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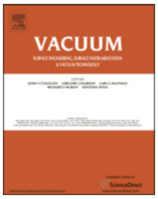

Raman and XRD studies of Ge nanocrystals in alumina films grown by RF-magnetron sputtering

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ABSTRACT

Germanium (Ge) nanocrystals (NCs) embedded in alumina thin films were produced by deposition on fused silica and silicon (111) substrates using radio-frequency (RF) magnetron sputtering. The films were characterised by both Raman and X-ray diffraction (XRD) spectroscopy. The deposition conditions were optimised in order to obtain crystalline Ge nanoparticles. In as-deposited films, the typical NC size was ~3 nm as estimated by means of X-ray diffraction. Raman spectra taken from as-deposited films revealed both amorphous and crystalline semiconductor phases. Annealing was performed in order to improve the crystallinity of the semiconductor phase in the films. After a 1 h annealing at 800 °C the mean NC size estimated from the XRD data and Raman spectra increased to ~6.5 nm. An increase in the crystallinity of the Ge phase was also confirmed by the Raman spectroscopy data.

1. Introduction

Over the last two decades, a lot of research has been dedicated to studying the quantum-confined electronic states in low dimension structures of group IV semiconductors like Ge. Nanocrystals (NCs) of indirect-gap semiconductors, such as Si and Ge are widely studied, as they would open new possibilities for the application of these materials in novel integrated optoelectronics and microelectronics devices. Several techniques are being used to fabricate Ge nanocrystals, such as RF co-sputtering [1–6], dc sputtering [7], ion implantation [8,9], evaporation–condensation [10], electron beam evaporation [11,12], chemical vapour deposition [13], and pulsed laser deposition [14]. In almost all these works the NCs have been grown inside a SiO_2 matrix, and very few studies are reported using alumina as a doped material.

SiO_2 is, without any doubt, one of the materials most studied and widely used as a gate dielectric in electronic devices. However, the constant shrinking of the thickness of gate dielectrics to below 2–3 nm has led to a search for alternative materials, whose dielectric constant is higher than that of SiO_2, but whose other properties remain similar to SiO_2 [14]. Because of its similar band gap energy value and more than twice as high dielectric constant, Al_2O_3 is a good candidate to replace SiO_2 as a gate dielectric material.

In this work we report results of structural study of Ge NCs embedded in alumina films, produced at 500 °C using a RF-magnetron co-sputtering technique. This study was performed using X-ray diffraction (XRD) and Raman scattering spectroscopy, while Rutherford backscattering spectrometry (RBS) was employed to study the elemental composition and stoichiometry of the composite films.

2. Experimental

Ge-doped alumina films were grown by a conventional co-sputtering method using an RF-magnetron Alcatel SCM 650 system. An alumina plate (purity of 99.99%, 50 mm diameter) was used as a target. An unpolished polycrystalline germanium sheet (99.999%) was placed over and at the centre of the Al_2O_3 plate, to produce the doped films. Fused silica (FS) and (111) silicon wafers were used as substrates and were kept at 500 °C during the deposition process. Prior to sputtering, a pressure of at least 1×10^{-6} mbar was reached inside the chamber and in situ argon plasma treatment of target and substrates was performed in order to clean the surfaces. Samples deposited on Si (111) substrates were annealed at 800 °C, during 1 h, under air pressure of approximately 4×10^{-3} mbar. The experimental parameters used to produce the Ge/Al_2O_3 films are presented in Table 1.

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Table 1
Experimental deposition parameters of Ge/Al_2O_3 RF-sputtered films

	Al_2O_3 + Ge
RF power (W)	50 and 80
Argon pressure ($\times 10^{-3}$ mbar)	2–6
Substrate temperature (°C)	500
% of target area covered by Ge	~8
Target to substrate distance (mm)	60
Deposition rate (nm/min)	~2.7–6.2
Annealing temperature and time	800 °C, 1 h

The crystallographic structure was investigated by X-ray diffraction in conventional θ–2θ geometry (Philips PW1710) and glancing incidence geometry (GIXRD) (Siemens D5000), using Cu K_α radiation. The identification of the crystalline phases was made using the *JCPDS* database cards: no. 4–0545 for Ge and no. 27–1402 for Si. Non-polarized Raman scattering spectra were obtained using a Jobin-Yvon T64000 system with an Olympus BH2–UMA microanalysis system and a CCD detector, in a backscattering geometry. Raman spectroscopy was performed at room temperature using the 514.5 nm line of an argon laser at a power of 200 mW. In order to identify the chemical elements present in the films and their atomic percentage in depth, RBS characterisation technique using a 2.0 MeV $^4He^+$ beam was employed.

3. Results and discussion

The RBS spectrum and fit of an as-deposited sample grown on Si (111) (under 4×10^{-3} mbar Ar pressure and 80 W RF power) is shown in Fig. 1. The fitting demonstrates that the sample shows a homogeneous composition profile, with approximately 16% of Ge atoms. Concentration values in the graph, presented in atomic%, are subject to a relative error of 5%. The other samples also showed homogeneous composition profiles, with Ge atomic percentage ranging from 16 to 20 at.%. The other two elements present (O and Al) also are distributed rather uniformly across the films.

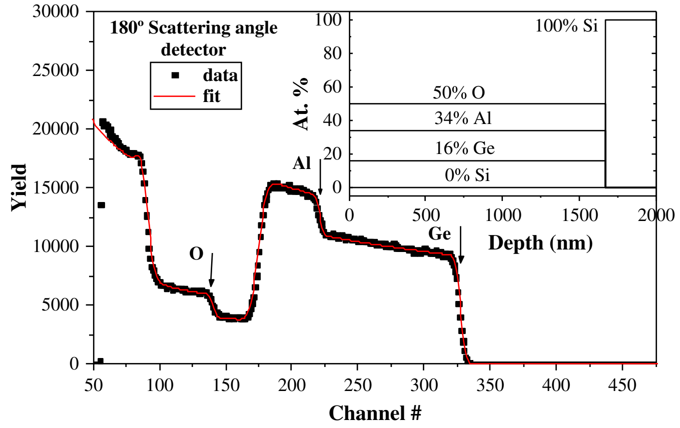

Fig. 1. RBS spectrum and fitting results for a film deposited on Si (111) substrate under 4×10^{-3} mbar Ar pressure and 80 W RF power.

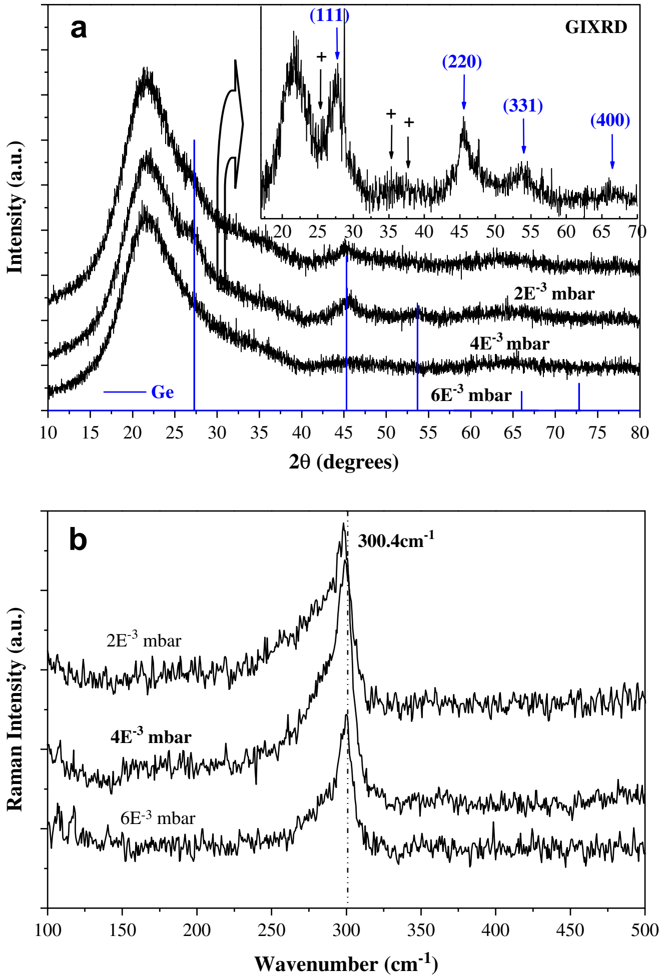

Fig. 2. X-ray diffractograms (a) and Raman spectra (b) from as-deposited Ge/Al_2O_3 films grown on FS substrates with an RF power of 50 W. GIXRD spectrum from one of the samples (obtained with one degree theta incidence) is shown in the inset for comparison with the conventional XRD. The peaks marked with the symbol "+" are attributed to a crystalline phase of the alumina matrix.

Fig. 2 shows the XRD (a) and Raman (b) spectra of Ge/Al_2O_3 as-deposited films grown on FS substrates at an RF power of 50 W and different argon pressures. It can be clearly seen that the optimal condition to grow NCs was obtained with an Ar pressure of $p_{Ar} = 4 \times 10^{-3}$ mbar. In this sample the (111) and (220) XRD reflection intensities are slightly higher, compared to the film deposited using $p_{Ar} = 2 \times 10^{-3}$ mbar. On the top right corner of Fig. 2(a), the GIXRD spectrum obtained from the 4×10^{-3} mbar sample is shown, clearly revealing (111), (220), (311) and (400) reflections corresponding to peaks from the diamond structure of germanium. The peaks marked with "+" are attributed to crystalline phase(s) coming from the alumina matrix, although it was not expected that these deposition parameters would be able to induce any crystalline phases in the alumina matrix [15]. XRD spectra of the sample deposited at 6×10^{-3} mbar did not reveal any clear peaks attributed to Ge. However, Raman spectra of all three samples indicate the presence of nanocrystalline Ge. The peak located at 298.9 cm^{-1} is identified as a confined phonon mode from Ge NCs. If compared to Raman spectra of bulk Ge ($\omega_{TO\text{-}LO} = 300.4$ cm^{-1}, FWHM ≈ 3.0 cm^{-1} [16]), the film produced with 4×10^{-3} mbar shows the best crystalline quality.

The results of Fig. 3 show that a combination of $p_{Ar} = 4 \times 10^{-3}$ mbar and RF power of 50 W is not optimal for producing Ge crystalline phase when films are deposited on Si (111) substrates. In fact, broad Raman spectra with a band centred at ≈275 cm^{-1} (Fig. 3(b)) are typical of amorphous germanium. However, when RF power of 80 W was applied, the presence of a Ge phase with the diamond structure becomes clear by XRD (111), (220), (311) and (331) reflections shown in Fig. 3(a). Raman spectroscopy revealing an asymmetric peak with a maximum at $\omega_1 = 297.3$ cm^{-1} (Fig. 3(b)) also confirms the presence of Ge NCs. A rough estimate of the NC mean size ($\overline{R}$) can be made from the shift between ω_1 and $\varpi_{LO\text{-}TO}$ using the bending parameters of bulk

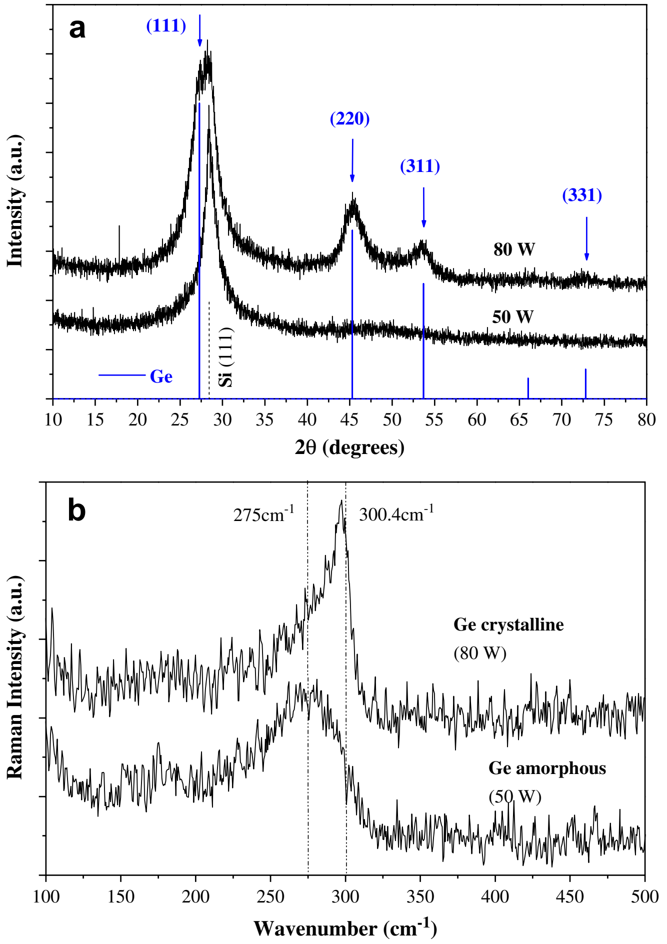

Fig. 3. X-ray diffractograms (a) and Raman spectra (b) from as-deposited Ge/Al_2O_3 films grown on Si (111) substrates with an Ar pressure of 4×10^{-3} mbar.

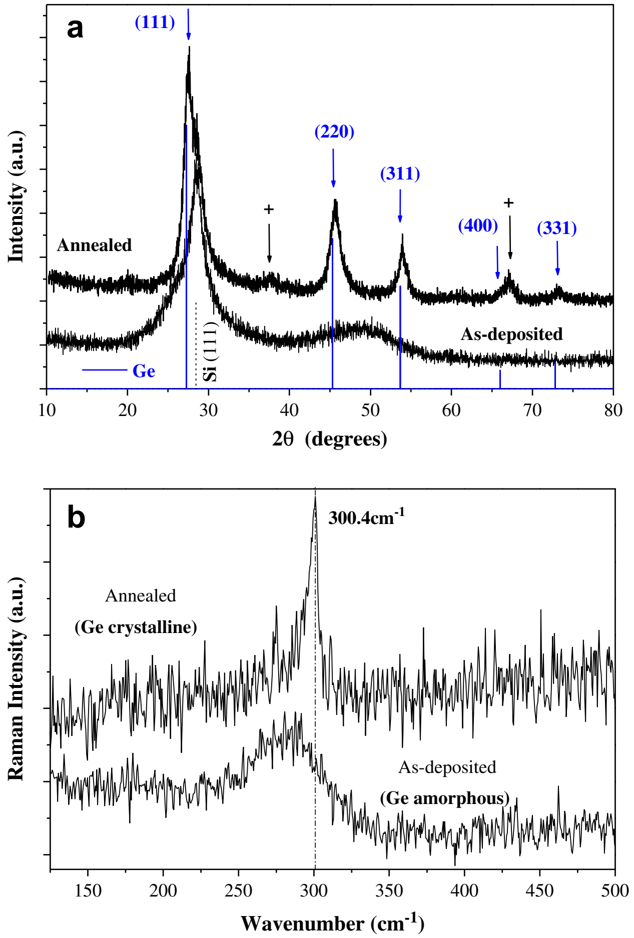

Fig. 4. X-ray diffractograms (a) and Raman spectra (b) of as-deposited and annealed films grown on Si (111) substrates.

optical phonon dispersion curve β_{LO}, according to the formula $\omega_1^2 = \omega_{\text{LO-TO}}^2 - \beta_{\text{LO}}(\pi/\bar{R})^2$. It gives ∼3.5 nm, in agreement with the value of 3 nm estimated from the XRD data using the well known Debye–Scherrer formula $D = 0.9\lambda/(B\cos\theta)$, where D is the average diameter of the NC, λ is the wavelength of the X-ray source, and B is the full width at half maximum (FWHM) of the X-ray diffraction peak at the diffraction angle θ.

It turned out possible to improve the crystallinity of the Ge phase by means of annealing at 800 °C for 1 h under a low air pressure of approximately 4×10^{-3} mbar. XRD and Raman results presented in Fig. 4 indeed confirm this. The NCs size was estimated to increase up to 6.6 nm. A high-resolution transmission electron microscopy (HR-TEM) image showing a spherical Ge NC in a similar sample is published elsewhere [17]. Again, the peaks marked with "+" are attributed to crystalline phase(s) of the alumina matrix, most probably a mixture of δ and γ alumina phases.

4. Conclusions

In conclusion, Ge nanocrystals embedded in Al_2O_3 matrix films were successfully produced by RF-magnetron sputtering. They were grown at 500 °C on fused silica and silicon substrates. RBS measurements performed on as-deposited films showed that the atomic percentage of Ge is homogeneous across the film and that, depending on the deposition parameters, it is between 16 and 20%. The use of an Ar pressure of 4×10^{-3} mbar was shown to improve the growth of the NCs when using fused silica substrates and 50 W RF power. However, with the same Argon pressure and substrate temperature, it was necessary to use a higher RF power value of 80 W in order to obtain Ge NCs in as-grown films deposited on Si (111) substrates. As expected, the annealed films exhibited an improvement in the crystallinity of the Ge phase. For the films grown on silica substrates NCs mean diameter values of 3 and 6.6 nm were obtained for as-deposited and annealed films, respectively, proving that this method of production is suitable for growing Ge NCs embedded in alumina matrix as well as for engineering their size.

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