Ge nanocrystals in magnetron sputtered SiO₂

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Ge nanocrystals in SiO₂ layers have in particular been produced by either ion implantation of Ge into SiO₂ layers or by magnetron sputtering of SiO₂ co-doped with Ge, in both cases followed by heat treatment. Only a few reports of Ge nanoclusters formed in chemical-vapor-deposited SiO₂, co-doped with Ge, have appeared [7–9]. In most of these systems, the onset of Ge nanocluster formation is found at temperatures of about 500 °C, and subsequent growth in size of the nanoclusters with increasing temperature has been reported. The formation of crystalline Ge nanoclusters has also been reported; however, it is not clear under which processing conditions the Ge nanoclusters become crystalline. In both ion implanted and magnetron sputtered Ge nanocluster/SiO₂ systems, non-uniform Ge nanocluster size distributions are reported in which the surface layer of the SiO₂ film is partly or completely depleted of nanoclusters [10].

Theoretically, nanocrystalline Ge (nc-Ge) has been shown to emit light more efficiently than Si nanocrystals [11, 12]. However, efficient interband radiation from nc-Ge has not yet been achieved, as it has in the case of Si nanocrystals. This lack of interband light from nc-Ge is believed to be due to defects associated with the Ge/SiO₂ interface which quench the light from nc-Ge [13].

The present investigation was undertaken in order to find optimal processing conditions of Ge nanoclusters in SiO₂ layers magnetron sputtered on Si substrates, in particular with respect to their structural characteristics. Such an investigation was felt appropriate with a view to establish a foundation for studies of the optical activity of the nanoclusters. Some of the questions we wanted to address were: (1) under which conditions is a uniform distribution of Ge nanocrystals formed throughout the SiO₂ layer, (2) which are the processing conditions for forming crystalline Ge nanoclusters, and (3) how well can the size distribution of the nanoclusters be controlled?

1 Introduction

During the last decade or so, group IV nanocrystals embedded in SiO₂ have attracted much attention. The main focus has been on Si nanocrystals in SiO₂ [1], but also Ge nanocrystals have been studied [2–4]. The primary reason to study group IV nanocrystals is twofold. Firstly, the nanocrystals have been shown to serve as efficient light emitters and are, therefore, interesting for optical applications. Secondly, these materials are fully compatible with silicon-based electronics that completely dominates the electronic industry. This makes group IV nanocrystals a promising candidate in optoelectronic applications. Moreover, the blue shift of the emitted light with decreasing nanocluster size is an interesting feature which has the potential of making it possible to tune the wavelength of the emitted light within certain limits [5, 6].

Received: 8 July 2005/Accepted: 14 December 2005
Published online: 13 January 2006 • © Springer-Verlag 2005

ABSTRACT Structural and optical properties of Ge nanocrystals in SiO₂ films created by magnetron sputtering and heat treatment have been investigated. The formation of nanocrystals is found to be influenced by the temperature of heat treatment and the Ge concentration in the films. After heat treatment at 1000 °C nanocrystals are present throughout the film, with the exception of a region close to the surface that does not contain nanocrystals. This effect is assigned to oxidation of Ge in this part of the film. The size distribution of the nanocrystals is analyzed by transmission electron microscopy for a range of deposition and heat-treatment parameters. By analyzing the transmission electron microscopy images, it is possible to estimate the fraction of nanoclusters that are crystalline for a given set of growth parameters. This analysis shows that all the nanoclusters are created in the crystalline state. Raman spectroscopy is employed to probe the Ge–Ge bonds. In combination with transmission electron microscopy, this information can be used to distinguish between growth modes such as nucleation or Ostwald ripening. The photoluminescence spectra exhibit a strong broad line at 625 nm, the presence of which is demonstrated to correlate to the presence of Ge nanocrystals.

PACS 61.46.+w; 78.55.-m; 78.67.-n

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sure from the argon ions used for sputtering was $10^{-2}$ mbar. The thickness of the films was 500 nm, and the Ge concentration in the films was either 1.3 at. % or 3.5 at. % as determined by Rutherford backscattering spectroscopy (RBS). Below, we will refer to these concentrations as the low and high concentrations, respectively. The heat treatment of the films was performed in a tube furnace under a flow of $N_2$ (and atmospheric conditions outside the furnace). The time of heat treatment was 30 min, and the films were allowed to cool down in the $N_2$ ambient to prevent oxidation at high temperatures. For each Ge concentration a series of films heat treated at 500, 600, 700, 800, 900, and 1000°C was prepared. RBS experiments were performed with a beam of alpha particles of energy 1.5 MeV. During RBS measurements the pressure was $10^{-5}$ mbar, and the sample was not heated during measurement. Secondary electrons were suppressed by an electron suppressor. Transmission electron microscopy (TEM) studies were performed using both cross-section (XS) and plane-view (PV) TEM samples with a Philips CM20 instrument with an accelerating voltage of 200 kV. The resolution of the TEM allowed us to monitor nanocrystals with sizes down to 2 nm. For high-resolution (HR) TEM a Jeol 3000F high-resolution transmission electron microscope (situated at Risø National Laboratory) was used. The TEM samples were prepared using a standard ion milling technique, and they were not heated during preparation. In the Raman studies we measured the Stokes shift of the incident 514.5-nm light from an Ar$^+$ laser. The spectra were recorded with a Renishaw RM series Raman microscope in the frequency range from 200 to 800 cm$^{-1}$ with a resolution of 1 cm$^{-1}$. For photoluminescence (PL) measurements the film was excited with the 488-nm line of an Ar$^+$ laser (power 10 mW). The spectra were taken at room temperature with a 1000M spectrometer from Yvon Jobin with a Si diode as the detector. The excitation light was removed with a 550-nm high-pass wavelength filter.

3 Results and discussion

3.1 Rutherford backscattering spectroscopy

In Fig. 1 the sections of the RBS spectra corresponding to backscattering from Ge in the films are shown. For simplicity, only the as-grown spectrum and spectra corresponding to temperatures with which changes are induced in the Ge profile are shown. The as-grown spectra show a homogeneous distribution of Ge throughout the films. It is evident that the distribution of Ge is not stable in the SiO$_2$ matrix at the highest temperatures. In the case of the low Ge concentration and 1000°C heat treatment (Fig. 1a), a significant pile-up of Ge both at the surface and at the Si/SiO$_2$ interface takes place. This pile-up is accompanied by a significant lowering of the Ge concentration in the central part of the film. In the case of the high Ge concentration, the spectra evolve in a more gradual manner. Here heat treatment at 1000°C results in a pile-up of Ge at the Si/SiO$_2$ interface along with a loss of Ge in the central part of the film. In the sub-surface region, an advancing depletion of Ge takes place accompanied by an increase in the Ge concentration at the surface. It will be demonstrated in Sect. 3.2 that the region of interest, with respect to the creation of nc-Ge during heat treatment at 1000°C in the case of the high Ge concentration, is between the dashed lines in Fig. 1b. This central region corresponds to the part of the film where the surface effects are not present. For both Ge concentrations it is also clear that there is less Ge left in the sample after heat treatment at 1000°C than in the as-grown case. This indicates that at 1000°C Ge has evaporated from the sample. At lower temperatures of heat treatment the long-range redistribution of Ge is much less pronounced.

The observed features can be explained within a model developed by Borodin et al. [14], which they have used to describe the evolution of a Ge ion-implanted profile in a SiO$_2$ layer during annealing. In this model only two species are mobile in the SiO$_2$ matrix at the temperatures in question, namely...