Available online at www.sciencedirect.com
ScienceDirect
Applied Surface Science 253 (2006) 385–388
applied surface science
www.elsevier.com/locate/apsusc

Characterization of Si nanocrystals into SiO_2 matrix

C. Gravalidis, S. Logothetidis *, N. Hatziaras,
A. Laskarakis, I. Tsiaoussis, N. Frangis

Aristotle University of Thessaloniki, Department of Physics, GR-54124 Thessaloniki, Greece

Available online 10 July 2006

Abstract

Silicon nanocrystals (nc-Si) have gained great interest due to their excellent optical and electronic properties and their applications in optoelectronics. The aim of this work is the study of growth mechanism of nc-Si into a-SiO_2 matrix from SiO/SiO_2 multilayer annealing, using non-destructive and destructive techniques. The multilayer were grown by e-beam evaporation from SiO and SiO_2 materials and annealing at temperatures up to 1100 °C in N_2 atmosphere. X-rays reflectivity (XRR) and high resolution transmission electron microscopy (HRTEM) were used for the structural characterization and spectroscopic ellipsometry in IR (FTIRSE) energy region for the study of the bonding structure. The ellipsometric results gave a clear evidence of the formation of an a-SiO_2 matrix after the annealing process. The XRR data showed that the density is being increased in the range from 25 to 1100 °C. Finally, the HRTEM characterization proved the formation of nc-Si. Using the above results, we describe the growth mechanism of nc-Si into SiO_2 matrix under N_2 atmosphere.

Keywords: Si nanocrystals; X-rays reflectivity; High resolution transmission electron microscopy; Optical density

1. Introduction

Si nanocrystals into SiO_2 matrix have recently attracted much attention because of their light-emitting ability that can be used for Si-based optoelectronic applications. The induced confinement of electron and hole carriers in nanoscale dimension enhances the luminescence efficiency due to the increasing recombination rate of carriers as well as the visible luminescence arising from quantum confinement effect [1]. These structures can be formed from $(SiO/SiO_2)n$ multilayer composed of alternating SiO and SiO_2 layers grown by CVD or by PVD methods [7–9] and subsequent heat treatment [4].

For the optimization of these systems (silicon nanocrystals (nc-Si) in SiO_2 matrix), various structural and optical characterization methods are needed [2–6]. In this work, X-rays reflectivity, fast fourier infrared spectroscopic ellipsometry and electron microscopy techniques were applied for the study of Si nanocrystals in SiO_2 matrix formed from SiO_2/SiO multilayer annealing.

2. Experimental

The SiO/SiO_2 multilayered films were deposited on nc-Si(1 0 0) wafers by e-beam evaporation of SiO and SiO_2 chunks of 99.999% purity in an ultra-high vacuum chamber with base pressure $<1.33 \times 10^{-7}$ Pa. The working pressure during deposition was varying with the e-beam current in the range of 1.33×10^{-4} Pa. The accelerating voltage of the e-beam was fixed at 7 kV and the beam current was equal to 50 mA. The deposition rate was reduced with deposition time for a constant current due to the mass reduction of the evaporated SiO chunks. The films grown we consisted of seven alternating layer of SiO and SiO_2. The partial pressure of the evaporated species the chamber was monitored by a multi-channel quadrapole mass spectrometer (QMS). The samples, after the growth, were annealed at 500, 800 and 1100 °C into N_2 atmosphere for 1 h.

The X-rays study was performed with a D-5000 Siemens diffractometer equipped with a conventional Cu Kα source, a reflectometry sample stage (RSS) and a Goebel mirror. The Goebel mirror transforms a divergent X-ray beam into a parallel and high brilliant one. No monochromator was necessary because Cu Kβ is suppressed by the mirror. The RSS consists of a translation stage on which an edge diaphragm and a vacuum-held holder are mounted. The edge

* Corresponding author. Tel.: +30 2310 998174; fax: +30 2310 998390.
E-mail address: logot@auth.gr (S. Logothetidis).

0169-4332/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2006.06.019

diaphragm is placed on the sample surface for suppression of the direct source beam.

The IR measurements, before and after annealing, were performed in the range of 900–4000 cm^{-1}, using a Jovin Yvon Fourier Transform IR Phase Modulated Ellipsometer adapted to the UHV deposition chamber using BaF_2 windows. The IR beam is produced by a commercial IR spectrometer (BOMEM-MB100) which includes a thermal source of SiC bars and a Michelson interferometer and is focused on the sample through an optical system of reflectors and lenses. A grid analyzer and a photo-elastic modulator, which modulates the IR beam polarization with a frequency of 37 kHz, define the polarization of the incident beam. After its reflection on the sample, the polarization of the IR beam is detected by a grid analyzer and then is focused on the detection head through a suitable optical system.

Finally, high resolution transmission electron microscopy (HRTEM) observations of cross-section specimens were performed in a JEOL 2011 electron microscope working at 200 kV. Cross-sectional samples were prepared first by mechanical etching and followed by ion milling with Ar^+ ions. The accelerating voltage was first 5.5 kV and was gradually decreased to 3.5 kV, as the thinning was going on. The angle of incidence of the beam was about 10° in the beginning and 3–4° at the last step of the thinning.

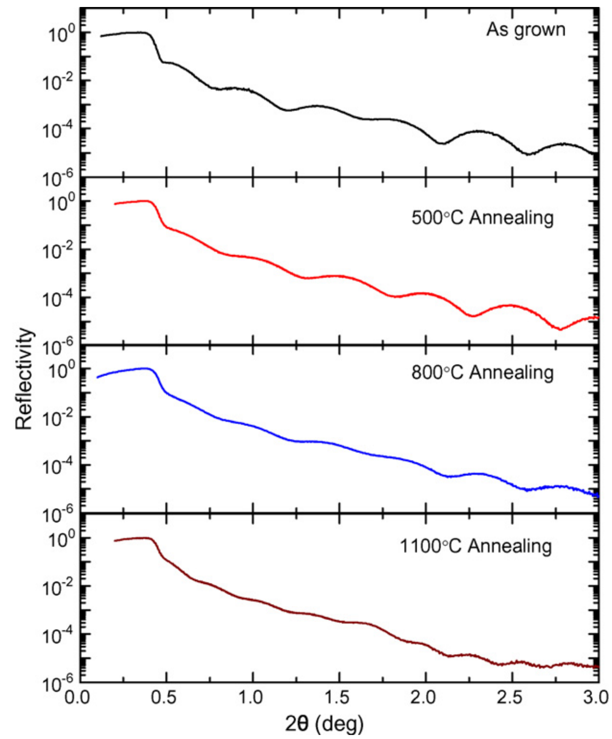

Fig. 1. The XRR spectra of the samples before and after annealing.

3. Results and discussion

The growth of the SiO/SiO_2 multilayer can be achieved by various techniques [10–12]. The high temperature annealing (up to 1100 °C) results the phase separation of the ultra-thin SiO layers and formation of Si nanoparticles surrounded by amorphous SiO_2, which described by the equation $SiO_x \rightarrow x/2\ SiO_2 + (1 - x/2)Si$ [11]. Alternatively, a-Si/SiO_2 systems can have the same results during annealing [13].

The processes take place during annealing can be divided to two stages [11,12]:

Stage 1 (300–900 °C): Rearrangement of SiO and SiO_2 components and initialization of the nc-Si nucleation.

Stage 2 (900–1100 °C): The phase separation of nc-Si and SiO_2 has finished and Si cluster are being further crystallized. Further, annealing does not have any effect on Si–O bond.

X-rays reflectivity (XRR) take advantage of the small wavelength ($\lambda_{Cu\ K\alpha} = 0.154$ nm) of X-rays, which is appropriate for the structural study of multilayered system. XRR was applied in the range from 0° to 3° and the spectra for the samples are depicted in Fig. 1. At angles below critical angle (θ_c), which is proportional to the mass density, there is the plateau indicating the region of the total reflection of X-rays and for angles above θ_c the reflectivity decays almost exponentially. Additionally, due to the layer thickness interference fringes appear in the spectrum. The data were fitted using a model consisted of $SiO_2/(SiO/SiO_2) \times 3$/c-Si and using Parrat's formalism combined with a Nevot-Croce factor for the description of the surface and interface roughness [14,15]. Thus, thickness, roughness and density of the film can be calculated. What was found from the above analysis is that for the SiO layers the thickness is decreasing and the average density of the multilayer is increasing with the increase of annealing temperature as it is shown in Fig. 2. This densification can be assigned to the dissociation of SiO_x, which enhances the formation of the denser SiO_2 and Si compounds. In the case of the sample annealed at 1100 °C the model used for the lower temperatures failed describe the data well. This is rather expected due to the phase separation and the breakdown of the layered structure that are taking place at this temperature. To overcome this problem we replaced the SiO layers with Si layers and the whole analysis gave a total thickness of 28 nm approximately. The phase separation that is taking place at this temperature is one of the reasons for the

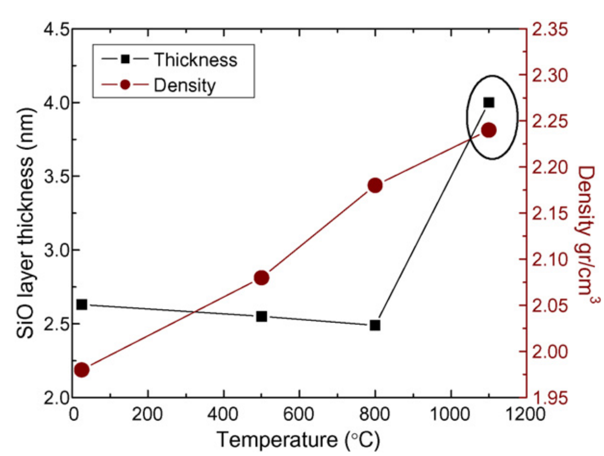

Fig. 2. The average density (circles) and the thickness (rectangle) of the SiO layers and with the annealing temperature. The point in the circle corresponds to the model $SiO_2/(Si/SiO_2) \times 3$/c-Si used for the description of the data.