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Influence of the deposition parameters on the growth of SiGe nanocrystals embedded in Al_2O_3 matrix

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ABSTRACT

$Si_{1-x}Ge_x$ nanocrystals (NCs), embedded in Al_2O_3 matrix, were fabricated on Si (100) substrates by RF-magnetron sputtering technique with following annealing procedure at 800 °C, in nitrogen atmosphere. The presence of $Si_{1-x}Ge_x$ NCs was confirmed by grazing incidence X-ray diffraction (GIXRD), grazing incidence small angle X-ray scattering (GISAXS) and Raman spectroscopy. The influence of the growth conditions on the structural properties and composition of $Si_{1-x}Ge_x$ NCs inside the alumina matrix was analyzed. Optimal conditions to grow $Si_{1-x}Ge_x$ ($x\sim 0.8$) NCs sized between 3 and 4 nm in Al_2O_3 matrix were established.

1. Introduction

Recently, Si, Ge and SiGe nanocrystals (NCs) embedded in dielectric matrices have been widely investigated due to their potential application in non-volatile memories and optoelectronics [1–7]. With a better carrier's confinement, NCs have a big potential to replace continuous floating gate in flash memory devices [5]. For this application, the characteristics of NCs layer, namely NCs diameter, uniformity, spatial distribution and density play an important role due to their strong influence on the electrical properties of the devices. SiO_2 matrix is one of the materials most used and studied as a gate dielectric in flash memory devices. However, the constant shrinking of the thickness of gate dielectrics has started a search for others high dielectric constant (high-k) materials. Among other dielectrics, Al_2O_3 has emerged as one potential candidate, since it combines a relatively high dielectric constant (~10), a wide band gap (6.2 eV), as well as a high band offset value of the Al_2O_3/Si barrier height (~2 eV) [8]. To the best of our knowledge there are only a few studies reported about SiGe NCs embedded in alumina matrix [9]. In most cases SiGe NCs have been produced in SiO_2 matrix and post annealed at high temperatures (>1000 °C) [10–12].

In this work, we present and discuss the effect of deposition and annealing conditions on the structural and compositional properties of SiGe NCs embedded in alumina grown by the RF magnetron co-sputtering technique. Thick films (~300 nm) have been produced in aim to optimize the best growth and annealing parameters to produce well calibrated NCs embedded in a thin Al_2O_3 oxide layer. Grazing incidence X-ray diffraction (GIXRD), grazing incidence small angle X-ray scattering (GISAXS) and Raman spectroscopy have been used in this study. Rutherford backscattering spectrometry (RBS) was employed to demonstrate the homogeneous composition of as-grown films. We have been able to produce well calibrated SiGe NCs in alumina matrix, in nitrogen atmosphere, at quite low annealing temperature (800 °C).

2. Experimental details

Nanostructures consisting of $Si_{1-x}Ge_x$ NCs inside an alumina matrix were grown at room temperature (RT) on n-type Si (100) substrates by RF-magnetron sputtering with an Alcatel SCM650 system, using a composite target, containing an Al_2O_3 (99.99%) plate of 50 mm diameter covered with several polycrystalline Si and Ge pieces on the surface. The surface ratio of the Si and Ge pieces in the Al_2O_3 target was 1:2. All films were produced at 4×10^{-3} mbar Ar^+ atmosphere and the target–substrate distance

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Table 1
Thickness, NC's size, Ge content (x) and Ge amount of Si_{1-x} Ge_x/Al_2O_3 samples estimated by different techniques. The NC's size and Ge amount (x) estimated from GIXRD, Raman, and GISAXS are in a good agreement.

Sample	Thickness(nm)	NCs size (nm)			Ge content x
	SEM	Raman	GIXRD	GISAXS	GIXRD
30–1	280	10 ± 0.5	–	–	–
50–1	300	10 ± 0.5	9.7 ± 0.8	9.9 ± 0.4	1.0
50–10	300	7.0 ± 0.5	–	10.6 ± 0.4	–
70–1	330	2.5 ± 0.5	3.1 ± 0.8	2.9 ± 0.2	0.8
70–10	330	3.0 ± 0.5	4.1 ± 0.8	3.8 ± 0.2	0.8
100–1	350	3.5 ± 0.5	3.1 ± 0.8	–	1.0

was kept at 90 mm. After deposition, the films were annealed at 800 °C in nitrogen atmosphere during 1 and 10 h inside a quartz tube in a commercial oven. The samples are labeled by X–Y, where X is the production power (W) and Y the annealing time (h), e.g. sample 30–1 was grown at 30 W of rf power and annealed for 1hour. Growth and annealing conditions of the samples, labeled 30–1, 50–1, 50–10, 70–1, 70–10 and 100–1, are listed in Table 1. The thickness of each sample estimated by scanning electron microscopy (SEM) is presented in Table 1.

GIXRD and Raman measurements were used to provide information about the crystallographic structure and the chemical composition of the NCs, and to estimate their size, while the GISAXS technique was used to study the NC size, shape and spatial arrangement. With these techniques we investigated the influence of the growth parameters on the properties of the NCs. Grazing incidence X-ray diffraction (GIXRD) was carried out in a Bruker AXS D5000 Diffractometer employing CuKα radiation (wavelength of 0.154 nm) at 1° grazing angle of incidence. The data were collected in the 15–50° 2θ range with a step size of 0.04 ° and a step time of 25 s. The Joint Committee of Powder Diffraction Standarts (JCPDS) database cards: 4–0545, 27–1402 and 15–7760 were used for the crystalline phase identification of Ge, Si and $Al_6Si_2O_{13}$, respectively.

Raman scattering spectra were recorded using a Jobin–Yvon T64000 system with an optical microanalysis system and a CCD detector, in the backscattering geometry. These measurements were performed at room temperature using the 514.5 nm line of an argon ion laser at a power of 0.2 mW on the sample surface. The silicon TO mode at 521 cm^{-1} was used as frequency calibration reference.

GISAXS measurements were performed at the SAXS beamline at the Elettra Synchrotron using 8 keV photon energy. Two-dimensional (2D) GISAXS maps were measured at incidence angles slightly above the critical angle for total external reflection.

3. Results and discussion

The RBS technique, using a 2.0 MeV $4He^+$ beam, was used to estimate the amount of Ge in the as-grown samples. The fitting [13] of the results (not shown here) for as-grown samples produced at 30, 50, 70 and 100 W of sputtering power demonstrates a homogeneous composition versus depth distribution. The atomic concentration of Ge estimated from RBS data is 11.4 ± 0.6, 10.9 ± 0.6, 14.3 ± 0.4, and 9.0 ± 0.5 at.% for the samples produced at 30 W, 50 W, 70 W, and 100 W, respectively. The others elements (Si, O and Al) also are distributed rather uniformly across the film. No significant change was observed in all element concentration after annealing process.

To investigate the inner structure of the formed NCs, GIXRD analysis was performed. GIXRD patterns of the annealed $Si_{1-x}Ge_x/Al_2O_3$ nanostructures are plotted in Fig. 1. By fitting the SiGe diffraction peaks with Lorentzian function, the positions and full

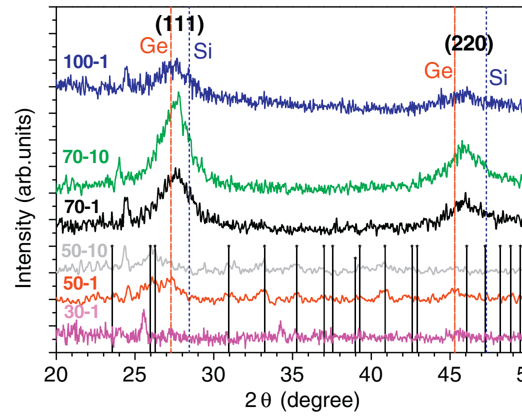

Fig. 1. GIXRD patterns of the annealed samples, from 30–1 to 100–1. The position of Si, Ge and mullite diffraction peaks are shown as vertical lines.

width at half maximum (FWHM) of the various peaks were determined. Both quantities vary from one sample to another, indicating the formation of $Si_{1-x}Ge_x$ NCs with various sizes and Ge content (x). The average size of the NCs was estimated from the FWHMs with the well known Debye–Scherrer equation [14]. Assuming that the contribution of elastic strain is negligible, the composition of the $Si_{1-x}Ge_x$ alloy was estimated using Vegard's rule. This empirical relationship assumes that a linear relation exists between the crystal lattice parameter of an alloy and the concentrations of the constituent elements [15]:

$$a_{SiGe} = xa_{Ge} + (1 - x)a_{Si}, \quad (1)$$

where a_{SiGe} is determined from the experimental data and a_{Ge} = 0.5658 nm and a_{Si} = 0.5431 nm are the Ge and Si bulk lattice parameters, respectively. The estimated values of the NCs size and Ge content (x) of the samples are summarized in Table 1.

The GIXRD pattern of sample 50–1, produced at 50 W of sputtering power and annealed at 800 °C during 1 h, display two peaks centered at 27.3 and 45.35 degrees corresponding to the (111) and (220) Ge Bragg peaks, respectively. This clearly evidences the presence of $Si_{1-x}Ge_x$ NCs with x close to 1, which indicates that most of the Si atoms have not been involved in the formation of the NCs.

Surprisingly, evidence for an $Al_6Si_2O_{13}$ (mullite) crystalline phase was observed, which normally araises at higher temperatures, >1000 °C, in the bulk or in thick films [16,17]. No significant change was observed in all element concentration after annealing process. The peak at around 24°, observed in all annealed samples, originates from the orientation of the Si substrate. Moreover, increasing the annealing time to 10 h at the same temperature (sample 50–10) led to a decrease of the intensity of the peaks assigned to Ge while that for mullite was not significantly affected. Therefore, it was impossible to prove the presence of $Si_{1-x}Ge_x$ NCs and estimate the Ge content from the pattern of this sample. However, in contrast to GIXRD, the presence of Ge NCs in sample 50–10 was confirmed by Raman measurements. From the pattern of sample 30–1, the observation of SiGe NCs and the estimation of the Ge content are very difficult. Thus, for samples 30–1 and 50–10 NCs sizes were estimated using the Raman technique.

Samples 70–1 and 70–10 produced at higher sputtering power (70 W) and annealed at 800 °C, during 1 and 10 h respectively, display two well pronounced GIXRD peaks near 27.6 and 46 degrees, which are located between the expected (111) and (220) Bragg peaks of Si and Ge diamond structure. Both samples display a Ge-rich $Si_{1-x}Ge_x$ alloy with x equal 0.8. In these two samples, the presence of mullite phase is not evident. This could be explained, that under such growth conditions, the Si atoms are more involved