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Optical characterization of CO₂-laser-ablated Si-rich SiOₓ

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Anomalous absorption and the corresponding change in the optical band gap of a CO₂-laser-ablated Si-rich SiO₂ (SiOₓ) film are studied. The optical band gap energy of as-grown nonstoichiometric SiOₓ is slightly reduced by increasing Si–Si bonds as compared to quartz. After rapid thermal annealing using a CO₂ laser, the dehydrogenation of SiOₓ film further increases the Si–Si bonding states and redshifts the optical band gap by 1 eV. Laser ablation is initiated at a laser intensity of >7.5 kW/cm², leaving numerous luminescent centers that are related to neutral oxygen vacancy defects, increasing the absorption coefficient and related optical band gap energy, and reducing the refractive index in partially annealed SiOₓ. © 2007 American Institute of Physics. DOI: 10.1063/1.2721141

The optical properties of Si-rich SiO₂ (SiOₓ) film grown by plasma-enhanced chemical vapor deposition (PECVD) are of great interest because of its extensive applications in Si-based photonics. Self-aggregation of Si nanocrystals (nc-Si) can typically be obtained in SiOₓ layer after a high-temperature furnace annealing over 1000 °C. However, the high annealing temperature used to induce the formation of nc-Si may exceed the thermal budget in complementary metal-oxide-semiconductor processes. Since SiOₓ exhibits an absorption coefficient of 1.2×10³ cm⁻¹ at a wavelength of 10.6 μm, a CO₂ laser annealing technology for synthesizing nc-Si in SiOₓ (Refs. 3–5) has recently emerged to overcome the concern about heat-induced damage of nearby integrated circuits. CO₂ laser rapid thermal annealing (RTA) thus provides a convenient approach for the in situ precipitation of nc-Si in SiOₓ. However, ablation occurs at a laser intensity of >6 kW/cm². The evolution of optical characteristics of the CO₂-laser-ablated SiOₓ film is not yet well understood. In this work, an ultraviolet-visible-near infrared (UV-VIS-NIR) transmission/reflection spectroscopic diagnosis is adopted to analyze anomalous absorption spectra, corresponding changes in optical band gap energy, and reciprocal band edge absorption of a CO₂-laser-ablated PECVD-grown SiOₓ film. Structural damage induced luminescent centers embedded in CO₂-laser-ablated PECVD-grown SiOₓ films were also characterized.

A 280 nm SiOₓ film was grown on a 1-mm-thick polished quartz substrate (GE, Type 219). The PECVD was operated at a N₂O/SiH₄ fluence ratio of 6 under an inductively coupling plasma power of 45 W and a chamber pressure of 120 mtorr. The N₂O fluence was maintained at 120 SCCM (SCCM denotes cubic centimeter per minute at STP) during 5 min of growth. The composition of SiOₓ was analyzed by Rutherford backscattering spectrometry, which yielded a calculated O/Si ratio of 1.25 and a total Si concentration of 44.44 at. %. After deposition, a continuous-wave CO₂ laser (LTT Corp., ILS-II) was adopted to perform annealing in ambient atmosphere for 1 ms with intensities from 1.5 to 13.5 kW/cm². Photoluminescence (PL) of the CO₂-laser-treated SiO₁.₂₅ film was excited by a HeCd laser with a laser intensity (P_laser) of 5 W/cm² at 325 nm. The beam spot sizes of the CO₂ laser for RTA and the HeCd laser for PL are about 500 and 30 μm, respectively. The transmittance and reflectance of the SiO₁.₂₅ films between 190 and 850 nm (with 0.1 nm resolution) were analyzed using a UV-VIS-NIR spectrophotometer (Shimadzu, UV-2401PC).

Several mechanisms related to the redshift in the absorption spectrum of CO₂ laser RTA SiO₁.₂₅ film are considered, including an increase in the number of Si–Si bonding states, dehydrogenation, precipitation of nc-Si, generation of oxygen-related defects, and variation in the composition of the SiO₁.₂₅ film. After deposition, a slight redshift of the as-grown SiO₁.₂₅ at a transmission of 50% increases from 300 to 320 nm in comparison with that of quartz substrate, as shown in the inset of Fig. 1. The absorption peak is at 300 nm with a full width at half maximum of 68 nm, which reveals the decrease in the optical band gap energy of the as-grown SiO₁.₂₅. As the mole ratio x decreases from 2.0 to 1.25, the valence and conduction band edges of the SiOₓ tailor into its forbidden region; the increased number of Si–Si bonding states is gradually overlaid with the oxygen nonbonding states and finally spread out into the Si valence band. As a result, the band gap energy of the PECVD-grown SiOₓ film declines because of the increase in the number of Si–Si bonds in the nonstoichiometric SiOₓ, which becomes more significant when nc-Si precipitates in the CO₂ laser RTA SiOₓ. Electron-energy-loss spectroscopy also yields evidence of the decrease in the excitation energy of the inner-shell electrons of the Si atom in the CO₂ laser RTA SiOₓ. The
modification on the absorption band edge as well as the optical band gap by detuning stoichiometry during growth or by self-assembling Si nanocrystals after CO2 laser RTA was thus confirmed. Therefore, the slight redshift in the transmission of as-grown SiO$_{1.25}$ in comparison with that of quartz substrate is caused by the increasing number of Si–Si bonds in SiO$_{1.25}$ near the valence and conduction band edges.

The wavelength of 50% transmission of annealed SiO$_{1.25}$ after CO$_2$ laser RTA at $P_{\text{laser}}=6$ kW/cm$^2$ is greatly increased from 320 to 457 nm in comparison with that of as-grown SiO$_{1.25}$. The peak of the change in the transmission of the annealed sample is significantly redshifted from 300 to 356 nm, associated with an increase in the peak absorption by a factor of 4, as presented in Fig. 1. At a CO$_2$ laser RTA intensity below the ablation threshold, the effect of increasing Si–Si bonding states on the clearly tuned blue-green absorption edge is thus stronger than any other effect. The near-band-edge absorption coefficient is further understood by decomposing the absorption coefficient ($\alpha$) from the transmission and reflection spectra according to the following equation:

$$\alpha = \frac{1}{d} \ln \left( \frac{\sqrt{(1-R)^4 + 4T^2R^2} - (1-R)^2}{2TR^2} \right),$$

where $d$ is the thickness of the film, $T$ is the transmission, and $R$ is the reflectance. CO$_2$ laser RTA at 6 kW/cm$^2$ caused a redshift of nearly 1 eV on the absorption band edge of the SiO$_{1.25}$ (see Fig. 2). Since the reactants are SiH$_4$ and N$_2$O, the as-PECVD-grown SiO$_{1.25}$ film contains a high concentration of hydrogen. Hydrogen passivation can be released from SiO$_{1.25}$ during CO$_2$ laser annealing. The loss of hydrogen causes compaction of SiO$_{1.25}$, a decrease in the thickness of SiO$_{1.25}$ during annealing, and a variation in the composition of SiO$_{1.25}$ film. The absorption spectra of hydrogen-passivated Si clusters were calculated by solving the many-body Bethe-Salpeter equation$^7$ with a symmetrized plane wave basis, while the ab initio nonseparable pseudopotential model$^8$ was adopted to accelerate computation efficiency. The calculated absorption band edge was also redshifted by almost 1 eV as the number of surrounding hydrogen atoms decreased from 36 to 24. Dehydrogenation not only reduces the thickness of the PECVD-grown SiO$_2$ film but also increases the number of Si–Si bonding states, contributing to the redshift of the optical band gap. Figure 3 plots the evolution on the optical band gap energy of the SiO$_{1.25}$ with increasing CO$_2$ laser RTA intensity, which is mainly attributed to nonstoichiometric growth, dehydrogenation, and Si precipitation in PECVD-grown SiO$_{1.25}$ under the ablation threshold. The slope of the laser-intensity-dependent change in the optical band gap is $-0.148 \text{ eV/kW/cm}^2$.

In contrast, the optical band gap energy of the PECVD-grown SiO$_{1.25}$ increases from 2.43 to 2.76 eV at a CO$_2$ laser RTA intensity of $>6$ kW/cm$^2$ (see Fig. 3), because the structural defects were generated under high-power CO$_2$ laser RTA induced ablation. Such CO$_2$ laser ablation at $P_{\text{laser}}$...
> 7.5 kW/cm² not only sputters the SiO₁.₂₅ film out of the substrate but also damages the surface structure without any regrowth. Therefore, the oxygen-defect-related PL at 455 nm is inevitably increased, as shown in Fig. 4. The SiO₁.₂₅ matrix is rapidly compressed during such rapid laser ablation, where numerous oxygen-dependent defects such as weak oxygen bond, neutral oxygen vacancy (NOV), and ionized oxygen (O2⁻) with PL wavelengths at 410–455 nm are generated by the damaged bonds of the SiO₂ matrix. The NOV defect may have an important role in the anomalous absorption because the PECVD-grown SiO₁.₂₅ matrix is originally in an oxygen-deficient environment. Obviously, the adsorption rate of O ions will be much smaller than that of Si ions at a high-temperature and in an oxygen-deficient environment provided by the CO₂ laser RTA of the SiO₁.₂₅ in ambient atmosphere. Such a phenomenon has never been observed on a SiO₂ film that was entirely annealed in a furnace under similar conditions, as furnace annealing usually causes a gradual but complete recovery on the compressing strain of the SiO₂ matrix close to nc-Si. Notably, the transmission change profile of the CO₂-laser-ablated SiO₁.₂₅ at P_laser > 7.5 kW/cm² is highly consistent with the NOV-defect-related blue-green PL spectrum at a peak wavelength of 450–455 nm (see Fig. 4). Such a blue-green PL spectrum has never been observed in the CO₂ laser annealed SiO₁.₂₅ at < 6 kW/cm², which result clearly confirms the contribution of NOV defects generated during CO₂ laser ablation. Additionally, the absorption coefficient of the SiO₁.₂₅ film at a wavelength of 455 nm increases by three times as the CO₂ laser intensity enlarges from 7.5 to 12 kW/cm² (see Fig. 5). This result again verifies the contribution of ablation-induced surface damage and structural defects at higher laser intensities. The incompletely annealed SiO₁.₂₅ with many oxygen-dependent defects also suffers from a slight decrease in the refractive indices from 1.87 to 1.79 as P_laser increases from 7.5 to 12 kW/cm². In Fig. 5, the threshold CO₂ laser intensity required to initiate the ablation of the SiO₁.₂₅ film can be clearly obtained from the evolution of both the refractive index and the absorption coefficient.

In conclusion, the anomalous absorption spectra and corresponding changes in optical band gap energy, band edge absorption, and structurally damaged related luminescent centers of the CO₂-laser-ablated PECVD-grown SiO₁.₂₅ film were characterized using UV-VIS-NIR transmission/reflection and PL spectroscopies. After PECVD deposition, a slight redshift in the transmission and the lower optical band gap energy of as-grown SiO₁.₂₅ in comparison with those of quartz substrate are due to the increase in the Si–Si bonding state in SiO₁.₂₅ near the valence and conduction band edges. Since the as-grown SiO₁.₂₅ film contains a high concentration of hydrogen, dehydrogenation not only reduces the thickness of the PECVD-grown SiO₁.₂₅ film but also enhances the number of Si–Si bonding states under CO₂ laser RTA below the ablation threshold (6 kW/cm²), hence contributing to a redshift of the optical band gap from 3.32 to 2.43 eV. As the CO₂ laser RTA intensity increases to > 6 kW/cm², the optical band gap energy of the PECVD-grown SiO₁.₂₅ increases oppositely from 2.43 to 2.76 eV due to the ablation-induced damage to the surface and the generated NOV defects. The absorption coefficient of the SiO₁.₂₅ film at a wavelength of 455 nm is increased by a factor of 3 as the CO₂ laser intensity is increased from 7.5 to 12 kW/cm². During ablation, the incompletely annealed SiO₁.₂₅ with numerous oxygen-dependent defects also suffers from a slight decrease in the refractive indices from 1.87 to 1.79 when P_laser increases from 7.5 to 12 kW/cm².

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