ideal material for Si processing conditions. However, a few studies have been reported on Ge NCs embedded in Al₂O₃ matrix [3].

In this work, Ge NCs embedded in Al₂O₃ were grown on a commercial RF magnetron Alcatel SCM 650 apparatus using a conventional co-sputtering method. Two materials, Al₂O₃ (99,99%) and polycrystalline Ge (99,99%), were simultaneously used as target to produce the doped films. Low electrical resistivity (3-6 Ω cm) n-type Si(111) 2 inches wafers were used as substrates. Prior to sputtering, a pressure of at least 1x10⁻⁶ mbar was reached inside the chamber and in situ argon plasma treatment of target and substrates was performed in order to clean the surface and remove any impurities. More details of the samples preparation can be found in pervious works [4,5]. The as grown films were annealed at 800 °C and 900 °C, during one hour, under air pressure at 1,0x10⁻⁶ and 1,0x10⁻³ mbar, in order to improve the cristallinity of the Ge phase and to achieve control over the NCs size. With the aim to study the cristallinity and distribution of the Ge NCs size Raman spectroscopy, X-ray, and high resolution transmission electron microscopy (HRTEM) techniques were used. X-ray diffraction in conventional θ–2θ geometry (Philips PW1710) was performed towards the crystallographic structure investigation, using Cu K_α radiation. The identification of the crystalline phases was made using the JCPDS (Joint Committee of Powder Diffraction) data base. Raman scattering spectra were obtained using a Jobin-Yvon T64000 system with an optical microanalysis system and a CCD detector, in a backscattering geometry. Raman spectroscopy was performed at room temperature using 514.5 nm and 488.0 nm line of an argon laser at a power of 50 μW focus on an area of the sample ~1 μm². After preparing cross-section specimens by standard procedures the structure of the samples was examined using HRTEM.

XRD diffraction shows the characteristic peaks of Ge diamond structure, which confirms the high cristallinity of our samples. Figure 1 illustrates the XRD diffraction of an as grown sample and after annealing. It is clear that the post grown annealing treatment leads to sharp peaks and a therefore better cristallinity. The average size of Ge NCs was estimated using the Debye-Scherrer equation [6]. Using Lorentzian functions to fit each XRD peak of the samples, we obtained mean diameter values of 3.0 nm and 5.3 nm for sample B (see table) before and after annealing, respectively. Figure 2 (a) shows a TEM image that has high density of Ge particles, while in figure 2 (b) it is possible see the lattice fringes from individual Ge NC, confirming that these Ge NCs have a good homogeneity and a spherical shape. A statistical average diameter was obtained from HRTEM pictures. The size distribution of Ge NCs is shown in figure 2 (c). The average size is 7 nm with a standard deviation of 3 nm. Figure 3 shows Raman spectra for all samples investigated in this study.

NCs sizes were deduced from Raman spectra using the Fauchet and Campbell model [7]. It should be noted that this model considers that the NCs are completely relaxed in the matrix. The simulated Raman spectrum is shown for sample A. The calculated Raman peak fits quite well the experimental one. A mean diameter of the NCs of 7 nm was used in the calculations, in agreement with X-ray diffraction finding. The phonon confinement theory [7] predicts a red shift and an asymmetric broadening of the Raman peaks for smaller sizes. This was observed in our Raman measurements. Nevertheless for samples with bigger sizes (~20 nm) the Raman peak presents a blue shift relative to Ge bulk ($300,4 \text{ cm}^{-1}$). The reason for this discrepancy is not clear at present. However, a possible explanation is the compressive stress exerted on Ge NCs due to the existence of Al_2O_3 matrix.

Table 1 shows the NCs size obtained through the different techniques used in this study. Analysing the data illustrated in table 1, it is possible to conclude that for the smallest Ge NCs, there is an agreement between the values obtained with these different used techniques. However, for larger NCs (>20nm) there is a quite discrepancy between the XRD and Raman.

Analysing carefully the XRD diffraction of D sample (figure 4 (b)), it is clear that the peaks are shifted for bigger angles, i.e., smaller lattice parameters, in relation to the diamond structure of Ge crystallites, which is an evidence that the sample is under compressive stress. The Raman spectrum (figure 4 (a)), for the same sample, shows a blue shift relative to Ge bulk, giving confirmation of the fact that the NCs are actually under the effect of compressive stress. This effect in Ge NCs due the SiO_2 matrix was already studied by other groups [8], but in Al_2O_3 matrix this effect has not yet been studied. So, the red shifts caused by phonon confinement would be compensated by the blue shifts which are caused by the compressive stress on the Ge NCs embedded in Al_2O_3 . The stress may also affect the linewidth of the Raman peak for this kind of systems [8]. Further detailed studies are in course in order to clarify both effects of the stress, and the amorphous phase or the microcrystalline one of the matrix on the peak position and the linewidth in Raman and XRD spectra.

In conclusion, Ge nanocrystals embedded in Al_2O_3 matrix were successfully produced by RF magnetron sputtering. By using the X-ray diffraction, Raman spectroscopy and HRTEM it is possible to estimate the Ge nanocrystals sizes. For smallest Ge NCs, there is a good agreement between the three techniques. However, for larger NCs there is a discrepancy between the XRD and Raman results.

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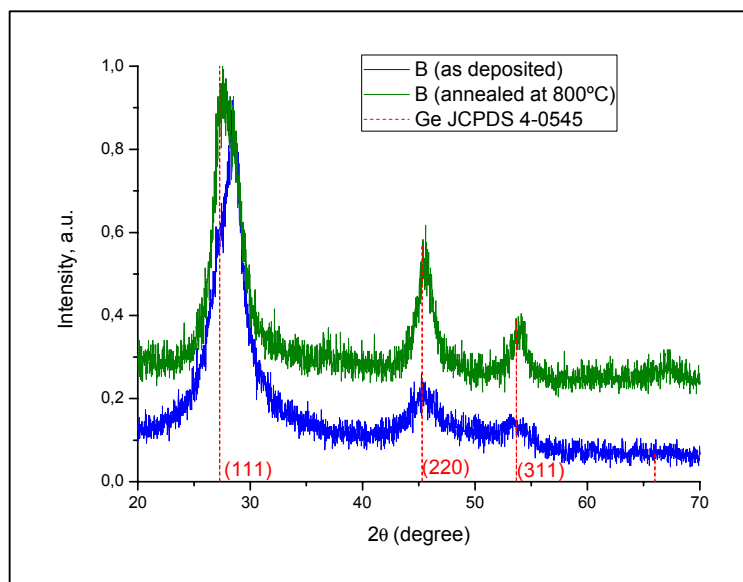


Figure 1: XRD diffraction of one sample showing the increase of the Ge NCs size before (3.0 nm) and after annealing (5.3 nm) in vacuum at 800°C during 1 hour under $P = 4 \times 10^{-3}$ mbar.

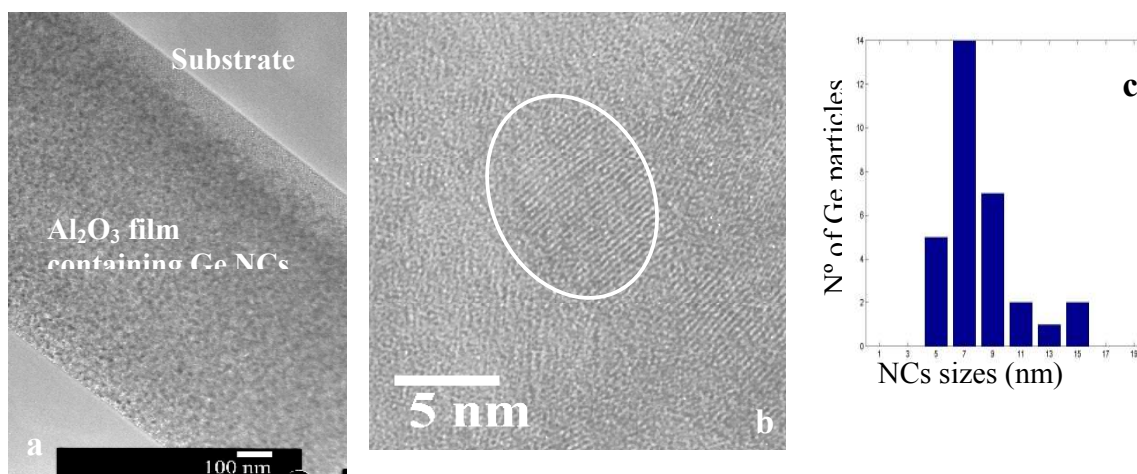


Figure 2: (a) A cross section TEM image gives an overview of the film. (b) HRTEM image where one can clearly see the lattice fringes of Ge NCs. (c) Histogram of the NC sizes distribution obtained from HRTEM images.

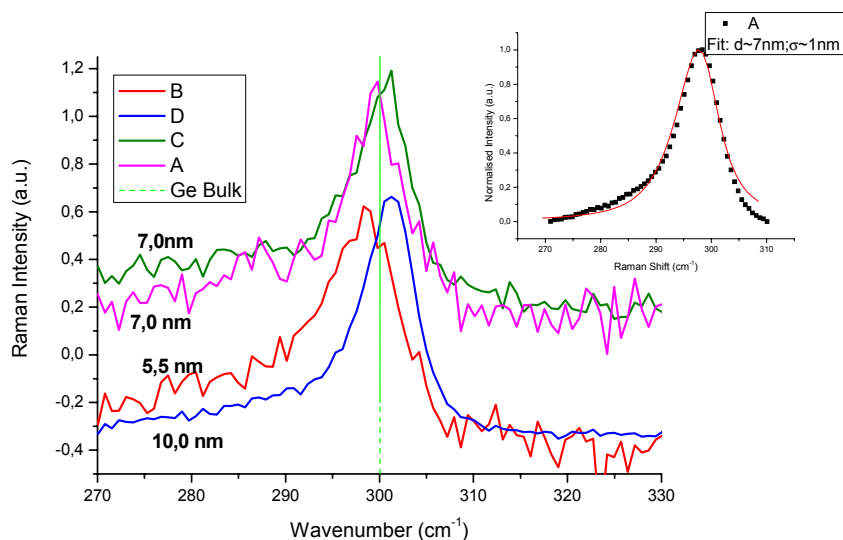


Figure 3: Raman spectra of all annealed samples. The inset shows the experimental (dots) and fitted curves (continuous line) for one sample.

Sample Name	Nanocrystals size (nm)		
	XRD	Raman	HRTEM
A	7,1	7,0	8,0
B	5,3	5,5	8,0
C	20,0	7,0	-----
D	17,0	10,0	-----

Table 1: Ge NCs size obtained from different techniques.

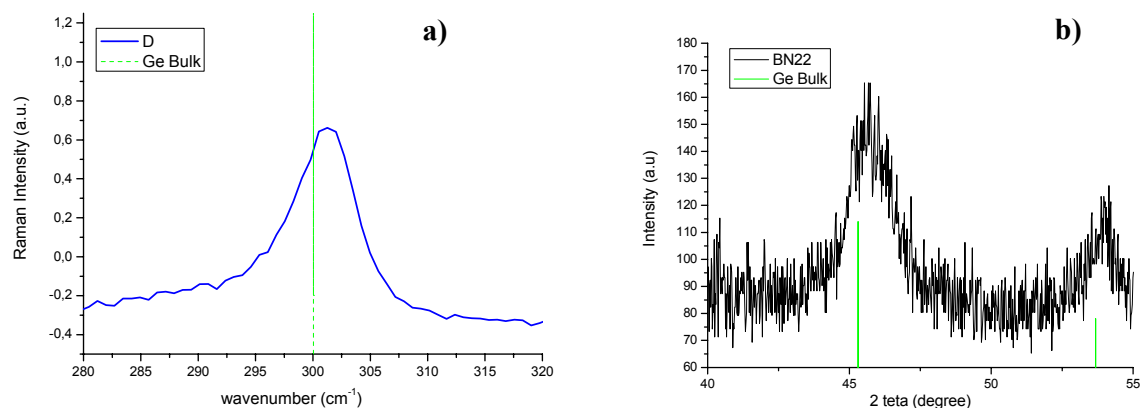


Figure 4: (a) Raman spectra of D sample, where a blue shift relative to Ge bulk is observed. (b) XRD diffraction of the same sample. The peaks positions are shifted related to the Ge polycrystalline reference.