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Luminescence of black silicon fabricated by high-repetition rate femtosecond laser pulses

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We studied the photoluminescence (PL) from black silicon that was fabricated using an 800 nm, 250 kHz femtosecond laser in air. By changing the scan velocity and the fluence of the femtosecond laser, the formation of the PL band between the orange (600 nm) and red bands (near 680 nm) could be controlled. The red band PL from the photoinduced microstructures on the black silicon was observed even without annealing due to the thermal accumulation of high-repetition rate femtosecond laser pulses. The orange band PL was easily quenched under 532 nm cw laser irradiation, whereas the red band PL was more stable; this can be attributed to "defect luminescence" and "quantum confinement", respectively. © *2011 American Institute of Physics*. [doi:10.1063/1.3641976]

I. INTRODUCTION

Silicon-based luminescent devices have received considerable attention[1,2] because they are more easily integrated with silicon-based circuits. However, the indirect bandgap of silicon makes it a poor light emitter. In the past few decades, many efforts have been devoted to developing new forms of silicon with highly efficient photoluminescence (PL), such as porous silicon[3,4] and silicon nanocrystals.[5–7] Another promising material is black silicon,[8] which has been produced by nanosecond,[9,10] picosecond,[11] or femtosecond[12,13] laser processing on the crystalline silicon. The PL of black silicon originates from the silicon-rich silica (SiO_x, $x < 2$) formed in the microstructures.[9,10] SiO_x has better chemical and structural stability compared with porous silicon and thus has attracted increasing interest.[14,15]

The PL of black silicon fabricated via nanosecond laser has been widely studied.[9,10] Recently, Wu and co-workers reported visible PL from black silicon fabricated in air via femtosecond laser.[16,17] The black silicon exhibited two luminescence bands: a green band and a red band. The red band appeared after annealing. The green band PL and the red band PL were attributed to "defect luminescence" and "quantum confinement", respectively. The work of Wu *et al.* suggests a potential application of femtosecond laser micromachining for the fabrication of silicon-based luminescent devices.[18,19]

In our work, the black silicon was fabricated using an 800 nm, 250 kHz femtosecond laser, and it exhibited separate orange (600 nm) and red (680 nm) luminescence bands even without annealing. The formation of the two PL bands could be controlled by selecting a suitable scan velocity and adjusting the fluence of the femtosecond laser. For higher scan velocities or larger laser fluences, it was prone to form microstructures emitting orange band PL. Conversely, it was prone to form microstructures emitting red band PL. The measurements of the dependence of the PL on the power of the 532 nm excitation light indicated that the orange band PL was easily quenched, whereas the red band PL was more stable. The orange band PL and the red band PL were ascribed to "defect luminescence" and "quantum confinement", respectively.

II. EXPERIMENTS

The sample was a 3-mm-thick silicon wafer that was cleaned in an ultrasonic acetone bath and then a methanol bath. The experimental setup was similar to that described in Ref. 20. A Ti:sapphire regenerative amplifier system (Coherent, RegA9000) was used as a light source and provided 800 nm, 120 fs laser pulses at a repetition rate of 250 kHz. The energy and access of the laser pulses were controlled using a variable attenuator and a mechanical shutter, respectively. The laser beam was perpendicularly focused on the silicon wafer via a 5× microscope objective (Nikon, NA = 0.15). The spot size on the silicon wafer surface was set at about 32 μm by adjusting the distance between the focus and the sample. The silicon wafer was positioned on a three-axis translation stage and moved in the plane perpendicular to the laser beam. The damage lines were scribed on the silicon wafer surface by femtosecond laser pulses in air. The PL spectra were measured using a three-dimensional nanometer scale Raman microspectrometer (Kyoto Instruments Inc., Nanofinder 30) equipped with a 532 nm cw laser as an excitation source. All measurements were performed at room temperature. The elements of the irradiated area were characterized using an electron probe micro-analyzer.

III. RESULTS AND DISCUSSION

A. Influence of the fabrication parameters

First, we investigated the dependence of the black silicon PL on the laser scan velocity. The femtosecond laser

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fluence was set at 1.5 kJ/m^2, and the scan velocities were set at 50, 200, 1000, and 3000 μm/s, respectively. The PL from the fabricated black silicon was excited by a 0.1 mW light at 532 nm. Figure 1 illustrates the PL spectra of the microstructures formed on the silicon wafer surface. As shown in Fig. 1, the PL intensity of the microstructures on the black silicon decreased with increasing laser scan velocity. More interesting, PL from the black silicon exhibited two kinds of luminescence spectra. The PL spectrum peak was located at a wavelength of 600 nm for a scan velocity of 3000 μm/s, and the PL spectrum peaks dramatically shifted to near 680 nm for scan velocities of 50, 200, and 1000 μm/s.

In addition, the influence of the femtosecond laser fluence on the black silicon PL was investigated. The scan velocity was fixed at 200 μm/s, and the femtosecond laser fluence was set at 0.5, 1.0, 1.5, 2.5, and 4.0 kJ/m^2. The PL was excited by a 0.1 mW light. As shown in Fig. 2, initially the PL intensity increased with increasing laser fluence while the PL spectrum peak was located near 680 nm. When the laser fluence was increased to 2.5 kJ/m^2, the PL intensity decreased rapidly to almost half of that for 1.5 kJ/m^2. In addition, the PL spectrum peak shifted to 600 nm, as observed in the black silicon formed at a scan velocity of 3000 μm/s. The intensity of the PL at 600 nm also increased with increasing laser fluence. Accordingly, we supposed that the luminescence from the black silicon fabricated by femtosecond pulses included two luminescence bands: an orange band at 600 nm and a red band near 680 nm. Furthermore, the PL band formation was dependent on the scan velocity and the femtosecond laser fluence. More interesting, when the black silicon was fabricated by the 250 kHz femtosecond laser, the red band PL was observed even without annealing, whereas when the black silicon was fabricated by the 1 kHz femtosecond laser, the red band PL was observed only after annealing.[16]

Moreover, the atomic ratio of oxygen to silicon (O/Si) in the photoinduced microstructures was also measured. Figures 3(a) and 3(b) show the dependence of the oxygen to silicon ratio on the scan velocity and the femtosecond laser fluence, respectively. As shown in Fig. 3(a), the oxygen to silicon ratio decreased with increasing scan velocity. When the scan velocity was increased to 3000 μm/s, the oxygen to silicon ratio decreased to 0.24. As shown in Fig. 1, the corresponding sample exhibited orange band PL. The oxygen to silicon ratio was larger than 0.24 for the sample emitting the red band PL. As shown in Fig. 3(b), the oxygen to silicon ratio increased with increasing laser fluence. When the laser fluence was increased to 2.5 kJ/m^2, the oxygen to silicon ratio increased to 0.79. As shown in Fig. 2, the corresponding sample exhibited orange band PL. The oxygen to silicon ratio was lower than 0.79 for the sample emitting the red band PL. For all of the measured samples, the ratios of oxygen to silicon were less than 2, which suggests that SiO_x has been formed in the silicon microstructures via the femtosecond laser pulse irradiation.[9,10,16] In addition, the silicon oxidation

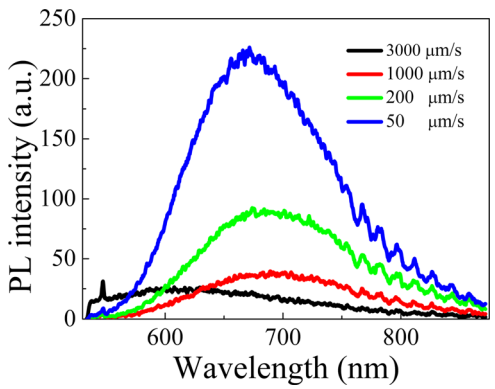

FIG. 1. (Color online) PL spectra from samples fabricated at scan velocities of 50, 200, 1000, and 3000 μm/s. The femtosecond laser fluence was set at 1.5 kJ/m^2. PL was excited by a 0.1 mW cw light at 532 nm.

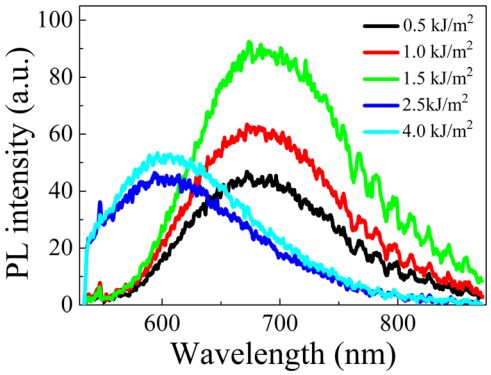

FIG. 2. (Color online) PL spectra from samples fabricated at femtosecond laser fluences of 0.5, 1.0, 1.5, 2.5, and 4.0 kJ/m^2. The scan velocity was set at 200 μm/s. PL was excited by a 0.1 mW cw light at 532 nm. The vertical scale is the same as in Fig. 1.

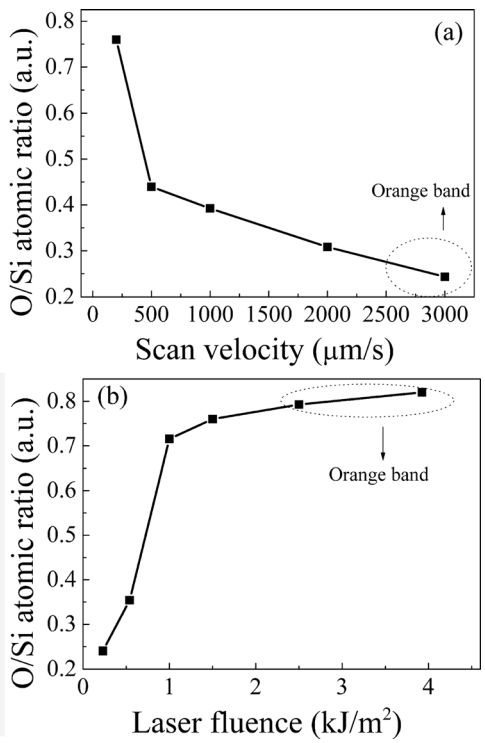

FIG. 3. The atomic ratio of oxygen to silicon in silicon microstructures induced by femtosecond laser for (a) different scan velocities and a laser fluence of 1.5 kJ/m^2 and (b) different femtosecond laser fluences and a scan velocity of 200 μm/s.

could be enhanced by either accumulating more laser pulses at the same zone or increasing the laser fluence.

B. Influence of the excitation power

In order to gain an understanding of the PL mechanism of black silicon, the influence of the excitation power at 532 nm on the PL spectra was investigated. The PL spectra under 1 mW excitation were measured for comparison with the PL spectra under 0.1 mW excitation. Figure 4 shows the PL spectra under 1 mW excitation when the sample used in Fig. 1 was employed. Under 1 mW excitation, the PL spectrum peaks were located at the red band for all of the samples. However, as shown in Fig. 1, under 0.1 mW excitation, the PL spectrum peak was located at the orange band for the sample made at a scan velocity of 3000 μm/s, whereas the PL spectrum peaks were located at the red band for samples made at scan velocities of 50, 200, and 1000 μm/s. That is, when the excitation power was set at 0.1 mW, the PL exhibited an orange or red band, depending on the femtosecond laser processing parameters. When the excitation power was increased to 1 mW, the PL exhibited only the red band.

The behavior discrepancy between the two bands under higher power excitation was probably due to their different mechanisms. The orange band PL and the red band PL could be attributed to "defect luminescence" and "quantum confinement", respectively.[16] In the PL measurements, it was observed that the orange band PL was easily quenched under 532 nm light irradiation at high power (over 1 mW), whereas the red band PL was more stable. Quenching of the orange band PL could be ascribed to the thermal effect, which was realized by the exciting light irradiation.[17] Accordingly, the change of the orange band PL excited by 532 nm cw light can be explained as follows: under irradiation with 1 mW exciting light, the temperature rose to about 400 K at the center of the irradiated zone. Due to the large thermal annealing effect of the exciting light, the orange band PL degraded dramatically. However, the intensity of the red band PL that existed simultaneously almost remained constant. Therefore, the PL shifted from the orange band to the red band under 1 mW excitation.

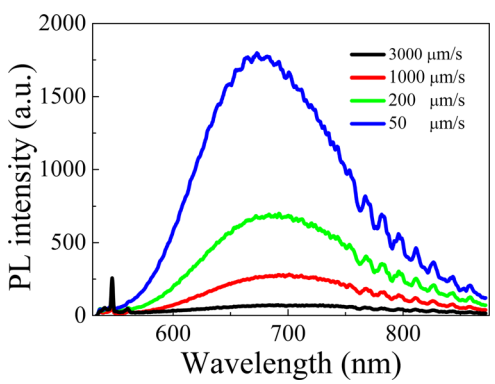

FIG. 4. (Color online) PL spectra under 1 mW excitation with a 532 nm cw light. The samples were fabricated at a femtosecond laser fluence of 1.5 kJ/m^2 and scan velocities of 50, 200, 1000, and 3000 μm/s. The vertical scale is the same as in Figs. 1 and 2.

Furthermore, due to the thermal accumulation effect of the 250 kHz laser pulse train,[21] black silicon emitting red band PL could be fabricated even without annealing. It was reported that the influence of the thermal accumulation began to appear when the repetition rate of the femtosecond pulse train exceeded hundreds of kHz.[22] Moreover, similar red band PL was also observed in black silicon fabricated with a nanosecond laser, which has a larger thermal effect than a femtosecond laser.[10] This might also prove that the thermal accumulation of laser pulses contributed to the formation of the red PL band.

IV. CONCLUSIONS

In conclusion, black silicon was fabricated using an 800 nm, 250 kHz femtosecond laser pulse train, and the resulting PL exhibited orange and red bands even without annealing. The formation of the luminescence band between the two bands could be controlled by changing the scan velocity or the femtosecond laser fluence. With a higher scan velocity or larger femtosecond laser fluence, the formed microstructures on the black silicon were prone to emit orange band PL under low power excitation. Conversely, it was prone to form microstructures emitting red band PL. The orange band PL was easily quenched under 532 nm cw light irradiation, whereas the red band PL was more stable due to its different PL mechanisms. The orange band PL and the red band PL can be attributed to "defect luminescence" and "quantum confinement", respectively.

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