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Multilayers of Ge nanocrystals embedded in Al_2O_3 matrix: Structural and electrical studies

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ABSTRACT

In this paper, Ge/Al_2O_3 multilayer systems were grown by pulsed laser ablation. The grown samples were annealed at 900 °C to promote the formation of Ge nanocrystals. Rutherford backscattering spectroscopy and transmission electron microscopy confirmed the presence of a multilayer system. Grazing incidence small angles X-ray scattering technique demonstrates the formation of Ge nanoclusters formed between alumina layers. Room temperature *I–V* measurements showed weak carrier trapping in the system. This was explained by the leakage caused by Ge diffusion through the multilayer.

1. Introduction

Nonvolatile memory (NVM) devices with a floating gate structure are being used widely at present. For NVM devices, a long retention time is very important. But for a conventional flash memory with a continuous floating gate, the retention time is limited by the charge leakage through weak spots in the tunnel oxide. Nanocrystals (NCs) floating gates have been demonstrated to lead to an improvement in the retention time compared with conventional continuous floating gates [1]. Ge NCs have attracted considerable attention because of their potential applications in NVM and integrated optoelectronics. Ge NCs can be more useful than Si NCs for improving the NVM function because of their smaller energy bandgap, inducing better retention and faster writing/erasing times [2,3]. Moreover, owing to the low carrier effective mass, the quasi/ballistic transport in Ge NCs may lead to a better device performance. A number of groups have already proposed integrated flash memories based on Ge NCs embedded in a SiO_2 matrix [4]. Since Al_2O_3 has a high dielectric constant and a large bandgap compared to SiO_2, it is a good candidate to replace silica in flash memory systems, and therefore to improve their performances [5]. However, only few studies have been reported on Ge NCs embedded in an Al_2O_3 matrix [6,7].

Several techniques are being used to fabricate Ge NCs within the insulating matrix, such as RF co-sputtering, ion implantation, electron beam evaporation, chemical vapour deposition. Nevertheless, few studies have been reported for samples grown by pulsed laser deposition (PLD) [8,9].

In this work, a set of $[Al_2O_3/Ge/Al_2O_3]$ multilayer samples were grown using a PLD technique. Samples with different numbers of multilayers have been produced and structurally characterized in order to achieve optimization of the growth parameters. Annealing was performed in order to improve the crystallinity of the semiconductor phase and to control the NC size.

Rutherford Backscattering Spectroscopy (RBS), Grazing Incidence Small Angles X-ray Scattering (GISAXS), Transmission Electron Microscopy (TEM) and Raman spectroscopy techniques have been used to characterize the structural properties of the multilayer samples including determination of the multilayer period and the properties of the NCs. Current–Voltage (*I–V*) technique was used to examine the electrical behaviour of the grown samples and to test their applicability to NVM applications.

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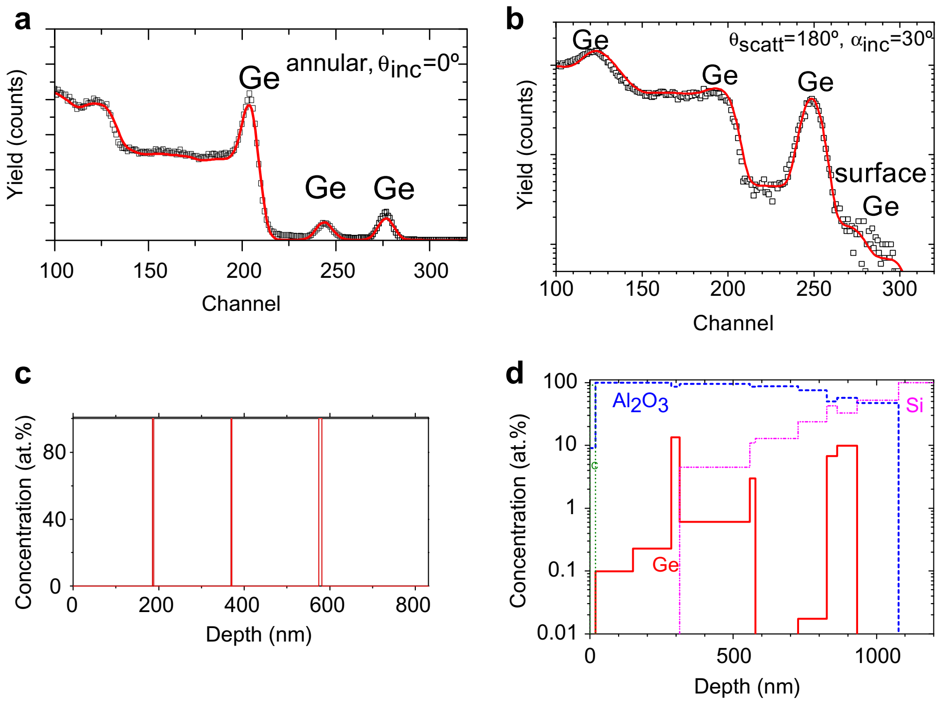

Fig. 1. (a) RBS spectrum (black circles) of the as-grown (Ge/Al_2O_3) three-layer sample collected at a 140° scattering angle. Fits assuming that the Ge is organised in NCs and mixed into the Al_2O_3 layers are shown. (b) RBS spectrum of the same sample after annealing. Corresponding fitted depth profiles for (c) the as grown sample and (d) the annealed sample.

2. Experimental parameters

$Al_2O_3/Ge/Al_2O_3$ multilayer structures were grown on p-Si (1 0 0) substrate at room temperature under vacuum pressure. Ge and Al_2O_3 targets were ablated with a wavelength of 248 nm, and an energy density of 4–5 J/cm^2. Pulse duration of 20 ns from a KrF excimer laser was used. The targets were rotated during the ablation in order to avoid, as far as possible, formation of deep craters in the targets. Different numbers of layers (from 1 to 10) with different Ge layer thicknesses (2–40 nm) in the multilayer system have been produced. All deposition parameters except deposition time, were the same for the all samples. In order to improve the Ge crystalline phase and to control the NC size, the samples were annealed at 900 °C under nitrogen pressure (6 mbar), for one hour.

The total films thicknesses were obtained by SEM and the thickness of each layer was acquired by RBS and TEM techniques. In order to identify the chemical elements present in the films and their atomic percentage in depth, RBS using a 2.0 MeV 4He$^+$ beam was carried out. GISAXS measurements were performed at the SAXS beamline of Elettra synchrotron, using monochromatic radiation with wavelength 0.154 nm. The incidence direction of the X-ray radiation was along the x axis, perpendicular to the detector ($y - z$) plane. Data were measured by a two-dimensional (1024 × 1024 pixel) CCD detector, with a sample-detector distance about 1.72 m. We have used several grazing incidence angles slightly above the critical angle of total external reflection. Raman scattering measurements were carried out at room temperature with an optical microanalysis system and a CCD detector in backscattering geometry, using the 514.5 nm line of an argon laser. Conventional TEM and high angle annular dark field (HAADF) images were acquired with a Tecnai F30 FEG-TEM microscope operating at 300 kV. TEM cross-sectional samples were produced by mechanical polishing followed by ion beam milling to have sufficiently large electron transparent areas.

For electrical measurements Al contacts with a thickness of 200 nm were thermally evaporated on the film surface under vacuum (~10^{-6} mbar). The back contacts to the substrate side were burned from Al foils by an electric sparks. *I–V* measurements were obtained at room temperature using Keithley 617 electrometer.

3. Results and discussion

RBS is a well-established technique to identify the depth profile of the elemental composition of thin films [10]. Fig. 1 shows RBS spectra with fits [11] of a three Ge layer sample, as grown (a) and after annealing at 900 °C (b).

It is clear from Fig. 1a that the layers are well separated. This figure offers also the possibility to estimate the thicknesses of the Al_2O_3 separation layers. Fig. 1c and d show the depth profiles of as grown and annealed Ge layers samples, estimated from the analysis of the RBS results. The three Al_2O_3 and Ge monolayers are well resolved. However, the depth profile graph of the annealed sample (Fig. 1d) indicates Ge diffusion through the Al_2O_3 separa-

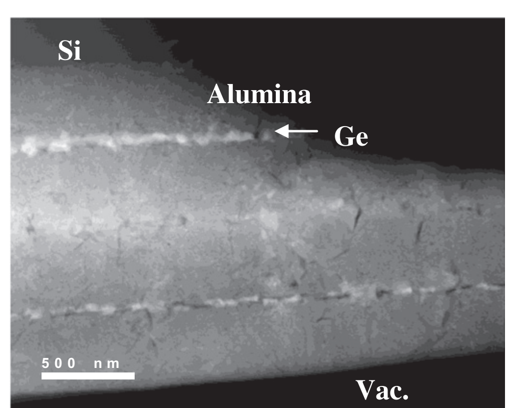

Fig. 2. HAADF-TEM image of a sample containing three layers after annealing.