Ge nanocrystals in alumina matrix: a structural study

RJ Kashtiban¹, SRC Pinto², U Bangert¹, AG Rolo², A Chahboun²,³, MJM Gomes³ and AJ Harvey¹

¹ Nanostructured Materials Research Group, School of Materials, The University of Manchester, P.O. Box 88, Manchester, M1 7HS, UK
² Physics Department, University of Minho, 4710 – 057 Braga, Portugal
³ Physics Department, Dhar Mehraz Sciences Faculty, BP 1796, Fès, Morocco

E-mail: reza.jalilikashtiban@postgrad.manchester.ac.uk

Abstract. Germanium (Ge) nanocrystals (NCs) embedded in alumina thin films were produced by deposition on silicon (111) substrates using radio-frequency (RF) magnetron sputtering. By changing growth condition and annealing parameters samples with large and small Ge-NCs were produced. The average size of NCs in the sample with larger NCs was estimated to be 7.2, 30.0 and 7.6 nm, and 5.0, 7.0 and 4.8 nm for the sample with smaller NCs, according to X-ray diffraction (XRD), Raman and high resolution transmission electron microscopy (HRTEM) results, respectively. Both, XRD and Raman peak positions of the larger NCs are shifted to higher angles and larger wave numbers in relation to the Ge bulk values, whereas the Raman peak was red-shifted for the smaller NCs indicating phonon confinement. HRTEM shows twinned structures, which is an indication of relaxation. Strain evaluation of the bigger NCs gave values < 0.5 % which is within the estimated error of the evaluation technique.

1. Introduction

Undesirable charge leakage in modern flash memories based on polycrystalline silicon prohibits the use of thin tunnel oxide layers for the reduction of the operating voltage. On the other hand a thick tunnel oxide requires a higher operating voltage, which is a major disadvantage. Si and Ge-NCs embedded in a SiO₂ matrix have attracted great attention because of their potential applications in high performance non-volatile memory devices and light emitting diodes [1-4]. Using isolated NCs in dielectric layers improves the retention time, and thinner oxide layers can be employed resulting in lower operating voltage and faster device speed [3]. Ge has a smaller band-gap than Si which makes it compatible with currently used metal oxide semiconductor (MOS) technology and also improves its write/erase speed [5, 6]. Promising non-volatile properties of Ge-NCs were reported by several groups [7-10].

Since Al₂O₃ has a high dielectric constant, twice that of SiO₂, the thickness of the oxide layer can be reduced to 2-3 nm. Moreover, Al₂O₃ exhibits good mechanical properties and can endure high temperatures; this makes it a good candidate for replacing silica in flash memory systems and thereby
Improve their performance. Most of the research on Ge-NCs has been done on Ge-NCs embedded in SiO$_2$ system [3, 5, 7, 9-12]. However, a few studies have been reported on Ge-NCs embedded in Al$_2$O$_3$ matrix [13, 14]. In this work we will study Ge-NCs embedded in alumina grown by the RF-magnetron co-sputtering technique.

2. Experimental

Conventional co-sputtering methods were used to grow Ge-NCs embedded in Al$_2$O$_3$ in a commercial RF magnetron Alcatel SCM650 machine. Al$_2$O$_3$ (99.99%) and polycrystalline Ge (99.99%) were used as targets to produce the doped films simultaneously on 2 inch n-type Si(111) wafers as substrates, kept at 500 °C. Prior to sputtering, a pressure of at least 1×10$^{-6}$ mbar was reached inside the chamber and in order to achieve a clean surface free of any impurities, in situ argon plasma treatment of target and substrate was performed. In order to improve the crystal structure of the Ge phase and achieve structures with large (sample A) and small (sample B) Ge-NC sizes, as-grown samples were annealed at 900 °C and 800 °C, for one hour, under air pressures of 8.0×10$^{-3}$ and 4.6×10$^{-6}$ mbar, respectively. More details are presented elsewhere [13]. Room temperature Raman spectroscopy was carried out using the 514.5 nm and 488.0 nm lines of an argon laser at a power of 50 µW focus on an area of the sample ~1 µm$^2$ in order to study crystallinity and size distribution of the Ge-NCs. In order to study the crystallographic structure of the materials X-ray diffraction in conventional $\theta$-2$\theta$ geometry was performed with a Philips PW1710 apparatus using Cu K$_\alpha$ radiation for sample A and sample B by grazing incidence X-ray diffraction (GIXD) in the European Synchrotron Radiation Facility (ID01 beam line, Grenoble, France) using 11 keV radiation at 0.15 degree of incidence to the sample surface. TEM and HRTEM images were acquired with a Tecnai F30 FEGTEM microscope operating at 300 kV.

3. Results and discussion

Figure 1 represents XRD and Raman spectra of samples A and B. The XRD curve confirms the diamond crystalline structure of Ge. Both, XRD and Raman peak positions of sample A are shifted to higher angles and larger wave numbers, respectively, in relation to the Ge bulk. This would indicate that the sample is under compressive stress exerted by the Al$_2$O$_3$ matrix. Raman spectra of sample B show a red shift, which is predicted by phonon confinement theory for small NCs.

The average size of NCs in sample A was estimated to be 7.2, 30.0 and 7.6 nm, and 5.0, 7.0 and 4.8 nm for sample B according to X-ray diffraction (XRD), Raman and high resolution transmission electron microscopy (HRTEM) results, respectively. Whereas TEM and XRD results are in agreement, the discrepancy with the Raman results is not clear. It might be partially caused by the elongated shape...
of the sample-A NCs (>10 nm along the long axis; the value above is a geometrical average) and also by the near-epitaxial relationship between Ge- and neighbouring Al₂O₃-crystallites, giving the appearance of larger crystalline regions.

Figure 2 shows a bright field (BF) and dark field (DF) TEM image of sample B. Formation of crystalline Ge-NCs within the alumina matrix can be seen in the DF image. The silicon substrate, the 600 nm thick alumina matrix and the glue can be seen clearly in the BF image. Diffraction contrast cannot reveal atomic-scale structure of the NCs and the alumina matrix and also not the exact NC sizes. In order to obtain this information, HRTEM images were acquired. A detailed size analysis was carried out on a statistical ensemble of Ge-NCs, which showed the majority of the NCs to be ellipsoidal with the major axis ~11 nm and the minor axis ~5 nm.

Figure 3(a) depicts a Ge-NC in sample B. Extensive twinning, observed in most of the NCs, indicates that stress relaxation has taken place and we therefore expect the NCs to be nearly unstrained. Figure (b) and (c) represent images acquired at different foci revealing the polycrystalline nature of the matrix. The circled Ge-NC is the same in both images. The existence of crystalline alumina phases complicates the interpretation of XRD measurements, because of the occurrence of additional peaks close to the position of Ge peaks which make the identification of the latter difficult.

Figure 3 (d) shows an image of big Ge-NC in sample A together with its Fourier transform (FT) pattern representing the (211) zone axis pattern of the diamond crystal structure. Different diffraction spots of this FT pattern were used to measure lattice plane distances in this NC to evaluate the strain which may be exerted by the alumina matrix.

To assess the existence of such strains in the Ge-NCs, HRTEM images of the Si substrate were taken as reference in order to estimate the error in the determination of lattice plane distances from FTs of HRTEM images. The lattice spacing of the Si substrate was determined using FTs of HRTEM
images with the sample aligned at the (110) zone axis for various reflections and in various locations and compared to calculated values of silicon ($λ = 5.43$ Å). Lattice spacings for Ge-NCs were then obtained from HREM images (FTs) taken at the same magnification as the Si images. Table 1 illustrates lattice planes distances and error values for both, substrate and NCs. As can be seen changes in the lattice distances of the NCs were within the error limit, and hence the strains would be below 1%. The shifts in the XRD peaks in fig. 1b would arise from strains around the $\frac{1}{2}$ % mark; this is the error limit of the HREM technique, and hence we would not be able to confirm these from lattice images.

| Planes | Silicon substrate | Ge-NCs |
|--------|------------------|--------|
|        | Exp. | Calc. | Error | Exp. | Calc. | Displacement |
| 111    | 3.110 | 3.135 | +0.7% | 3.240 | 3.262 | +0.6% |
| 220    | 1.890 | 1.919 | +1.5% | 1.970 | 1.990 | +1.0% |
| 113    | -    | -    | -     | 1.690 | 1.700 | +0.5% |

Table 1. Error values of technique based on Fourier method applied to HRTEM images, and percentage of evaluated strain in the sample A.

4. Conclusion

Ge-NCs embedded in Al$_2$O$_3$ films were successfully produced by RF-magnetron sputtering. Samples with two different NC sizes (on average $\sim$5 and $\sim$8 nm) were produced by changing the annealing temperature and gas flow pressure. Raman and XRD results indicate strain in the bigger NCs, however, peaks from the polycrystalline alumina matrix obscure the exact position of the Ge-peaks in the XRD results. Furthermore, the shifts, if genuine, are concomitant with strains $< \frac{1}{2}$ %, which is below the accuracy of HRTEM-based lattice constant determination. HRTEM suggests unstrained structures for the small NCs, because plastic relaxation and extensive nano-twinning have taken place. This explains red shift in the Raman peak position of the sample and is a sign of relaxed NCs.

References

[1] Tiwari S, Rana F, Chan K, Shi L and Hanafi 1996 H Appl. Phys. Lett. 69, 1232
[2] Lu TZ, Alexe M, Scholz R, Talalaev V, Zhang RJ and Zacharias M 2006 J. Appl. Phys. 100, 14310
[3] Kanjilal A., Hansen JL, Gaiduk P, Larsen AN, Cherkashin N, Claverie A, Normand P, Kapelanakis E, Skarlatos D and Tsoukalas D 2003 Appl. Phys. Lett. 82, 1212
[4] Tiwari S, Rana F, Hanafi H, Hartstein A, Crabbe EF and Chan 1996 Appl. Phys. Lett. 68, 1377
[5] Batra Y, Kabiraj D and Kanjilal D 2007 European Physical J.- Appl. Phys. 38, 27
[6] Lee PF, Lu XB, Dai JY, Chan HLW, Jelenkovic E and Tong KY 2006 Nanotechnology 17, 1202
[7] Baron T, Pelissier B, Perniola L, Mazen F, Hartmann JM and Rolland G 2003 Appl. Phys. Lett. 83, 1444
[8] Kanoun M, Souifi A, Baron T and Mazen F 2004 Appl. Phys. Lett. 84, 5079
[9] Rolo AG, Chahboun A, Conde O, Vasilievskiy MI and Gomes MJM 2008 Physica E 40, 674
[10] Hong SH, Kim MC, Jeong PS, Choi SH and Kim KJ 2008 Nanotechnology 19, 305203
[11] Choi WK, Chew HG, Ho V, Ng V, Chim WK, Ho YW and Ng SP 2006 J. Cryst. Growth 288, 79
[12] Park CJ, Cho KH, Yang WC, Cho HY, Choi SH, Elliman RG, Han JH and Kim C 2006 Appl. Phys. Lett. 88, 71916
[13] Caldelas P, Rolo AG, Gomes MJM, Alves E, Ramos AR, Conde O, Yerci S and Turan R 2008 Vacuum 82, 1466
[14] Yerci S, Kulakci M, Serincan U, Turan R, Shandalov M and Golan Y 2008 Journal of Nanoscience and Nanotechnology 8, 759