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Structural and optical properties of Si-nanoclusters embedded in silicon dioxide

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Abstract

In this paper we report on light emission from silicon nanostructures embedded in silicon oxide prepared by rf co-sputtering in argon of pure silicon and silicon dioxide. The concentration of excess silicon was varied in the range 0.5–1.8%. Specimens were subjected to thermal anneals up to 1100 °C in nitrogen atmosphere. The effects of annealing on photoluminescence spectra and crystallization of a-Si as well as the chemical feature of the Si 2p core level were studied. Stable blue and green luminescence was observed with intensities strong enough to be visible to the naked eye from samples which were excited by ultraviolet light. In the as-deposited samples and after anneals below 600 °C, the luminescence around 440 nm is ascribed to structural defects in the SiO_2 film. For anneals above 600 °C the emissions at wavelengths 370, 445 and 537 nm were attributed to excitons bound at structural defects in an interfacial layer between a silicon nanoparticle with crystalline core and surrounding amorphous SiO_2.

Keywords: Nanosilicon; Photoluminescence; XPS

1. Introduction

In recent years extensive studies have been devoted to the physics and engineering of nanostructures embedded in crystalline solids. Such studies were stimulated strongly by the novel aspects of electron quantum confinement. In addition, small particles have a large surface-to-volume ratio which as well affects their properties. Based on new fundamental parameters, such as for the electron-band structure, new phenomena may be observed. As an example, the enlargement of the valence-to-conduction-band gap in semiconductors and the fact that transitions between them can become vertical in k space has resulted in new optical properties, hitherto not existent, and of eminent importance for a material like silicon. The realization of silicon-based structures which emit light in the visible range, from the near infrared corresponding to the bulk silicon band gap at 1.1 μm to within the near ultraviolet (UV) has an enormous potential for optoelectronic applications. As such structures can be realized with techniques compatible with microelectronics processing the interest from engineering side is huge.

A number of techniques have been applied for the production of nanostructures. This has started with the method of anodic oxidation pioneered by Canham to produce porous silicon, emitting luminescent red light [1]. However, porous silicon is mechanically fragile and due to absorption of gases and impurities not stable. Alternative methods have therefore been explored. Silicon nanoparticles were produced by direct breakdown of silane (SiH_4) molecules in an intense laser beam [2,3]. Crystalline silicon particles collected on a substrate were subsequently oxidized. Straightforward implantation of silicon ions into silicon dioxide layers has also been used for controlled creation of silicon-rich non-stoichiometric glassy layers [4–7]. Methods of plasma-enhanced chemical vapor deposition were used as well, also allowing the doping of layers by impurities as nitrogen and hydrogen [8,9]. Another effective method is the co-sputtering of silicon dioxide

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and pure silicon [10–12]. In all cases the option of thermal anneal of produced structures, typically in a range of temperatures up to 1200 °C, is employed beneficially.

Results obtained in the various studies differ vastly, even within an equal technique of preparation. A multitude of light emission wavelengths has been reported. Effects of temperature of annealing also show little similarities. Apparently, the results depend sensitively on details of production parameters. Control over the parameters and their tolerances to obtain a desired result still largely has to be established.

In this paper, with the intention to clarify the origin of the light emission from silicon nanoclusters embedded in silicon dioxide thin films, a systematic study on the dependence of photoluminescence (PL) properties on various experimental parameters such as silicon concentration and annealing temperature were carried out. Also, comparison of the PL spectra of the Si,SiO_2 co-sputtered film with those of the thermally grown oxide and the sputtered SiO_2 film were made and is reported.

2. Sample preparation and spectrometer

Samples were fabricated by rf magnetron co-sputtering of silicon and silicon dioxide. On an SiO_2 target (99.99% purity) with a diameter of 3 in several small chips of silicon, each with area of 5 mm^2, were placed. The silicon source material is n type, doped with *P* to the resistivity of 5–10 Ω cm. The number of silicon chips, from 2 to 17, is used for control of the concentration of Si in the produced SiO_2:Si films. The silicon chips are arranged in such a way that best uniformity is obtained in the sputtered films. Films were deposited on thermally oxidized silicon substrates with 3 in diameter. By varying the duration of sputtering time films with thickness in the range 30–800 nm were produced. Thermal annealing treatments were given to the samples in a temperature range of 300–1200 °C and for durations of time from 30 min to 2 h. PL intensity was measured using SPEX Fluorog-3 model 322. PL was excited by illumination at wavelengths of either 265 or 365 nm from a 450-W xenon short arc focussed to a spot diameter on the sample of 0.6–1.5 mm. Emitted light was dispersed by a double 1200 groove/mm gratings monochromator, and detected with photomultiplier tube. Samples were kept at room temperature during PL measurements.

3. Results and discussion

Immediately after deposition already a bright luminescence, visible to the naked eye, is observed from the SiO_2:Si film. Fig. 1 shows the emission of a 400 nm thick layer with a silicon concentration of 1.3%, produced by sputtering from 12 silicon chips in the target. There is a maximum emission at 440 nm (2.82 eV). The brightness of the blue emission is shown to be comparable to the red light emission of a porous silicon sample with the maximum at

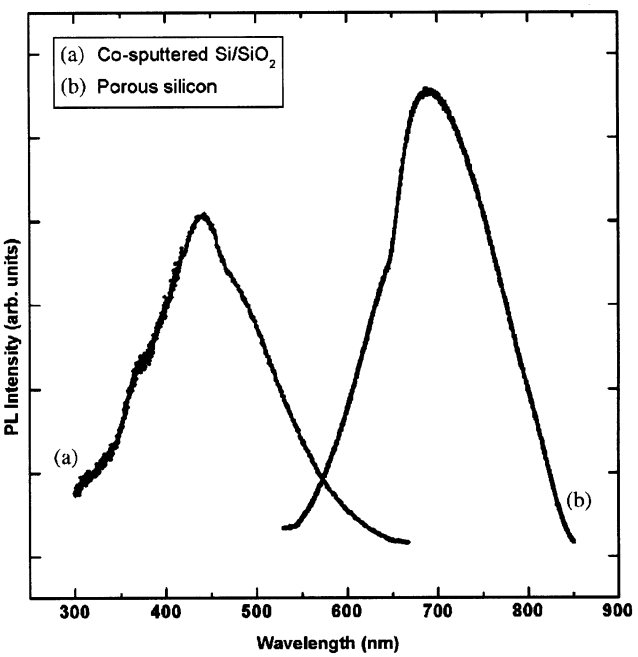

Fig. 1. PL spectrum of (a) an as-deposited SiO_2:Si film, thickness 400 nm, Si concentration 1.3%, compared to (b) porous silicon. Samples at room temperature. UV light excitation at 265 nm.

690 nm (1.80 eV), measured in the same set-up. For a similar study of co-sputtered as-deposited samples no such emission was reported [10].

The thermal stability of the luminescence was probed by annealing the samples at increasing temperatures. It was found that anneal at 600 °C for 1 h completely removes the light emission. Upon further anneal treatment at higher temperatures luminescence reappears. A clear emission is again obtained by anneal at 800 °C. The spectrum shown in Fig. 2 for a sample with 1.3% silicon concentration exhibits three bands with maxima at 370 nm (3.35 eV), 445 nm (2.79 eV) and 537 nm (2.31 eV), respectively. Increase of anneal temperature to 1000 °C enhances the 370 and 445 nm emissions considerably, but has no effect on the 537 nm band. A further increase of anneal temperature to 1100 °C almost completely removes all luminescence.

Results of luminescence were found to depend also strongly on the concentration of the excess silicon in the SiO_2 layers. Spectra for co-sputtered silicon concentrations of 0.5%, 0.9%, 1.3% and 1.8% are shown in Fig. 3. All samples had the thickness of 400 nm and were annealed for 1 h at 800 °C. The intensity increases when the concentration rises from 0.5% to 1.3%, but non-linearly, and falls rapidly for the higher concentration of 1.8%. Also the number of peaks in the spectra, probably related to luminescent centers or mechanisms, changes from one for the lowest concentration, via two for the intermediate concentrations to three for the most non-stoichiometric composition, in the spectral range from 400 to 650 nm.

Additional experiments were performed in which the film thickness was varied and others in which the time

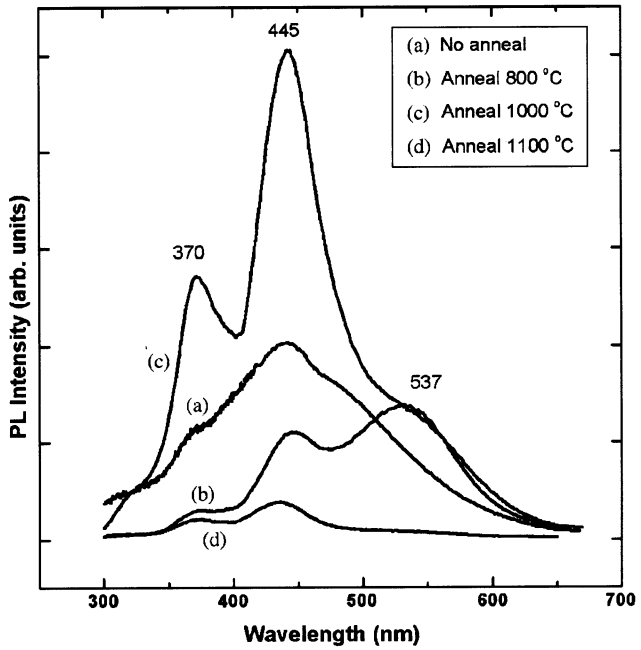

Fig. 2. PL of Si/SiO_2 co-sputtered films. Shown is the spectrum of an as-deposited SiO_2:Si film, and after anneal in nitrogen atmosphere at 800, 1000 and 1100 °C. Films with Si concentration of 1.3% and thickness of 400 nm. All spectra excited by 265 nm UV light and observed at room temperature.

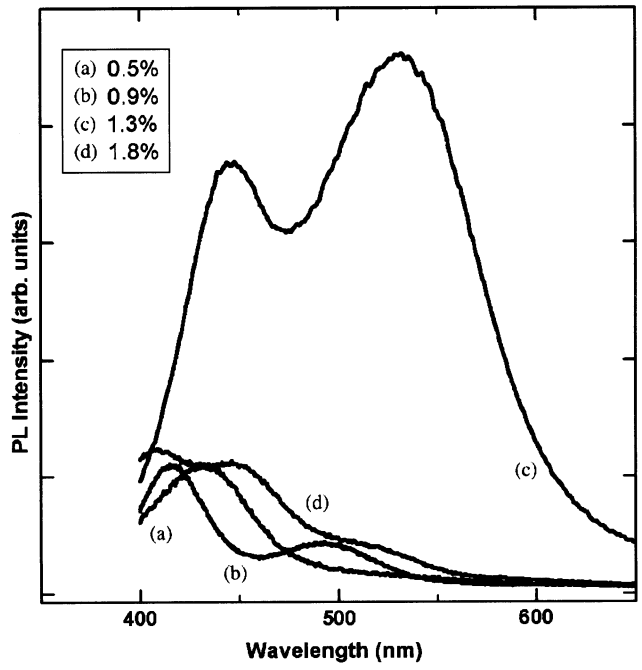

Fig. 3. Dependence of the PL spectra on silicon concentration in the SiO_2:Si co-sputtered films. All samples thermally annealed at 800 °C for 1 h in nitrogen atmosphere. Film thickness 400 nm. Luminescence excited by UV light of 365 nm wavelength.

dependence of center growth or loss was recorded in an isochronal anneal sequence. As such experiments were less systematic yet, they will not be reported here.

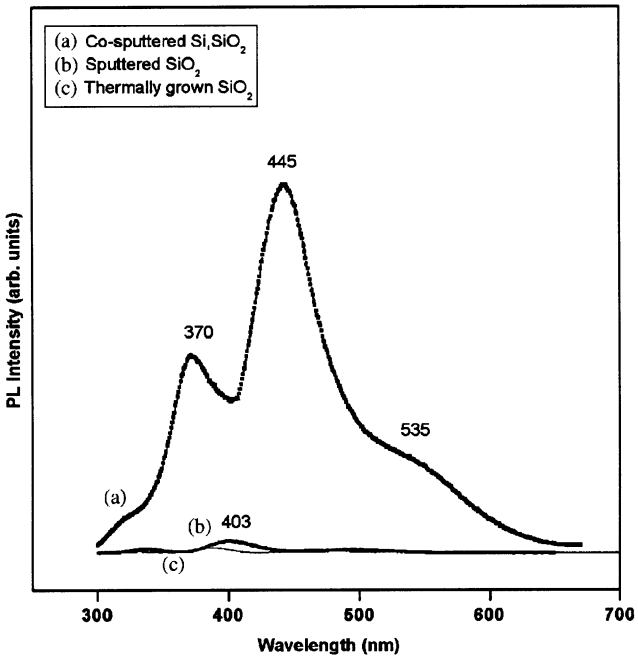

Fig. 4. A comparison of the PL spectra and intensities of (a) Si/SiO_2 co-sputtered film, (b) SiO_2 sputtered film, and (c) thermally grown silicon dioxide film. All films have thickness 400 nm.

Visible luminescence has been reported to be emitted from UV excited plain SiO_2 layers [13]. In spite of that observation it is generally assumed and confirmed that some silicon-related nanostructures are required for the efficient light emission process. In order to verify this assumption for the present kind of experiments sputtered films were prepared without the simultaneous co-sputtering of silicon. The result as presented in Fig. 4 demonstrates the strongly reduced optical activity of such a film. Also an oxide grown thermally does not show any appreciable light emission. Fig. 4 presents the comparison for the film, which was annealed at 1000 °C for 1 h. A similar result is obtained for the as-grown film. It supports the conclusion that light emission requires the presence of some kind of silicon-related defect or nanostructure.

The existence of silicon nanocrystals in the SiO_2:Si films was identified by X-ray photoelectron spectroscopy (XPS) measurement. Typical XPS spectrum of silicon 2p core level of the SiO_2:Si film is shown in Fig. 5. Only the signal of SiO_2 around 103.5 eV is detected in the as-deposited film. A peak at 99.5 eV, which results from the crystalline silicon phase, is observed after annealing the sample at 1000 °C for 1 h in nitrogen gas environment. It is important to note that the formation of nanocrystalline silicon particles correlates with the remarkable increase of the 370 and 445 nm PL bands (Fig. 2).

It was found in the experiments that after a thermal anneal at 600 °C all optical activity was absent. This observation indicates a natural division between a mechanism active at low temperatures and another one following the high-temperature treatment. In the low-temperature

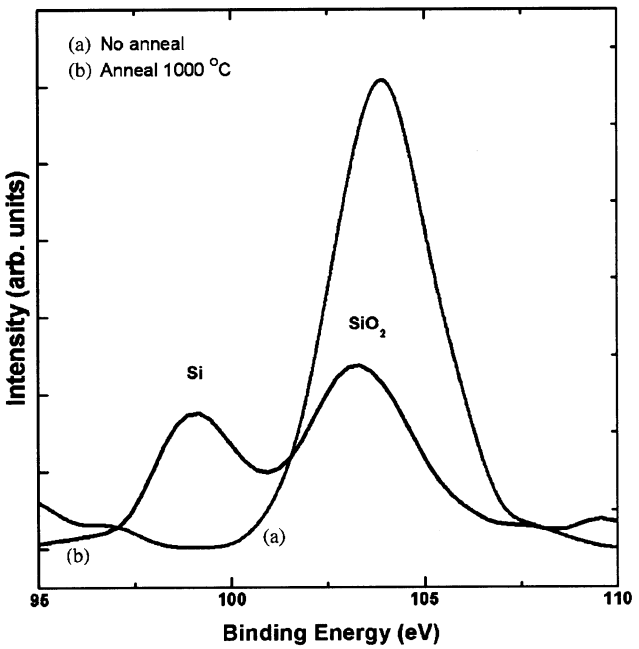

Fig. 5. Typical XPS spectra of the silicon 2p core level for the co-sputtered Si/SiO_2 films which were as-deposited, annealed in N_2 at 1000 °C.

regime there has been no opportunity yet for the as-deposited silicon atoms in the film to form clusters. Isolated silicon atoms are expected to be present. The related film will show a similarity to films as produced by ion implantation. The non-stoichiometric excess of silicon atoms will lead by necessity to vacancies on oxygen sites. The E′ center is a well-known example of such a defect. E′ centers can be monitored in electron paramagnetic resonance by the associated spectrum with isotropic g factor $g = 2.0023$. Following ion implantation the disappearance of the EPR signal of E′ centers in parallel with diminishing luminescence was found to occur at 600 °C thermal anneal [7,14]. In analogy to this result the luminescence activity in as-deposited co-sputtered samples is ascribed to a small structural defect. This defect is not necessarily the E′ center as the luminescence observed after ion implantation occurs at a different wavelength. Defect-related luminescence does not shift in wavelength upon annealing, in agreement with the observations made.

Upon thermal anneal at the higher temperatures above 600 °C, the silicon atoms tend to aggregate into clusters with crystalline core. The process has been observed in many studies by transmission electron microscopy [2,3,6,8,13]. These silicon nanoparticles with the core made only of silicon are embedded in the silicon dioxide matrix. There exists an interfacial region with an intermediate chemical composition SiO_x, with $0<x<2$, typically SiO. The band gap in this interface layer is smaller than that of the silicon core which is increased above the bulk silicon value of 1.18 eV by quantum confinement. The gap in the insulator silicon dioxide is near 8 eV. Excitons created by the excitation light will be trapped in the interface layer binding themselves there to structural defects [2]. Observed luminescence is due to the electron–hole recombination of these bound excitons. The energy will depend on the trapping defect. In the present experiment the observed emissions are at 370, 445 and 537 nm. In the initial stages of high-temperature anneal the luminescence intensity will increase as the result of gradual formation of more silicon nanoparticles. Most efficient for luminescence are the smaller-sized nanoparticles. At further thermal anneal at higher temperatures the increased size of nanoparticles will lead to decrease of luminescence as actually is observed in the experiment. As the emitted energy will be determined by the structural defects the wavelength does not change with annealing status, in agreement with observations in this and similar experiments, in contrast to its intensity. The prevailing explanation for luminescence of porous silicon is the phenomenon of quantum confinement. For this process a dependence of emission wavelength on nanoparticle size is expected. Theory predicts an energy of 2.0 eV for core diameters of 4 nm, decreasing to 1.3 eV for the 10 nm core size [2]. As such shifts were not observed for the co-sputtered samples, quantum confinement is not proposed as the effective luminescence mechanism.

Acknowledgements

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