Nanocrystals: Silicon and Germanium
Silicon nanocrystals formed by ion implantation and annealing of fused silica wafers show a strong, broad photoluminescence (PL) peak centered at a wavelength between 750 and 900 nm, depending on the processing conditions. This luminescence has been extensively investigated and trial device structures based on these materials have been built. However, relatively few studies also report the optical absorption spectra. In fact, the absorbance of these specimens is quite low (usually < 10%) at wavelengths greater than 450 nm (i.e., at the pump wavelengths typically used for PL studies). This suggests that in numerous studies of Si nanocrystals produced by ion implantation, only a small fraction of the nanocrystals is responsible for the observed PL at the typical pump wavelengths. In this study, we investigated how the PL spectrum and intensity depend on the power and wavelength of the pump laser. We find that the PL intensity approaches saturation at high pump fluences, and that the peak emission wavelength is sensitive to the excitation power. These observations can be attributed to the dynamics of the excitation/recombination processes at different energies, and indicate that considerable care must be taken when comparing the emission spectra of different specimens. Our data are uniformly consistent with a mechanism of light emission involving subgap states (i.e., radiative trap sites) and are not supportive of a “pure” quantum confinement model.

INTRODUCTION

The light emitting properties of silicon nanocrystals formed by ion implantation and annealing of fused silica have been extensively investigated in recent years. Optical gain has been reported in ion-implanted specimens, suggesting the possibility of future Si-nanocrystal-based lasers [1]. Ion implantation can be used to dope Si nanocrystal composites with erbium – a technique that shows some promise for future 1.5 μm fiber amplifiers [e.g., 2,3]. Films of pure and Er-doped silicon nanocrystal composites have recently been embedded within multiple distributed Bragg reflectors to produce highly directional and spectrally narrow emission [4,5].

Despite these promising developments, the physical mechanism responsible for the spectrally broad red-infrared photoluminescence peak is still debated. Several researchers have proposed that the luminescence is due to bandgap recombination that occurs at higher energies than in bulk silicon, due to the quantum confinement effect [6-8]. For example, the luminescence energy from Si nanocrystals in SiO2 was reported to narrow slightly and shift to shorter wavelengths when the part of the specimen that contained the largest nanocrystals was oxidized or etched away. The temperature dependence of the luminescence has been attributed to radiative recombination from the shorter-lived singlet and longer-lived triplet exciton spin states in the quantum confinement model [8-10]. However, work has not supported this model, instead attributing the luminescence to radiative electron-hole recombination at surface traps [e.g., Ref. 11]. Theoretical models are consistent with the broad red PL band arising from recombination at surface Si=O double bonds [12,13]. The bonding geometry at the nanocrystal surface can...
produce stable electronic states in the gap, as suggested for porous silicon [14], dominantly as a result of hole trapping [15]. Electron spin resonance measurements have shown that Si dangling surface bonds are the main non-radiative recombination site [16]. The large Stokes shift between the absorbing and emitting states in Si nanocomposites produced by ion implantation is further evidence in favor of emission from radiative sub-gap trap sites [17].

The absorption onset for silicon nanoparticles produced by ion implantation is below 450 nm [1,17]; however, many previous photoluminescence studies have employed excitation light sources having wavelengths longer than 450 nm to stimulate the PL. This suggests that in many previous studies, only the largest nanocrystals may actually have been excited. In the present work, therefore, we examined more closely the relationship between absorption and photoluminescence of silicon nanocrystals formed by Si implantation of fused SiO 2, and more carefully characterized the PL emission.

**EXPERIMENTAL**

Two optical grade fused quartz wafers were implanted at room temperature with silicon ions. Specimen A was implanted at energies of 35, 70, and 135 keV to fluences of 1.7 x 10 16, 3 x 10 16, and 7.5 x 10 16 ions/cm², respectively. The multiple energies and doses were used to obtain a flatter implanted-element concentration profile than would be obtained with a single energy. Specimen B was implanted at the same energies, but the fluences were increased to 3.2 x 10 16, 5.6 x 10 16, and 1.5 x 10 17 ions/cm², respectively. After implantation, the specimens were annealed at 1100 °C for one hour in flowing Ar + 10% H 2 in order to induce precipitation of implanted silicon. This temperature and annealing atmosphere was chosen in order to maximize the luminescence efficiency [18].

Continuous wave (CW) photoluminescence experiments were performed using an Ar ion laser at wavelengths of either 488 or 514 nm, or a HeCd laser operated at 442 or 325 nm. Time-resolved PL measurements were done using a diode-pumped solid-state laser emitting ~10 ns pulses at 349 nm. The PL spectra were collected and analyzed using a fiber-optic digital CCD spectrometer. The luminescence spectra were corrected for the CCD array sensitivity by normalizing with respect to a black body light source of known color temperature. Optical absorption measurements were taken using a deuterium-tungsten lamp interfaced to the same spectrometer system. Finally, the microstructure of the specimens was characterized on a JEOL 2010 transmission electron microscope (TEM) with a LaB 6 filament.
RESULTS AND DISCUSSION

The Si nanoparticles in specimen A averaged ~1.5 nm in diameter, with a few particles as large as 2.5 nm (Fig. 1). As expected due to the higher implanted ion fluence, the nanocrystals in specimen B were larger, averaging ~2.4 nm in diameter. Because the smallest silicon nanocrystals show poor contrast and can be difficult to detect when embedded in SiO₂, there may be more nanocrystals smaller than 1 nm than appear in the images or histograms.

For both specimens, the absorption spectrum is nearly featureless between 400 and 1000 nm (Fig. 2). Specimen A shows a slow and nearly linear increase in absorption from < 1% to ~5% at on going from 700 nm to 370 nm, after which the absorption increases more rapidly with decreasing wavelength. Specimen B shows similar absorption characteristics, except that the region of rapidly increasing absorption starts at ~420 nm. For both samples, the peak of the photoluminescence occurs in the near infrared and is shifted by approximately 2 eV with respect to the strong absorption band. The net PL emission intensity was greater for specimen A, despite the lower implanted ion fluence. Both the absorption and peak photoluminescence occur at slightly higher energies in specimen A, which has the smaller particles.

Several other effects were also measured. In both samples, the PL intensity decayed by between 5 and 10% under over a period of several seconds, under 2 W CW laser illumination (Fig. 2, inset). This PL decay is reversible and recovers to nearly the initial value after a laser-off period of ~1 min. Based on previous temperature measurements of the photoluminescence intensity [8], specimen heating by ~25 degrees during laser illumination would be sufficient to decrease the PL intensity by almost 10%.

The photoluminescence was not polarized, in contrast to the case of porous silicon [19], which, due predominantly to the elongated nature of the particles, shows polarization “memory” with respect to the excitation source. A recent theoretical analysis showed that the degree of linear polarization of silicon nanocrystals is highly sensitive to the size and shape of the particles [20]. The lack of polarization memory in the implanted specimens is due to the random orientations and generally spherical shapes of the particles in Fig. 1.

Finally, we also attempted to measure any changes in the optical absorption spectra that might occur in the presence of ~80 mW of combined 325 + 442 nm CW laser excitation, using the experimental setup shown in Fig. 3. Our initial results showed a decrease in the absorption at wavelengths longer than the excitation wavelength, which was consistent with the idea that nanocrystals already containing electron-hole pairs would show absorption bleaching. However,
when the effect of photoluminescence on the absorption spectra was fully eliminated, we were, in fact, unable to any observe CW absorption bleaching within the sensitivity range of our setup.

The time-resolved PL experiments showed photoluminescence decay times on the order of tens of microseconds (Fig. 4). For simplicity, the decay curves were fit by a non-linear least-squares method to a stretched exponential, giving time constants of ∼45 μs. The decay rate for specimen B appears slightly faster than for specimen A (inset to Fig. 4), although this difference is close to the detection limit. The similarity in the luminescence decay curves for the different size distributions is not consistent with the pure quantum confinement model. If the recombination were across the fundamental bandgap, the smaller nanocrystals (sample A) might be expected to exhibit faster PL decay, due to the closer spatial proximity of charge carriers and the more direct nature of the bandgap for small silicon nanoparticles [11]. Furthermore, since the rate of surface trapping is on the order of picoseconds [21], the observed microsecond lifetimes cannot be due to differences in the trapping rates themselves.

The absorption energies are consistent with the quantum confinement model for silicon. The fact that the absorption onset of specimen A occurs at higher energies than that of specimen B is attributable to the effects of the smaller particle size on the bandgap energy. However, the extremely large Stokes shift between the absorption and emission energies implies the presence of radiative sub-gap states. Smaller shifts (on the order of 100 meV) can be due to Coulomb and exchange interactions, but a Stokes shift of ∼2 eV that is due to anything other than a trap state is unlikely. The fact that specimen A, with the smaller particles, luminesces at slightly higher energies could be interpreted as being due to bandgap emission from smaller particles, but this interpretation is not consistent with the absorption spectra.

The shape and peak energy of the photoluminescence spectrum was independent of the CW excitation wavelength (power = 20 mW), from 325 to 514 nm (the spectra are not shown, due to limited space). Care was taken to use excitation fluxes for the different wavelengths that were as similar as possible, to avoid any flux-dependent spectral shifts. Exciting at different wavelengths is an effective means of size selection, where only the nanocrystals with band gap energies smaller than the incident photon energy (i.e., larger
nanocrystals) can be excited. The fact that we observed no difference in the emission spectrum for different pump wavelengths is inconsistent with the pure quantum confinement model for light emission from silicon nanocrystals. However, models that incorporate the subgap trap state do show a variation in the energy of the subgap state with particle size [12], which appears to contradict the lack of a spectral shift observed in these samples.

Despite the lack of variation of the PL with excitation wavelength, the PL spectrum was sensitive to the excitation power (Fig. 5). With increasing 488 nm excitation power, the peak luminescence wavelength of specimen A blueshifted from 790 to 770 nm. Even at mW power levels, inserting a lens into the optical path to produce a higher flux on the specimen was sufficient to cause a spectral blueshift of up to 20 nm. By using bandpass filters we found that the PL decayed more rapidly on the short wavelength side of the emission peak, which would explain the spectral blueshift at increased pump powers. This rather sensitive dependence of the PL spectrum on incident photon flux requires caution when comparing spectra excited under different pump conditions.

Previous work on silicon nanocrystals formed by ion implantation showed a linear dependence of the PL intensity on excitation power [22]. In that work, the highest excitation flux was only \(7 \times 10^{19}\) photons/cm\(^2\)/s, whereas in the present work, we increased the power density to over 2W in a ~1 mm\(^2\) beam, corresponding to a flux of up to \(40 \times 10^{19}\) photons/cm\(^2\)/s, and we observed a gradual approach to luminescence saturation. The excitation-power-dependence of the photoluminescence intensity can be modeled with rate equations that describe the creation and recombination of electron-hole pairs [2]. Careful application of the rate equations permits the extraction of the optical absorption coefficient, if parameters such as the time decay constant, volume density of the nanocrystals, and the number of electron-hole pairs per nanocrystal are known. We have obtained the first two parameters from the time-decay and TEM measurements. The average number of electron-hole pairs per nanocrystal is not known, but based on the lack of induced CW absorption bleaching (Fig. 3) and extremely high powers required for PL saturation, this number might be large.

CONCLUSIONS

The following experimental results are consistent with models in which the light emission is due to carrier recombination at trap sites: (i) the large Stokes shift between the emitting and absorbing states, (ii) the lack of any dependence of the PL peak on CW pump wavelength, and (iii) the luminescence decay measurements. We point out that in most previous studies, only a small fraction of silicon nanocrystals were actually excited, due to the use of laser wavelengths at which most of the nanocrystals do not absorb. Finally, numerous papers have assumed that the light emission from Si nanocrystals produced by ion implantation is a result of electron-hole recombination across the fundamental energy gap, shifted to higher energies as a result of quantum confinement. Our results are not consistent with this model.
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REFERENCES

A New Pathway for Si Nanocrystal Formation: Oxi-Reduction Induced by Impurity Implantation

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ABSTRACT

In this work we show the feasibility of producing silicon nanocrystals by means of a new method based on the oxi-reduction of silicon dioxide induced by the presence of an impurity and annealing. The choice of magnesium as the impurity relies on its chemical properties of oxi-reducing the SiO$_2$ matrix while avoiding the formation of Si-based compounds. The samples were obtained by $3 \times 10^{16}$ and $1 \times 10^{17}$ at/cm$^2$ ion implantation into fused silicon dioxide followed by annealing in vacuum at 900 °C for 2 or 10 h. Rutherford backscattering spectrometry (RBS) characterized the chemical content and the Mg depth distribution. In all cases, photoluminescence measurements that showed a broad band starting around 1.8 eV with increasing emission intensity for lower energies, indicating the presence of Si nanocrystals. The analysis of the photoluminescence data in the framework of the quantum confinement theory suggests the existence of relatively large Si nanocrystals. The presence of these nanocrystals was also confirmed by Raman spectroscopy.

INTRODUCTION

Light-emitting semiconductor nanostructures have the potential of total integration of optical and electronic devices with expected great impact in telecommunication systems. Among the candidate materials, silicon nanostructures have been investigated both on their synthesis as well as on their properties. In 1990, visible photoluminescence (PL) at room temperature from anodically etched Si, the so-called “porous silicon”, was first reported [1]. A few years later, Si$^+$ implantation into fused silica followed by annealing was shown to produce intense PL output [2,3]. The presence of an emission band at 1.7 eV that appeared only after high temperature annealing was ascribed to the presence of Si nanocrystals. Moreover, it has been observed that the PL emission from Si nanocrystals shifts to lower energies for larger nanocrystals, and this behavior has been explained by some authors as due to the quantum confinement of the electron wavefunction [1-8]. Several other models have been proposed to explain this light emission, such as interface states, defects, siloxene species, etc. In addition to these approaches, several other procedures were employed to obtain Si nanocrystals, among them sputtering deposition, plasma enhanced chemical vapor deposition, laser ablation and molecular beam epitaxy. It is the aim of this work to show the feasibility of using the oxi-reduction method to the synthesis of Si nanocrystals. In this method, the implanted species reduce the matrix releasing its non-oxygen component that subsequently agglomerates in the form of nanoparticles. Annealing is expected...
to enhance this process by increasing the diffusion rate and so of the rates of nucleation and growth of the nanoparticles. This method was recently employed to obtain Al nanoparticles in Al2O3 by implantation of Y⁺ or Ca⁺, though the authors did not succeed in obtaining Si nanocrystals in SiO2 [9].

EXPERIMENTAL PROCEDURES

The samples were obtained by Mg⁺ implantation into commercial fused silicon dioxide plates with doses of 3 x 10¹⁶ and 1 x 10¹⁷ at/cm². The implantation energy was 80 KeV leading to a projected range of ~130 nm with a straggling of ~40 nm according to calculations using the TRIM code [10]. During implantation, the sample temperature remained close to room temperature as checked by a thermocouple device. After implantation the samples were annealed in vacuum (base pressure of ~2 x 10⁻⁷ Torr) at 900 °C for 2 or 10 hours. They were allowed to cool in vacuum before removal to ambient environment. The samples were characterized for chemical content and Mg depth distribution by means of 2 MeV He⁺ Rutherford backscattering spectrometry (RBS). The samples were characterized by photoluminescence (PL) and Raman scattering spectroscopies using a Renishaw RM2000 system (spectral resolution ~2 cm⁻¹) with an Ar⁺-ion laser (λ = 488 nm) as the excitation source. The optical absorption spectra in the near UV-visible range were obtained with a Cary 5E spectrometer. These measurements were carried out in air at room temperature.

RESULTS AND DISCUSSION

RBS data showed that within the experimental error, the retained dose corresponds to the nominal one and that the Mg depth profile is well described by a Gaussian distribution that slightly broadens for higher implantation doses. Moreover, no additional impurities were detected in the SiO₂ samples.

The photoluminescence results are presented in Figures 1 and 2 for each implantation dose, respectively. All spectra present a broad PL band starting around 1.8 eV with increasing emission intensity towards lower energies in agreement with earlier reports of PL measurements of Si nanocrystals capped with or embedded in SiO₂ [7]. The observed PL emission band was assigned to the recombination of quantum-confined carriers in Si nanocrystals. Also, defects in ion implanted silica are not known to emit light in this region of the spectrum [11,12]. The experimental spectra were fitted by one Gaussian curve shown as a continuous line in Figs. 1 and 2, and the fitting parameters, namely the peak position and the full width at half-maximum (FWHM), obtained this way are presented in Table I. These results were interpreted according to the quantum confinement model that relates the PL peak position (in eV) to the average size of the nanocrystals as follows [4-6]:

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E_{PL} = E_{gap} + 3.73/d^{1.39}
\]

where \(E_{gap} = 1.17\) eV is the band gap of crystalline silicon and \(d\) is the diameter of the nanocrystal in nm. Also, as suggested by studies of porous silicon, the width of the PL band is related to the size distribution of the nanocrystals [13]. These results are also presented in Table I and suggest that increasing implantation doses leads to larger average sizes and broader size