

Influence of Deposition Conditions on Silicon Nanoclusters in Silicon Nitride Films Grown by Laser-Assisted CVD Method

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Abstract—Crystalline-silicon-nanocluster-embedded silicon nitride films were deposited at low temperature using a laser-assisted CVD (LACVD) system with various reactant gas flow rates and assisting laser power densities. The photoluminescence (PL) performances of the resultant films were studied, showing a systematic spectra blue shift, and the enhancement of PL intensity with the increase of the reactant NH_3/SiH_4 gas flow rate ratio and the assisting laser power density used in the film deposition. The spectra blue shift can be ascribed to the decrease of the size of the nanoclusters in the films. It is also deduced that both the reduction of the amount of nonradiative centers in the nanoclusters and the increase of the number density of the nanoclusters in the film are responsible for the enhancement of the PL intensity. The film growth process is also briefly discussed.

Index Terms—Laser-assisted CVD (LACVD) system, photoluminescence (PL), quantum confinement effect, Si nanoclusters, silicon nitride matrix.

I. INTRODUCTION

THE DISCOVERY of bright visible emission from porous silicon [1] greatly stimulates the investigation on silicon nanostructure systems due to their potential applications for silicon-based LEDs and optoelectronic ICs (OEIC). In recent years, various silicon nanostructure systems such as porous silicon [2] and silicon nanostructure embedded in silicon oxide matrix [3], [4] and in silicon nitride matrix [5], [6] have been studied. Among the aforementioned systems, silicon-nanocluster-embedded silicon nitride film attracts more attention, recently. It is mainly due to the fact that the silicon nitride, in comparison with silicon oxide, has narrower bandgap, which would benefit the injection of the carriers into silicon nanoclusters embedded in the film as active layer of LEDs. Various methods for depositing silicon-nanocluster-embedded films have been studied. However, in all the cases, a high-temperature process is used for forming silicon nanoclusters, which evidently would degrade the performances of some other devices that have

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been integrated on the same chip. In the previous paper [7], we have reported that silicon-nanocluster-embedded silicon nitride films can be deposited at low temperature using a laser-assisted CVD (LACVD) method. This low-temperature method avoids the disadvantage of the high-temperature processes in the usual methods, and hence, is compatible with the current electronic and optoelectronic integration technology.

The origins of the light emission of the resultant films is one of key problems for photonic materials, but due to the complexity of the film structure, controversial models have been proposed, such as crystalline or amorphous silicon nanoclusters [3]–[6], defect centers in silicon nitride matrix [8], interface states between silicon nanocluster and silicon nitride matrix [9] etc. In our previous report [7], the photoluminescence (PL) of the silicon nitride films deposited by LACVD system, at various NH_3 flow rates, was analyzed and attributed to silicon nanoclusters embedded in the silicon nitride matrix. In this paper, an extensive investigation is presented, where our attention will be focused on the influence of the film deposition conditions, including reactant gas flow rates, not only NH_3 , but also SiH_4 , and the assisting laser power density, on the structure and the PL properties of the resultant films. Based on the PL performances of the films, in combination with the film structure and bonding configuration, the dynamics of the film deposition process was briefly discussed.

II. EXPERIMENTAL PROCEDURE

The LACVD system used in this paper was constructed by guiding an external CO_2 laser beam into the chamber of a conventional plasma-enhanced CVD (PECVD) system. The substrate was illuminated with the CO_2 laser beam at an incident angle of 88° in order to prevent heating the substrate. The detailed LACVD system configuration has been reported elsewhere [7]. In the film deposition process, the temperature of the substrate holder was approximate to 85°C . In this paper, the argon-diluted SiH_4 (4%) and pure NH_3 were used as the reactant gases to deposit thin films. During the deposition process, the total working pressure and RF power were maintained at 500 mtorr and 100 W, respectively. The films were deposited on (1 0 0)-oriented p-type silicon substrates with a resistivity of about $20\ \Omega\cdot\text{cm}$. To investigate the influence of the deposition conditions, three series of samples were deposited. The first series was deposited at conditions of a fixed flow rate of SiH_4 of 250 sccm and a laser power density of $2.02\ \text{W}/\text{cm}^2$, but with the flow rate of NH_3 varied from 20 to 50 sccm. The second series was deposited at the

conditions of the same laser power density and the fixed flow rate of NH_3 of 50 sccm, but with the flow rate of SiH_4 varied from 200 to 300 sccm. For the third series, the power density of the assisting laser beam varied from 1.21 to 2.82 W/cm^2 , while the flow rate of SiH_4 and NH_3 were fixed at 250 and 50 sccm, respectively. To avoid the complication in the comparison of film properties, such as the PL, Fourier transformation IR (FTIR), and time-resolved PL (TRPL), the thicknesses of the deposited films were mostly kept at about 300 nm. Some films of thickness about $1 \mu\text{m}$ were also deposited on sapphire substrates, which were used for Raman scattering measurement to avoid the interference of the scattering signal from silicon substrate. The PL spectra of the deposited films were measured at room temperature using a He-Cd laser with a wavelength of 325 nm as an excitation source. The Raman spectra were measured under the excitation of the second harmonic (532 nm) of a continuous wave Nd:YAG laser. The transmission electron microscopy (TEM) measurements were performed to show the structures of the resulting silicon-nanocluster-embedded films. The bonding configurations of the deposited films were realized from the FTIR spectroscopy measurement. The time-resolved PL spectra of the samples, excited by the triple harmonic of a femtosecond-pulsed Ti : sapphire laser system, were measured with a time-correlated single-photon counting system.

III. EXPERIMENTAL RESULTS AND DISCUSSIONS

The PL spectra of the silicon nitride films deposited under various conditions are shown in Fig. 1. All the PL spectra exhibit a single structureless band, which shifts systematically with the film deposition conditions. As shown in Fig. 1(a), for the first-series silicon nitride films, the PL band moves to higher energy side and the intensity increases for films deposited at a higher flow rate of NH_3 . The PL behaviors, as well as the TEM results of the films, have been examined in the previous paper [7], and the observed PL behavior was attributed to the effects of the variation in size and density of the nanoclusters. It seems contrary to the first series that the PL spectra of the second-series samples, as shown in Fig. 1(b), move to lower energy side and the PL intensity decreases for films deposited at a higher flow rate of SiH_4 . However, it is noted that in both cases, the PL behavior follows the same regulation that the emission band shifts to higher energy side (blue shift) and the intensity of the PL enhances for films deposited at a higher NH_3/SiH_4 flow rate ratio. The systematic changing of the PL spectra also exists for films deposited at various laser power densities, as shown in Fig. 1(c), where the PL band moves to higher energy side and the intensity of the PL enhances for samples deposited with higher laser power density. In view of the conclusion obtained in [7], the systematic blue shift and intensity enhancement of the PL emission of the second and third series of samples imply that there is a similar variation of the size and density of the silicon nanoclusters embedded in these films. Raman spectroscopy is an efficient method to determine the presence and the size of silicon nanoclusters embedded in films [10], [11]. Fig. 2 shows the Raman spectra of the silicon nitride films deposited under various conditions. All of the Raman lines locate near 520 cm^{-1} ,

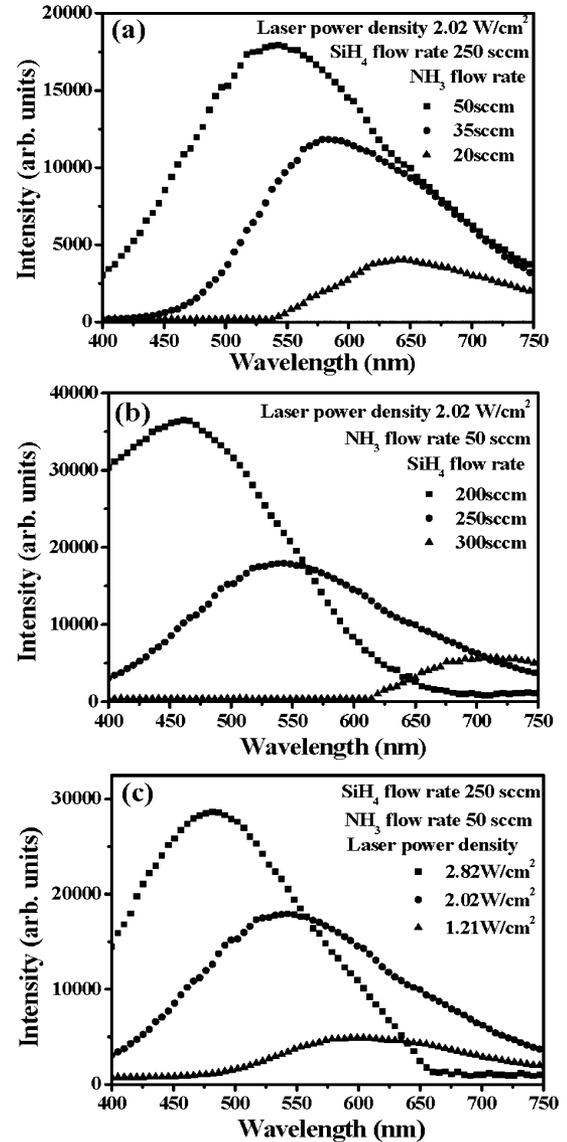


Fig. 1. PL spectra of samples deposited at various (a) NH_3 flow rates, (b) SiH_4 flow rates, and (c) laser power densities.

which correspond to crystalline silicon nanoclusters in the film. It can be seen that the Raman signal becomes broad, moves to lower frequency, and is less asymmetric, indicating the reduction of the size of Si nanoclusters [10], [11] for films deposited with higher NH_3/SiH_4 flow rate ratio and laser power density. This observation confirms the conclusion derived previously from the PL regulation [as shown in Fig. 1(a)–(c)] and supports the interpretation that is based on the quantum confinement effect.

The TEM measurements confirmed the observation of the PL and Raman spectra. Fig. 3 displays the representative TEM images of the films to show the variation of the size and density of the nanoclusters in the films deposited with various deposition conditions. Fig. 3(a) shows the TEM image of the film deposited at a laser power density of $2.02 \text{ W}/\text{cm}^2$, and flow rate of SiH_4 and NH_3 being 250 and 50 sccm, respectively. Whereas Fig. 3(b) corresponds to the film with a SiH_4 flow rate of 200 sccm, keeping other parameter same as that of Fig. 3(a). Finally, Fig. 3(c)

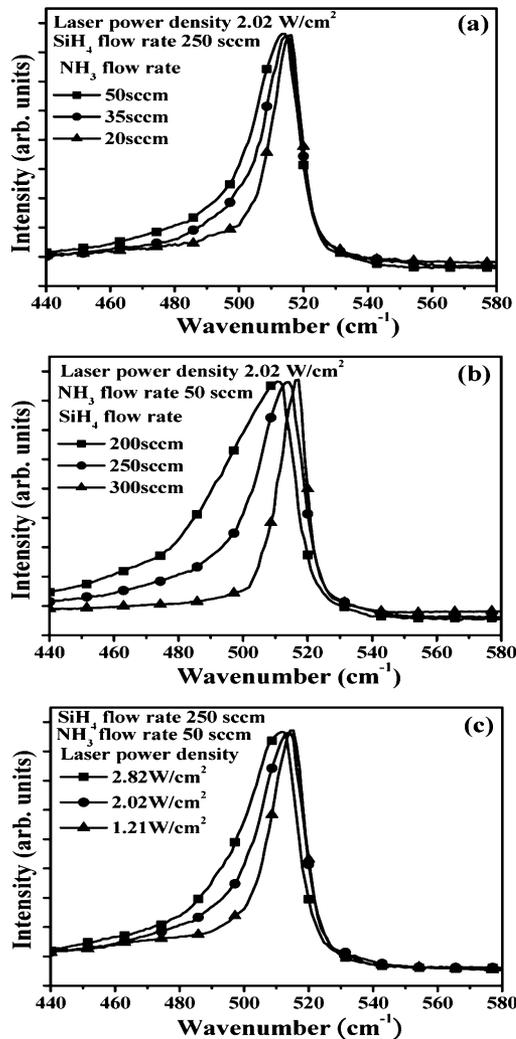


Fig. 2. Raman spectra of samples deposited at various (a) NH_3 flow rates, (b) SiH_4 flow rates, and (c) laser power densities.

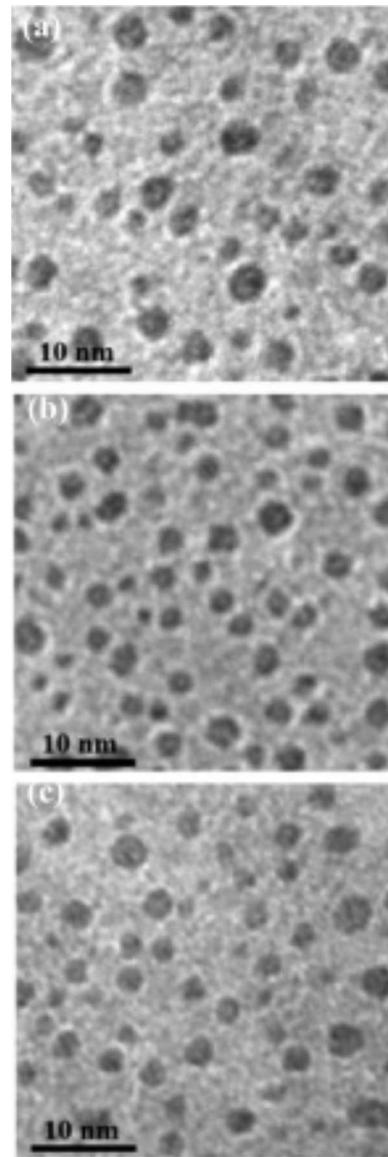


Fig. 3. TEM images of silicon nanocluster embedded films deposited at (a) flow rate of SiH_4 and NH_3 being 250 and 50 sccm, respectively, and the laser power density of 2.02 W/cm^2 , (b) flow rate of SiH_4 and NH_3 being 200 and 50 sccm, respectively, and the laser power density of 2.02 W/cm^2 , and (c) flow rate of SiH_4 and NH_3 being 250 and 50 sccm, respectively, and the laser power density of 2.82 W/cm^2 .

indicates the TEM image of the films deposited at a laser power density of 2.82 W/cm^2 with other parameter same as that of Fig. 3(a). The statistically averaged size and number density of the crystalline silicon nanoclusters in the film can be deduced from the corresponding TEM image, and the results deduced for three series of films are depicted in Fig. 4 (a)–(c), respectively. It can be seen that the average cluster size decreases and the number density of the clusters increases when the film is deposited with higher NH_3/SiH_4 flow rate ratio and laser power density. Now, we can say that the blue shift of the PL emission observed for all the three series samples is closely related to the decrease in the average size of the clusters in the film when the NH_3/SiH_4 flow rate ratio and laser power density used in the film deposition increases, which supports the conclusion that the PL emission of the LACVD-deposited silicon nitride films is originated from the silicon nanoclusters embedded in the films. And the intensity enhancement of the PL is partially related to the increase in the amount of nanoclusters in the film.

The exact mechanism responsible for the variation in size and density of the formed nanoclusters is still not clear. However,

the IR absorption spectra of the films deposited under various conditions can provide some hints to the chemical reaction dynamics in the film deposition. The FTIR spectra of the three series of silicon nitride films are shown in Fig. 5 (a)–(c), respectively. The FTIR spectra consist of the bands at $825\text{--}850 \text{ cm}^{-1}$ (Si–N stretching mode), $1155\text{--}1180 \text{ cm}^{-1}$ (N–H rocking mode), $2010\text{--}2325 \text{ cm}^{-1}$ (Si–H stretching mode), and $3250\text{--}3410 \text{ cm}^{-1}$ (N–H stretching mode) [5], [6]. It is noted that the intensity of the Si–H stretching mode decreases for films deposited at a higher NH_3/SiH_4 flow rate ratio. It implies that the existence of relatively more NH_3 molecules favors the dissociation of Si–H bonds in the deposition process, and hence, reduces the amount of Si–H bonds residing in the formed film, which is consistent

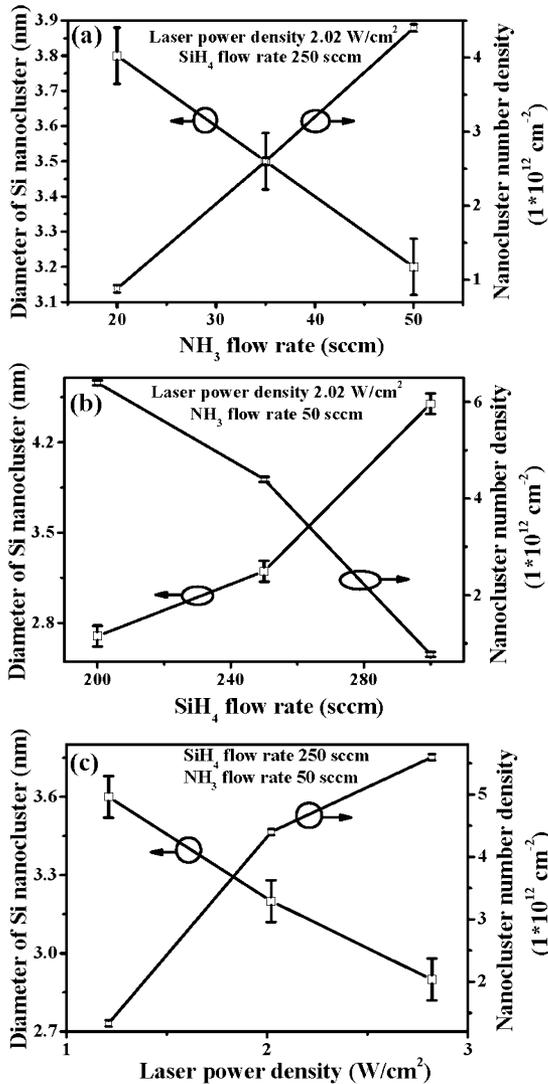


Fig. 4. Diameter and number density of Si nanoclusters in films deposited with various (a) NH_3 flow rates, (b) SiH_4 flow rates, and (c) laser power densities.

with the results reported in the literatures [5], [12]. Moreover, the intensity of the absorption band of the Si–H stretching mode also decreases with the increase of the laser power density used in the deposition, as shown in Fig. 5(c). This can be thought of as the result of the promoted decomposition of the Si–H bonds of the SiH_4 gas molecules by CO_2 laser illumination [13], [14]. Furthermore, the enhancement of the Si–H bonds decomposition, due to higher NH_3/SiH_4 flow rate ratio and laser power density, implies that the decomposed silicon radical will have more chance to bond with each other, which favors the nucleation of silicon clusters, and hence, increases the cluster number during the growth process. The increase of the number density of the silicon nanoclusters in the film has been thought of as an important reason for stronger PL of the film deposited at a higher NH_3/SiH_4 flow rate ratio and laser power density. It is also believed that the increase of the number of the nucleation sites tends to reduce the dimension of the grown silicon nanoclusters due to the limited amount of decomposed silicon radicals that are available for cluster growth in the film deposition process.

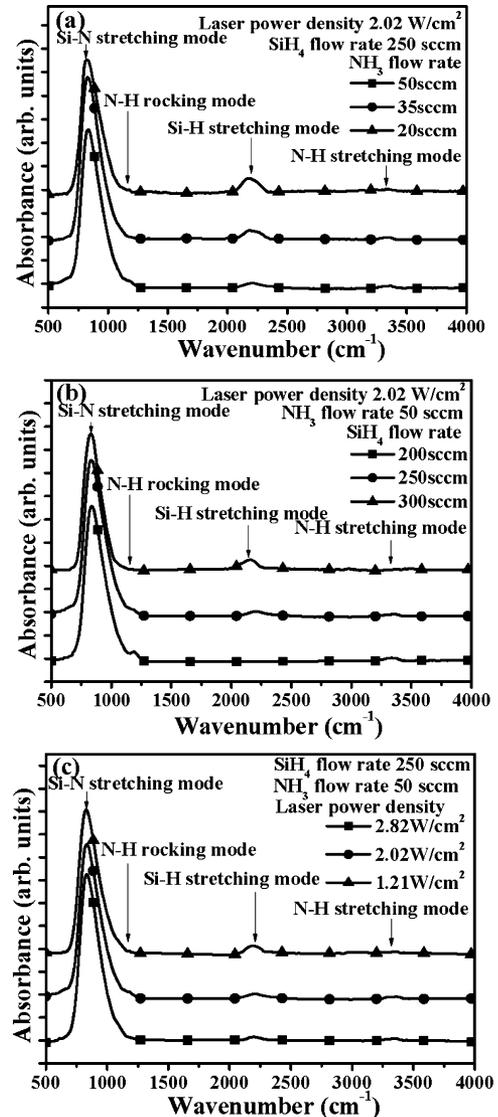


Fig. 5. FTIR spectra of samples deposited at various (a) NH_3 flow rates, (b) SiH_4 flow rates, and (c) laser power densities.

The temporal evolution of the PL peak intensity for films deposited at various NH_3 flow rates, SiH_4 flow rates, and laser power densities are shown in Fig. 6(a)–(c), respectively. It is clear that the carrier lifetime τ , estimated by the fluorescence lifetime, increases with the increase of the NH_3/SiH_4 flow rate ratio and laser power density. In general, the carrier lifetime τ can be expressed as follows [15]:

$$\frac{1}{\tau} = \frac{1}{\tau_r} + \frac{1}{\tau_{nr}}$$

where τ_r and τ_{nr} is the radiative lifetime and nonradiative lifetime, respectively. It is known that as the size of the silicon nanoclusters decreases, the radiative recombination rate $1/\tau_r$ of the nanocluster increases correspondingly [16], which would reduce the PL lifetime τ . However, the measured temporal evolution of the PL showed a slower decaying, implying a smaller deactivation rate, for films deposited at a higher NH_3/SiH_4 flow rate ratio and/or higher laser power density. This fact indicates

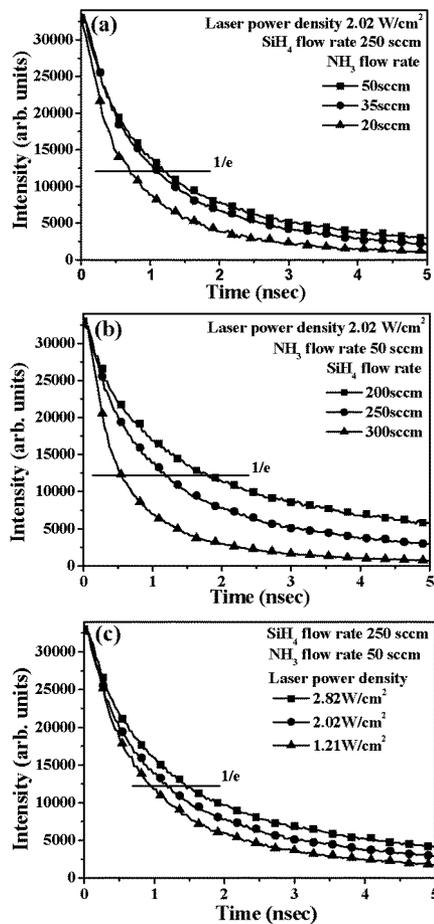


Fig. 6. Temporal evolution of the PL intensity for films deposited at various (a) NH_3 flow rates, (b) SiH_4 flow rates, and (c) laser power densities.

that for the film deposited at a higher NH_3/SiH_4 flow rate ratio and/or higher laser power density, the nonradiative recombination rate must be smaller, which suggests that a less amount of nonradiative centers exists in silicon nanoclusters. In other words, deposition of the films under the conditions of a higher NH_3/SiH_4 flow rate ratio and laser power density can improve the crystalline structure of the silicon nanoclusters. The aforementioned discussion indicates that the enhancement of the intensity of the PL relates not only to the increase of the number density of the silicon nanoclusters, but also to the improvement of the crystallite quality of the silicon nanoclusters.

IV. CONCLUSION

The PL performances of the silicon nanoclusters embedded in silicon nitride films deposited by LACVD method at various deposition conditions were systematically studied. It is found that the emission band shifts to higher energy side, and the PL intensity increases with the increase of the reactant NH_3/SiH_4 gas flow rate ratio and the assisting laser power density within the range used in the film deposition. The observed spectra shift of all the three series of samples can be ascribed to the decrease of the size of the nanoclusters in the films, which supports the conclusion deduced previously that the PL emission of

the LACVD-deposited films originates from silicon nanoclusters [7]. It is also deduced that the reduction of the amount of nonradiative centers in the nanoclusters, as well as the increase of the number density of the nanoclusters in the film are responsible for the enhancement of the PL intensity. The film growth process is briefly discussed, showing that Si-H bond decomposition is promoted by NH_3 molecules and laser assistance, which controls the growth dynamics. It appears that the LACVD method is of potential interest for depositing silicon-nanocluster-embedded silicon nitride films for optoelectronic applications, especially because the size of silicon nanoclusters, and hence, the emission color can be controlled by varying reactant gas flow rate and the laser power density used in the deposition process.

REFERENCES

- [1] H. Kim, C. M. Gilmore, J. S. Horwitz, A. Pigue, H. Murata, G. P. Kushto, R. Schlaf, Z. H. Kafafi, and D. B. Chrisey, "Transparent conducting aluminum-doped zinc oxide thin films for organic light-emitting devices," *Appl. Phys. Lett.*, vol. 76, pp. 259–261, Jan. 2000.
- [2] L. T. Canham, "Silicon quantum wire array fabrication by electrochemical and chemical dissolution of wafers," *Appl. Phys. Lett.*, vol. 57, pp. 1046–1048, Jul. 1990.
- [3] M. V. Wolkin, J. Jorne, P. M. Fauchet, G. Allan, and C. Delerue, "Electronic states and luminescence in porous silicon quantum dots: The role of oxygen," *Phys. Rev. Lett.*, vol. 82, pp. 197–200, Jan. 1999.
- [4] A. Irrera, F. Iacona, G. Franzo, S. Boninelli, D. Pacifici, M. Miritello, C. Spinella, D. Sanfilippo, G. Di Stefano, P. G. Fallica, and F. Priolo, "Correlation between electroluminescence and structural properties of Si nanoclusters," *Opt. Mater.*, vol. 27, pp. 1031–1040, Oct. 2005.
- [5] C. D. Presti, A. Irrera, G. Franzo, I. Crupi, F. Priolo, F. Iacona, G. D. Stefano, A. Piana, D. Sanfilippo, and P. G. Fallica, "Photonic-crystal silicon-nanocluster light-emitting device," *Appl. Phys. Lett.*, vol. 88, pp. 033501-1–033501-3, Jan. 2006.
- [6] B. H. Kim, C. H. Cho, T. W. Kim, N. M. Park, G. Y. Sung, and S. J. Park, "Photoluminescence of silicon quantum dots in silicon nitride grown by NH_3 and SiH_4 ," *Appl. Phys. Lett.*, vol. 86, pp. 091908-1–091908-3, Feb. 2005.
- [7] Y. Q. Wang, Y. G. Wang, L. Cao, and Z. X. Cao, "High-efficiency visible photoluminescence from amorphous silicon nanoparticles embedded in silicon nitride," *Appl. Phys. Lett.*, vol. 83, pp. 3474–3476, Aug. 2003.
- [8] T. C. Tsai, L. Z. Yu, and C. T. Lee, "Electroluminescence emission of crystalline silicon nanoclusters grown at a low temperature," *Nanotechnology*, vol. 18, pp. 275707-1–275707-5, Jun. 2007.
- [9] C. M. Mo, L. Zhang, C. Xie, and T. Wang, "Luminescence of nanometer-sized amorphous silicon nitride solids," *J. Appl. Phys.*, vol. 73, pp. 5185–5188, Jan. 1993.
- [10] L. D. Negro, J. H. Yi, L. C. Kimerling, S. Hamel, A. Williamson, and G. Galli, "Photonic-crystal silicon-nanocluster light-emitting device," *Appl. Phys. Lett.*, vol. 88, pp. 183103-1–183103-3, Jan. 2006.
- [11] G. Faraci, S. Gibilisco, P. Russo, and A. R. Pennisi, "Modified Raman confinement model for Si nanocrystals," *Phys. Rev. B*, vol. 73, pp. 033307-1–033307-4, Jan. 2006.
- [12] P. Mishra and K. P. Jain, "Raman, photoluminescence and optical absorption studies on nanocrystalline silicon," *Mater. Sci. Eng. B*, vol. 95, pp. 202–213, Sep. 2002.
- [13] N. M. Park, S. H. Kim, G. Y. Sung, and S. J. Park, "Growth and size control of amorphous silicon quantum dots using SiH_4/N_2 plasma," *Chem. Vap. Deposition*, vol. 8, pp. 254–256, Jun. 2002.
- [14] H. S. Tsai, G. J. Jaw, S. H. Chang, C. C. Cheng, C. T. Lee, and H. P. Liu, "Laser-assisted plasma-enhanced chemical vapor deposition of silicon nitride thin film," *Surf. Coat. Technol.*, vol. 132, pp. 158–162, Aug. 2000.
- [15] W. B. Steward and H. H. Nielsen, "The infrared absorption spectrum of Silane," *Phys. Rev.*, vol. 47, pp. 828–832, Apr. 1935.
- [16] P. S. Chen, T. H. Lee, L. W. Lai, and C.-T. Lee, "Schottky mechanism for Ni/Au contact with chlorine-treated *n*-type GaN layer," *J. Appl. Phys.*, vol. 101, pp. 024507-1–024507-4, Jan. 2007.
- [17] K. Watanabe, K. Sawada, M. Koshiba, M. Fujii, and S. Hayashi, "Photoluminescence decay-dynamics of Si nanoparticles prepared by pulsed laser ablation," *Appl. Surf. Sci.*, vol. 197–198, pp. 635–638, Sep. 2002.

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