Nano-engineered Crystalline Silicon for Enhanced Photoluminesence and 1.28\(\mu m\) Laser Action—a Study of Mechanisms

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ABSTRACT

1.278\(\mu m\) laser emission has been observed in a SOI structure which has been nanopatterned to contain an array of nanopores. The optical transition is known to be associated with phononless recombination mediated by the bistable, carbon-related \textit{G}-center. A physical model is proposed to explain the enhanced optical activity of the \textit{G}-centers in the presence of the nanopore array. The effects of the SOI, strain, dielectric modification and breaking of phonon \textit{k}-selection rules on the optical properties of the nanopatterned silicon are addressed. Temperature limitations are discussed.

Keywords:

1. INTRODUCTION

Silicon is an indirect band gap semiconductor, making it an inefficient light emitter. Due to the significant role played by silicon in the electronics industry, there is much interest in enhancing the optical capacities of silicon. Recent efforts have been devoted to improving the active photonic properties of silicon,\textsuperscript{1–8} including a most recent observation of low-temperature laser emission at 1.28 \(\mu m\).\textsuperscript{9} The laser emission was observed from a silicon-on-insulator (SOI) structure that had been periodically nanopatterned to contain a hexagonal array of nanopores. We present here a study of the relevant physical mechanisms in the nano-engineered crystalline silicon and examine how each contributes to laser action.

2. NANO-PATTERNING FOR LIGHT EMISSION IN CRYSTALLINE SILICON

2.1. Fabrication

The periodically nanopatterned silicon structure was fabricated in undoped crystalline electronic-grade silicon-on-insulator (SOI) using a highly-uniform self-assembled nanopore array as an etch mask as shown in fig. 1.

The anodic aluminum oxide (AAO) nanopore etch mask was placed atop a thin SOI layer which was insulated from the thick silicon substrate by 3\(\mu m\) of silicon-oxide. The nano patterning was achieved via reactive ion etching (RIE) which introduced nanopores to the silicon, as shown in fig. 1c.

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2.2. Contributions of Nanopatterning to Optical activity

Several features of the nanopatterned SOI structure give it properties which are different from those of bulk silicon. Five such features stand out as most significant. First, the presence of the 3µm buried oxide layer provides electrical and optical confinement. Second, the RIE formation of the nanopores and the accompanied lattice deformation have been shown to lead to phonon confinement and breaking of phonon k-selection rules.\textsuperscript{10,11}

Third, the presence of the nanopores, which are localized regions of vacuum embedded in the silicon lattice, gives rise to a reduced effective dielectric environment with extended screening length near the pore walls. Fourth, the lattice within a 4 5nm layer of the pore walls has been shown to be strained,\textsuperscript{10} which leads to lowering of the band edge and to excition confinement in the vicinity of the pore walls. Fifth, it is believed the RIE procedure used to introduce the nanopores created many defect states below the conduction band edge, including emissive centers known as G-centers which are optically active at 1.278µm.

It is difficult at this time to separate the relative contributions of these physical elements to the observed laser action. The current model proposes that the G-centers that were created in this nano-patterning process are more plentiful, highly concentrated, and stand an increased chance of being populated due to the carrier confinement and carrier collection from the surrounding unperturbed crystalline silicon as a result of the high-strain and the modified dielectric environment in the emissive zone. In addition, the breaking of phonon k-selection rules accelerates the relaxation of the collected carriers and therefore enhances their capture by the emissive G-centers.

3. OPTICAL ACTIVITY AND DISCUSSION OF PHYSICAL ELEMENTS

Fig. 2a shows the lasing line at 1.278 µm in the edge-emission of the slab waveguide pumped by a continuous-wave 514 nm argon-ion laser. Fig. 3 shows the photoluminescence (PL) spectrum of both the nanopatterned sample with the laser line and an unpatterned control sample. It was demonstrated that the nanopatterned sample emitted spatially-coherent stimulated emission.\textsuperscript{9}

The 1.278 µm line is a well-known zero-phonon line\textsuperscript{12} resulting from an optical transition within the G-center. The G-center is a bistable point defect comprised of two carbon atoms and one silicon atom. A schematic is shown in fig. 4. G-centers are known to be formed after bombardment of the silicon lattice by gamma rays, electrons, neutrons or ions. In the present study they are believed to have been formed during the RIE procedure executed to obtain the pores.

While much about the optical properties of G-centers has been known for some time,\textsuperscript{12} the effects of the nanopatterning may be elemental to the ability of the nanopatterned silicon to achieve lasing action. It is hypothesized that the key physical elements of the nanopatterned silicon structure mentioned above increase electronic population of the G-centers embedded in the surfaces of the pores, while minimizing the overall damage to the crystal and thereby keeping the total optical loss of the patterned sample at a minimum. Elements of the hypothesis are illustrated in fig. 5.
Figure 2. (a) Edge-emission spectra at 10 K. The inset illustrates the G-center mediated direct recombination pathway. (b) Cross-sectional TEM of the nanopatterned SOI structure. The scale bar is 45 nm. (c) High-resolution TEM (HRTEM) of the nanopatterned silicon surface layer region indicated in (b). The arrows indicate vacancy sites in the side-wall of a nano-pore.

Figure 3. PL spectra of nanopatterned SOI (red) and unpatterned SOI (black). The 1.278$\mu$m line is very pronounced in the nanopatterned sample and is absent in the unpatterned control sample.
**Figure 4.** Schematic of the bistable G-center. In the non-emissive configuration one silicon and one carbon share the center lattice site. In the emissive B configuration a carbon atom occupies the lattice site and a silicon atom becomes an interstitial.

**Figure 5.** (a) Schematic of effects of nanopores. The G-centers populate the strained walls. Carriers are pulled to the region of smaller band gap. (b) The band structure of bulk silicon showing the tail of states below the conduction band. Phonon assisted transitions occur from these tail states to the G-centers. The direct optical transitions are from the G-centers to the valence band.
3.1. The Role of SOI

The optical and electrical confinement introduced by the SOI no doubt plays a large role in enhanced optical activity. While much has been known about emissive centers in silicon for decades, the recent development of SOI technology offers an incredible advantage for technologies which hope to utilize emissive centers for optically-active silicon devices. By creating emissive centers in a thin layer of silicon atop a 3 $\mu$m buried oxide layer one ensures that all carriers created by optical excitation remain in the thin, active layer. The same nanopatterning procedure executed in bulk silicon gives reduced optical activity in the 1.278 $\mu$m line as compared with SOI because optically excited carriers in the bulk silicon are free to diffuse away from the top optically-active layer, thus encountering a greater probability for non-radiative recombination.

Further, the reduced index of refraction of the oxide layer as compared with the silicon layer leads to optical confinement in the top active layer. This optical confinement is necessary to achieve stimulated emission and is provided by the slab waveguide structure of the SOI.

3.2. Phonon Confinement, Breaking of Phonon $k$-selection Rules

Raman spectroscopy has shown\textsuperscript{10,11} that the array of nanopores in the silicon lattice alters the phonon spectrum and breaks the phonon $k$-selection rules (see fig. 6). It has been shown that phonon-assisted light emission at the band edge was indeed enhanced at 300K by the nano-patterning, indicating the role of phonon-selection rule breaking in the nanopatterned silicon. This breaking of phonon $k$-selection rules may lead to enhanced population of $G$-centers by increasing the probability for an electron in the silicon conduction band to transition to the $G$-center, which is .17eV below the silicon conduction band edge (see fig. 2a).

3.3. Modified Dielectric Environment

The nanopore walls are thin transition layers between the dielectric environment of crystalline silicon and free space. The effect of such a dielectric transition on the electronic behavior of the $G$-center, and ultimately to laser, is one of reduced screening. This reduced screening causes the exciton binding energy to be more negative in the vicinity of the pores. This spatial exciton energy gradient draws electron-hole pairs to the pore walls, which are densely packed with $G$-centers introduced during RIE.
3.4. Strain
TEM analysis confirms that the nanopore walls are strained.\textsuperscript{11} The effects of strain on optical activity will likely be similar to those of the modified dielectric environment in that the strained regions near the pore walls will have a narrowed band gap, leading to exciton confinement in the vicinity of the pore walls.

3.5. Introduction of Sub-Bandgap States and Optically-Active Complexes
The RIE procedure which created the nanopore array and introduced the emissive $G$-centers also introduced many other defect states just below the silicon conduction band edge. Photocurrent spectroscopy reveals the presence of an Urbach tail (fig. 7), the signature of such sub-band states. The presence of these states may increase the probability for an electron in the silicon conduction band to populate a $G$-center by effectively lowering the silicon conduction band minimum, bringing it closer to the level of the $G$-center (see fig. 5).

In addition, the RIE procedure was also responsible for the introduction of the optically-active $G$-centers. Because the RIE introduction of pores only disturbs the silicon lattice near the pore walls, the majority of the silicon retains its pristine quality. This element of controlled introduction of optically-active complexes is crucial because it introduces radiative recombination pathways efficiently without also introducing competing non-radiative recombination pathways.

4. DISCUSSION AND CONCLUSIONS

4.1. Summary
TEM, Raman, PL, and photocurrent spectroscopy studies have established the underlying mechanism for lasing to be that of a $G$-center-mediated, phononless, direct recombination and have led to a hypothesis explaining the enhanced optical activity. The hypothesis proposes that the pores introduce strain, modified dielectric environment and breaking of phonon $k$-selection rules that lead to increased population of the $G$-centers created in the RIE process. As important is that the nanopatterning technique maximally preserves the crystallinity of the engineered silicon by keeping most of the structure in its unperturbed crystalline state where carriers can be generated, preserved, and then subsequently collected by the nearby emissive zones within exciton diffusion length. The extreme uniformity of the nanoarray, the absence of dopants, and the presence of the thick underlying...
oxide layer help keep the total optical loss at a minimum. Also, the SOI structure gives electrical and optical confinement, both beneficial to laser action. Indeed, Raman, PL, TEM, and Photocurrent spectroscopy studies all add support to the hypothesis and show that the ratio of radiative to non-radiative recombination events increased after the introduction of nanopores to the SOI wafer.

4.2. Temperature Dependence

The temperature dependence of luminescence from G-centers has been documented, and it has been shown that the luminescence from G-centers takes a marked decrease at 50K and is entirely extinguished by 100K. This agrees well with the observed temperature dependence of the nanopatterned silicon laser which achieved a maximum operating temperature of 80K. This physical limitation, dictated by the capture kinetics of the G-centers versus non-radiative recombination pathways, stands as a formidable barrier to room-temperature operation. However, elements of the existing functionality may offer insight into how the operating temperature may be raised.

The discussed silicon nanostructure is one example of utilizing physical elements such as strain and breaking of k-selection rules to increase optical activity of interstitial complexes embedded in the silicon medium. Nanopatterned SOI fortuitously combines these elements in such a way as to allow for laser action at 1.278 µm at T<80K. Future research must be focused on analyzing each of the physical elements of the model separately to discover how to maximize the contribution of each to laser action. In particular, exploring new ways to locally introduce strain will be crucial to increasing the operating temperature of such point defect silicon lasers because the ability of strained regions to trap excitons, even at high temperatures, is a promising technique to aid in the population of optically active point defects at higher temperatures.

4.3. Future Research

Nanopatterned silicon is a physical system in which many independent physical elements are present and compound each other to give unique properties. But in order to maximally utilize the contribution of each physical element to optical activity, the contribution of each physical element must be understood independently. Therefore, systems which decouple the physical elements must be created and studied. For example, it is hypothesized that the strain fields near the pore walls contribute to electronic population of G-centers by drawing excitons into the vicinity of the G-centers which are embedded in the pore walls. However, as is argued above, the reduced electronic screening near the pore walls also draws excitons to the vicinity of the pores. To understand the ability of the strain or dielectric modification to independently aid in population of G-centers it will be necessary to devise structures which incorporate as few of the physical elements as possible, allowing independent analysis of the contributions of each of the relevant contributors to optical activity. Then, having obtained a better understanding of the roles played by the various modifications of the silicon lattice, it will be possible to devise new structures which effectively combine the benefits of SOI technology, breaking of phonon k-selection rules, modified dielectric environment, strain and controlled introduction of emissive complexes to produce maximal optical gain, minimal optical loss and the highest possible operating temperature.

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REFERENCES


