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Mechanism of light emission in low energy ion implanted silicon

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ABSTRACT

A silicon wafer implanted with a single low energy (42 keV) silicon ion beam results in strong luminescence at room temperature. The implantation results in the formation of various luminescent defect centers within the crystalline and polymorphous regions of the wafer. The resulting luminescence centers (LC) are mapped using fluorescence lifetime imaging microscopy (FLIM). The emission from the ion-implanted wafer shows multiple PL peaks ranging from the UV to the visible; these emissions originate from bound excitonic states in crystal defects and interfacial states between crystalline/amorphous silicon and impurities within the wafer. The LCs are created from defects and impurities within the wafer and not from nanoparticles.

1. Introduction

Silicon, an indirect bandgap semiconductor, is known to have over one hundred luminescence centers (LCs) [1]. Although various luminescence centers in silicon are reported, none of these are deemed suitable for practical application due to a lack of basic understanding on the nature of these emissions. Efficient light emission from Si may play an important role in many technological innovations including monolithically integrated optoelectronic circuits and inexpensive LEDs. Silicon is both inexpensive and well integrated in industry for its electrical properties, making it an attractive material for industrialization of optoelectronic devices.

Light emission from silicon was previously observed from silicides, dangling bonds, quantum confinement, and porous silicon (PS) [2–5]. Ion beam implantation, followed by other treatments such as annealing, is currently a prevalent technique for formation of light emitting silicon systems [6]. The origin of light emission in ion-implanted Si based semiconductors has been primarily attributed to originate from nanoparticles that are formed on annealing of the samples following the implantation process [2,6,7]. These emissions are predominantly considered due to indirect or quasi-direct transition in the near-infrared wavelength region and have recently been observed in the UV wavelength regime [2]. These conclusions are based on observation of nanoparticle formation using transmission electron microscopy and resulting far field luminescence from the implanted sample. However, to the best of our knowledge no investigations were done on luminescence from ion beam implanted samples on the microscopy of the light emission from these ion-implanted samples that had traces of nucleation of nanoparticle formation in the substrate. These nanoparticles in ion-implanted samples are reported to typically emit via intraband transitions [8], and surface traps on the interfaces of Si NCs and the surrounding dielectric [6]. These transitions are dominated by Auger recombination process and are generally inefficient at room temperature. There are also recent unsubstantiated reports of UV emission due to the direct transition from the ion-implanted silicon nanoparticles [2]. In this study, we present the spatial map of the light emission from ion-implanted silicon using high resolution optical microscopy in the UV–visible region. By investigating the origin of emission at various energies, we find that the contribution from defect bound excitons result in strong light emission.

Irradiation with energetic particles, including ions, is known to create various luminescent defect centers within the lattice of silicon [1,9,10]. Luminescent defect states generally have excellent photostability, high quantum yield, and may be formed within the smallest amount of crystalline matter or any macroscopic size sample [11].

2. Experimental

Phosphorous doped, n-type Si(1 0 0) wafers were obtained from University Wafer, Boston, MA,USA. The wafers were implanted by Core Systems, Sunnyvale, CA,USA with Si^+ ions with an energy of 45 keV, current of 22 μA, 7° tilt, and an ion dose of $5\times10^{15}\,cm^{-2}$ into an area of 133.4 cm^2 of the wafer. The implanted wafer was also etched in potassium hydroxide (KOH)

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solution to remove any implanted silicide layer as well as a portion of the amorphous silicon matrix.

The internal structure of the implanted wafers was observed with a high resolution analytical TEM (AHRTEM). Annealing was performed in a chemical vapor deposition (CVD) chamber with an Argon atmosphere. Far field PL from the wafers was mapped using a Fluorescence Lifetime Imaging Microscope (FLIM) PicoQuant MicroTime 200 with a 370 nm semiconductor laser diode. Temperature dependent PL was taken with a Horiba-Jobin Yvon's TRIAX 320 spectrometer and the excitation was provided by an Omnichrome 56 series continuous wave HeCd laser. Time resolved photoluminescence was measured with a Hamamatsu synchroscan streak camera with a resolution of 30 ps. The excitation source for lifetime measurements was a Spectra Physics Mai-Tai Ti: Sapphire mode-locked laser. The 700 nm laser output was doubled with a nonlinear BBO (β-Barium Borate) crystal to 350 nm.

3. Results

3.1. Structure and morphology

High resolution transmission electron microscopy (HRTEM) micrographs reveal that this ion implantation initially results in the formation of an amorphous layer with its depth depending on the penetration distance or the momentum of the implanted ions. However the crystalline nature can be recovered by annealing the samples at 700 °C. PL from the wafer was observed after just the implantation, after implantation and annealing, and after etching the wafer in KOH. Since TEM shows no nanoparticles for all samples (Fig. 1a) the luminescence observed from silicon in this experiment is not associated to the formation of nanoparticles as reported in various previous reports [2,6–8]. Instead the LCs are lattice defect sites formed at the interfaces within the amorphous layer within the wafer and show no signs of photo bleaching. The emission is stable and the wafer may be stored in air for months and sonicated in organic solvents without any discernable changes to the emission. Fig. 1a shows the sample structure after implantation for both pre-annealed and after annealing at 700 °C. The depth of the implanted region is found to be ~115 nm using TEM as shown in Fig. 1a-i, which is in agreement with the Stopping and Range of Ions in Matter (SRIM) simulations software [12]. Defect and interfacial states are created throughout the amorphous region. Fig. 1a-ii shows a close up of Fig. 1a-i to enthsize the none uniform nature of the amorphous region near the surface of the wafer. However after annealing the sample at 700 °C in Argon, the properties of the implanted layer changed. A flat interface between the SiO_2 layer and crystalline Si is observed as shown in Fig. 1a-iii. This region however may not be excited optically due to the absorption of the silicon layer above it. The amorphous layer is no longer present, however many feature analogous to the irregularities of Fig. 1a-ii are visible even at lower magnification. The resulting wafer was found to luminesce from the ultraviolet to the visible wavelength region. Annealing resulted in a higher concentration of LCs, but no new emission energies and no emission energy shifts were observed due to annealing. Etching in potassium hydroxide, thereby removing the oxide layer, also had no effect on the nature of the emission. The emission from the annealed samples is significantly brighter due to formation of the crystalline layer and the localization of defects. Thus light emission from silicon was achieved using only silicon as the implantation source and target.

3.2. Spatial distribution of luminescence centers

In order to spatially map the optical emission from the Si implanted sample, luminescence microscopy with submicron resolution was performed. Fig. 1b presents a typical $30 \times 30\ \mu m^2$ fluorescence imaging microscopy map of the sample surface at room temperature for the unannealed sample. Luminescence was observed at a single emission energy, 2.97 eV, the false color scale represents the average lifetime of the observed emission. Black regions in the image correspond to parts of the sample surface has very weak or low light emission, and thus they have no measureable PL lifetimes. Far field measurements confirm this scattered distribution of the emission centers. The distribution of the LCs throughout the silicon wafer arises from the self-assembly of LCs which are governed by the concentration of impurities and defect centers along the crystalline silicon lattice.

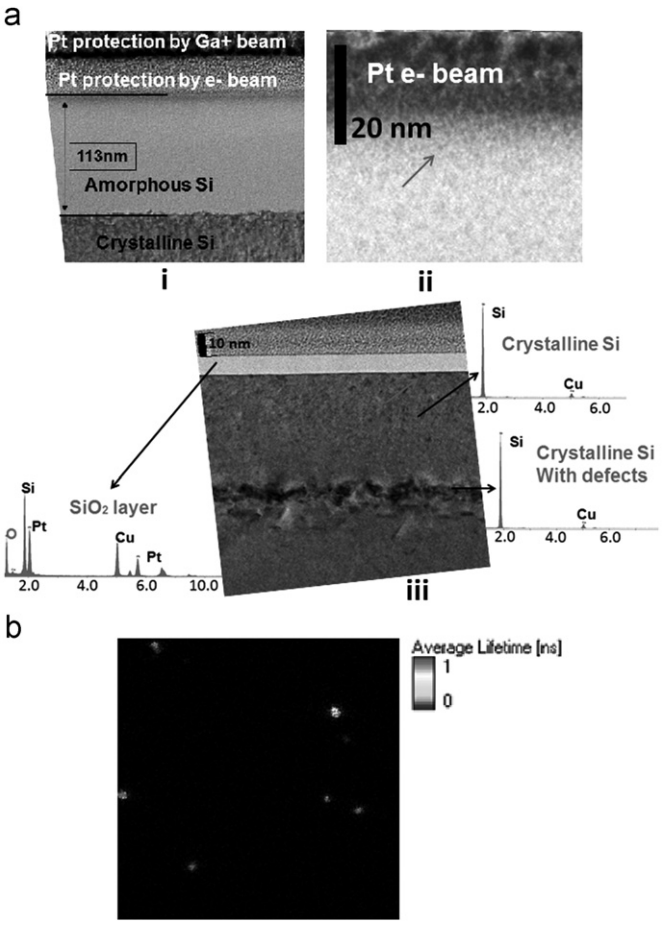

Fig. 1. (a) HRTEM image of silicon ions implanted with 42 keV energy on a silicon substrate (i) pre-annealed (ii) high magnification of (i) at the surface; (iii) post-annealed with EDX from different regions. (b) Spatial mapping of luminescence: FLIM image of a 30 $\times 30\ \mu m^2$ region of the wafer, observed at 2.97 eV of the silicon wafer as implanted with silicon. The color bar also indicates the electron–hole recombination lifetime of the carriers (for interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

3.3. Temperature dependence and time resolved photoluminescence spectra

Photoluminescence (PL) was taken at temperatures ranging from 15 to 300 K (Fig. 2). The blue luminescence (Fig. 2a) originates from known silicon oxide defect states, and along with the Energy-dispersive X-ray spectroscopy (EDX) (Fig. 1a-iii) and Fourier transform infrared spectroscopy (FTIR) (Fig. 3) data, is proof of the presence of oxygen within the wafer. Oxygen is a common impurity in silicon wafers, and it is observed in the present system. The presence of the infrared absorption band at ~1250 cm^{-1} which is due to the -SiO_3 group has been reported