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Structural and optical study of Ge nanocrystals embedded in Si_3N_4 matrix

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Abstract

Ge nanocrystals were fabricated in Si_3N_4 matrix by rf (radio frequency) magnetron sputtering, followed by post-annealing in a conventional tube furnace filled with N_2. Ge content was varied between 30-50vol% in Ge-rich silicon nitride (GRN) layer with variation of annealing temperature between 600-900 ºC were applied to study the crystallization properties. The structure of the Ge nanocrystals was studied by Raman spectroscopy, glancing incidence x-ray diffraction (GIXRD) and transmission electron microscope (TEM). The composition and bonding status of Ge nanocrystals was confirmed by x-ray photoelectron spectroscopy (XPS). TEM images, Raman and XRD results show that the crystallization transition is dependent on temperature and Ge content. Crystals in 50vol% annealed at 900 ºC were found as partially oxidized with 2at% of oxygen during the annealing process. This was shown by the XPS result. However, absorption measurement did not show evidence of quantum confinement of the Ge crystals.

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Keywords; Germanium; disk-shaped nanocrystals; GIXRD; Raman; TEM

1. Introduction

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As an alternative to silicon (Si) quantum dot, germanium (Ge) has been one of the promising candidate for quantum dot formation in the areas of photovoltaic, electronic and optoelectronic devices [1, 2].

The advantage of Ge over Si is the lower processing temperature and in effect, greater compatibility with other processes. This reduces the thermal budget and hence the manufacturing cost. The smaller electron and hole effective masses of Ge also allows greater theoretical quantum confinement than Si. The disadvantage is the cost and lower abundance of Ge compared to Si. Quantum dot fabrications have been realized by many techniques like co-sputtering with post-annealing [3-5], in-situ formation by molecular beam epitaxy [6, 7] and chemical vapor deposition [8]. In this work, Si_3N_4 is selected as a compromised matrix for band gap engineering and carrier mobility to replace SiO_2 matrix, which has already been much studied [3, 9-11]. The crystallization behavior for Ge nanocrystals in Si_3N_4 matrix was investigated by structural and optical characterization.

2. Experimental details

The 20 alternating bilayers of 5nm Ge-rich silicon nitride (GRN)/ 3nm Si_3N_4 were co-sputtered by radio frequency (rf) magnetron sputter (AJA International) on (100) silicon wafer substrates and quartz slides with a deposition rate in a range of 1-2 nm/min. The rf suppliers (13.56MHz) were connected to Si_3N_4 (4 in., 99.999 %) and Ge (4 in., 99.999 %) targets. Ge volume content of the GRN film was controlled by varying the rf power from 30 vol % to 50 vol % in increments of 10 vol %. The base pressure was 6.0×10^{-7} torr and working pressures during film deposition was 3.0×10^{-3} torr with argon (Ar). A post-annealing process was conducted by a conventional tube furnace with N_2 with an annealing temperature from 600 ºC up to 900 ºC in increments of 100 ºC, for 1 hour. Raman spectroscopy (Renishaw, 514nm) and glancing incidence x-ray diffraction (GIXRD) (Philips X'Pert Pro) using CuKα radiation were performed to study the phase and crystalline properties of the Ge nanocrystals. GIXRD was operated at a voltage of 45 kV and a current of 40 mA and using a 1/16º divergent slit, a parallel plate collimator of 0.27º acceptance and a soller slit of 0.04 rad aperture. Crystalline Ge was detected by glancing incidence x-ray diffraction; 2θ scan with a critical angle (ω=0.295°). The structure of the nanocrystals was observed by transmission electron microscope (TEM) (Philips CM200) at 200kv. The TEM specimen was prepared by a small angle cleavage method for the cross-sectional and plan-view observations. For the compositional analysis, x-ray photoelectron spectroscopy (XPS) (ESCALAB 220IXL) detected the elements consisting the film and quantified their contents. Spectrophotometer (PerkinElmer) measured optical properties; transmission and reflection values. Samples on silicon wafer substrates were used for XPS, TEM and GIXRD and those on quartz slides were used for Raman spectroscopy and optical measurement.

3. Results and discussion

3.1. TEM investigation

The structural properties of the Ge nanocrystals were studied by TEM. 5nm GRN layer and 3nm barrier layer were identified in the TEM images. TEM images of Ge content 30 and 40 vol% annealed at 900 ºC did not show any visible nanocrystals. However, a crystallization transition was observed in the 50vol% sample with temperature variation from 800 ºC to 900 ºC. Figure 1 (a) and (b) show spherical Ge crystals formed at 800 ºC at low and high magnification and Figure 1 (c) and (d) show disk shaped crystals formed at 900 ºC at low and high magnification. We observed homogeneous lattice fringes across the specimen.