

Enhanced photoluminescence from nanopatterned carbon-rich silicon grown by solid-phase epitaxy

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(Received 23 May 2007; accepted 5 July 2007; published online 3 August 2007)

Photoluminescence from the dicarbon G center in nanopatterned silicon is investigated. Enrichment of silicon with carbon atoms has been achieved by solid-phase epitaxy. When this carbon enrichment is combined with nanopatterning, the authors found a 33-fold increase in the G line emission intensity to a level that is comparable to the band-edge photoluminescence. Significant linewidth broadening is observed and is attributed to lattice strain associated with the nanopatterning. © 2007 American Institute of Physics. [DOI: 10.1063/1.2766843]

Silicon photonics is a rapidly developing field of technology that will enable the fabrication and integration of optical components with silicon complementary metal-oxide semiconductor technology.¹⁻⁴ Recently, stimulated emission and optical gain, characteristics of lasing, at 1.28 μm have been observed in periodic nanopatterned crystalline silicon under optical excitation at cryogenic temperatures.⁵ The source of this emission is attributed to the bistable carbon-substitutional-carbon-interstitial (C_sC_i) complex known as the G center. The emissive G centers were found as early as 1960's in irradiated silicon.⁶ Early studies were interested in investigating the effects of radiation damage via electron, ion, or gamma ray bombardment, mostly for the purposes of assessing, containing, and suppressing the undesirable consequences in electronic applications.⁷⁻¹⁰ These bombardment techniques necessarily inflict damage on the entire lattice and thereby increase both the electronic and optical losses. Previously, electroluminescence from G centers was demonstrated in an electron-irradiated p - n junction.¹¹

Substitutional carbon atoms are necessary for G -center formation and occur naturally in silicon wafers at concentrations between 10^{15} and 10^{17} at./cm³ depending on the crystal growth technique.⁹ A G center is created when a mobile interstitial carbon atom (C_i) binds with a substitutional carbon atom (C_s). The process is understood to proceed as follows: silicon interstitials (Si_i) are created as the result of a damage event. A mobile Si_i can then migrate to a C_s . The C_s then gives its lattice site to the Si_i in a process known as the Watkins exchange mechanism.¹² The resulting mobile C_i can then migrate until it binds to a C_s forming a C_sC_i pair, known as the G center. Thus, G -center creation depends both on the density of C_s present in the lattice¹³ and on the density of introduced Si_i 's.

In Ref. 5 a membrane of anodized aluminum oxide (AAO) containing a hexagonal array of throughpores was placed on a silicon-on-insulator (SOI) wafer and subsequently used as an etch mask for reactive ion etching (RIE).

The result was a hexagonal mesh of nanopores with 50 nm diameter and 100 nm pitch. In Ref. 5 it was unclear whether the carbon from which the G centers were created came from the native carbon in the silicon or from an external source introduced during the RIE process. Understanding and controlling the mechanisms involved in the creation of G centers by nanopatterning are critical to the further investigation into properties and possibilities of G -center luminescence in this system.

In the present study, the G centers are intentionally introduced via nanopatterning. The advantage of G -center introduction via nanopatterning for the purpose of fabricating light-emitting devices is that the damage to the lattice is contained in thin shells at the walls of etched pores⁵ while leaving the majority of the lattice in its pristine form. We report G -center photoluminescence from nanopatterned carbon-rich SOI obtained by solid-phase epitaxy. A 33-fold increase in G line intensity compared to unprocessed SOI is observed. These results indicate that the G centers are formed from carbon in the silicon crystal prior to the RIE

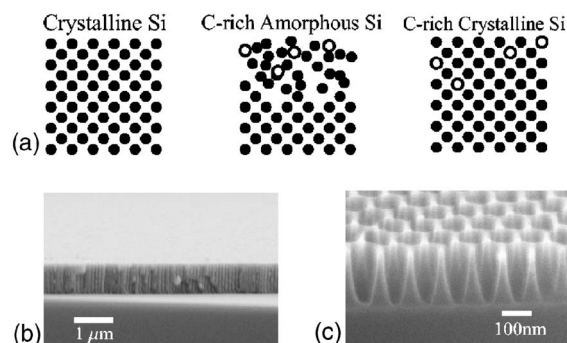


FIG. 1. Schematic of the fabrication process. (a) A pristine Si lattice is amorphized by bombarding with Si ions and is then implanted with C ions. The crystal is subsequently regrown by annealing using the undamaged bottom layer as a seed layer. (b) SEM image of an AAO membrane atop a SOI wafer. (c) SEM image of an array of nanopores in the SOI wafer resulting from RIE through the AAO etch mask. In this image the AAO has been removed.

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TABLE I. Parameters for implantations utilized for C-enriched Si fabrication. The rapid thermal annealing (RTA) was performed in an N_2 ambient in the temperature range of 650–900 °C for 10 s. The best results were obtained for RTA performed at 800 °C.

Step	Species	Dose (cm^{-2})	Energy (keV)	Target temperature (°C)	Mean implant depth (nm)	End of range depth (nm)
Amorphization	Si	10^{15}	65	-120	95	200
Implantation	C	10^{14}	18	24	60	120

process and also suggest a way to increase the emission efficiency of this system.

Carbon doping of silicon using conventional ion implantation is limited by the low solid solubility of carbon in silicon (on the order of 10^{17} at./ cm^3). Carbon ion implantation at levels exceeding the solid solubility results in a precipitation of SiC. Instead, solid-phase epitaxial (SPE) regrowth is employed. This method takes advantage of the increased carbon solubility at the interface between crystalline silicon and amorphous silicon.¹⁴ The silicon crystal is “preamorphized” by Si+ ion implantation prior to the C+ ion implantation. The crystal is then annealed to induce SPE regrowth. Substitutional carbon concentrations of up to 7×10^{20} at./ cm^3 were achieved using this method.¹⁵ In this work, *p*-type SOI (250 nm Si on a 3 μm buried oxide layer, 20 Ωcm , commercially available from Soitec) was used. The details of the C-enriched Si fabrication are given in Table I.

The concentration of the implanted carbon atoms was approximately 10^{19} at./ cm^3 , 400 times more than the manufacturer-specified carbon content of 2.5×10^{16} at./ cm^3 . Substitutional carbon in silicon is usually detected by its local vibrational mode IR absorption at 607 cm^{-1} .⁹ In this study, the maximal absorbance at 607 cm^{-1} expected if all implanted carbon atoms were incorporated into substitutional sites was less than 0.1%. This low absorbance was due to the fact that only a thin layer (~ 100 nm) of carbon-rich silicon was present in the samples, making the detection of this ab-

sorbance line below the sensitivity limit of available Fourier transform infrared instrumentation. Therefore, we could not meaningfully and quantitatively evaluate the fraction of C that was actually incorporated as C_s .

The periodically nanopatterned C-enriched Si structure shown in Fig. 1(c) was fabricated using the highly uniform self-organized AAO nanopore membrane as an etch mask.^{5,16} The freestanding AAO membrane was lifted from an aqueous solution by a C-enriched Si wafer and subsequently etched in an RIE machine. The RIE conditions were as follows: Cl_2 , 20 SCCM (SCCM denotes cubic centimeter per minute at STP); BCl_3 , 5 SCCM; 50 mTorr; 100 W; 24 °C; and 6 min. A schematic of the fabrication process and a scanning electron microscopy (SEM) image of the patterned C-enriched Si are shown in Fig. 1. Figure 2 shows the photoluminescence spectra at 25 K of the nanopatterned C-enriched Si on SOI and of similarly nanopatterned SOI without carbon enrichment. The 514 nm line of an argon ion laser was used for excitation. The excitation power was 200 mW and the beam spot size was 3 mm in diameter. The emitted photoluminescence was collected using a 3 in., F/4 concave mirror and focused onto a spectrometer. The resolution of the spectrometer was calibrated using a narrow-line (200 kHz) external cavity semiconductor laser and was determined to be 0.13 ± 0.02 nm. A cooled InGaAs photodiode array was used to measure the intensity of the photoluminescence (PL). The phonon-assisted band-edge PL at 1130 nm

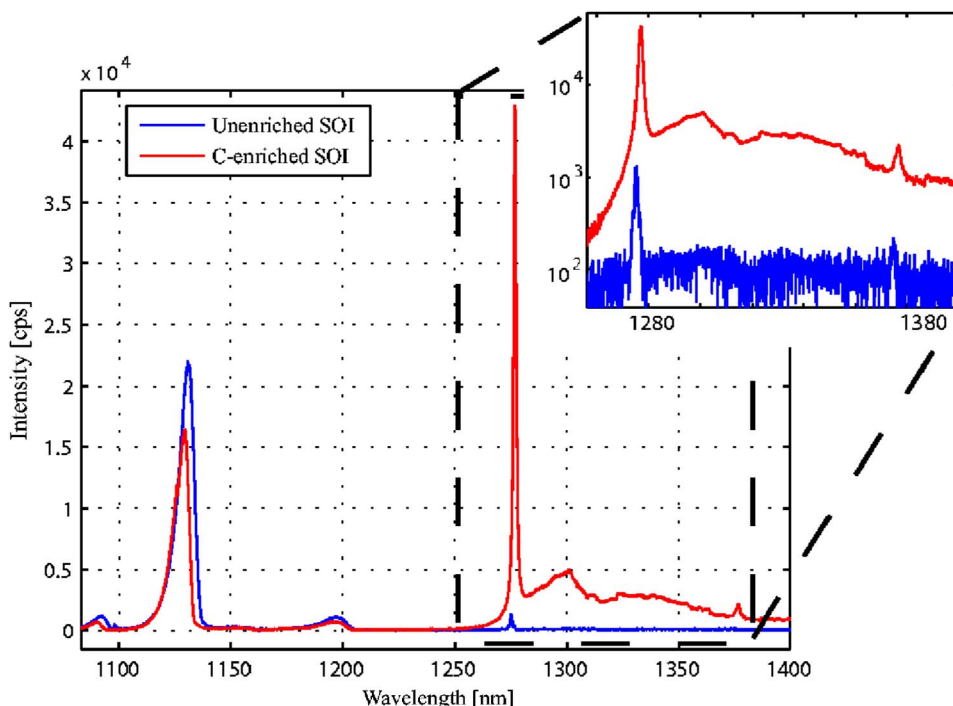


FIG. 2. (Color online) Photoluminescence spectrum at 25 K of nanopatterned Si and nanopatterned C-enriched Si. The inset shows a semi-log plot of the region containing the G line and phonon replicas.

is similar for both samples and serves as a good reference for comparing the two sets of data. The similarity in the band-edge emission linewidth and peak height is indicative of crystallinity being recovered after the SPE. In the reference nanopatterned SOI sample the G line intensity is 1300 counts/s while in the C-enriched sample the G line intensity is 43 000. While the results in Fig. 2 display the most intense G line observed, G line intensities exceeding 20 000 counts/s were consistently obtained. The wide band extending from the G line to longer wavelengths consists of several phonon replica modes of the G line.^{10,17}

These results confirm that the carbon in the silicon crystal is responsible for the creation of G centers and also provides a path for increasing the efficiency and gain of this material. The measured linewidths of 1.5 ± 0.1 nm (C enriched) and 1.1 ± 0.1 nm (unenriched) are considerably broader than the reported linewidth of 0.1 – 0.2 nm at 25 K.^{9,18} This linewidth broadening is likely due to the variety of strain environments⁹ experienced by G centers located in the pore walls. Transmission electron microscopy images showing evidence of compressive strain in the pore walls are presented in Ref. 19. The linewidth broadening in the C-enriched nanopatterned SOI versus the reference nanopatterned SOI is likely due to the presence of a variety of strain environments caused by C_i 's C_s 's, and other residual damages present after amorphization, C implantation, and SPE regrowth. In addition to leading to linewidth broadening, the presence of compressive strain in the pore walls would decrease the band gap locally, which may lead to the funneling of excitons from the pristine bulk crystal to the regions dense with G centers near pore walls,²⁰ facilitating efficient filling of G centers.

The temperature dependence of the G line emission at temperatures above 40 K can be modeled according to^{10,18,21}

$$I_G(T) = I_0 [1 + C \exp(-E_a/kT)]^{-1}, \quad (1)$$

where I_0 is the intensity at 40 K. Equation (1) models a two level system where the excited state of the G center is thermally depopulated into a higher level separated by E_a , and C is the ratio of degeneracy between these two levels. Previously obtained values for E_a and C are 55 ± 3 meV and $(2-8) \times 10^4$, respectively,²¹ 35 ± 5 meV (C not given),¹⁸ and 68 ± 6 meV and 8.9×10^6 .¹⁰ The G line intensity of the two samples presented in Fig. 2 was measured at temperatures between 40 and 80 K and fitted according to Eq. (1). The obtained values were $E_a = 39$ meV and $C = 8300$ for carbon-enriched Si and $E_a = 40.1$ meV and $C = 3500$ for nonenriched Si. The two values of E_a we obtained are very close and within the range of previously obtained values. The relatively small values of C are not yet understood. However, the large variations of this constant in previous reports imply

that it is very much affected by the measurement setup employed.

In conclusion, we have demonstrated that nanopatterning of carbon-rich silicon created via solid-phase epitaxial regrowth after amorphization and carbon implantation can lead to a significant increase in the intensity of the G line emission. An increase by a factor of 33 was achieved in our studies, and samples with intense G line were consistently manufactured. We hypothesize that the nanopatterned system is intrinsically beneficial for efficient optical activity. Utilizing the nanopatterning technique to create G centers allows for a large surface area with which the energetic ion etchants can interact with the crystal to create silicon self-interstitials which lead to G centers while maintaining the crystallinity, band structure, and carrier lifetime of the crystal away from the etched surfaces of the pores. In this way, the unetched regions of the crystal act, under pumping, as a carrier reservoir to the G centers embedded in the pore walls.

The authors thank Michael Aziz, Federico Capasso, Gordon Davies, and George Watkins for helpful discussions and added insights. This work was made possible by the support from the Office of Naval Research and Chagaan Baatar.

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