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The optical properties of single-crystalline α-Si$_3$N$_4$ nanobelts synthesized via catalyst-assisted pyrolysis of polymeric precursor were characterized by absorption, photoluminescence (PL) and photoluminescence excitation (PLE). The optical absorption spectrum showed that the nanobelts exhibited indirect absorption behavior with optical band gap of $\sim$5.0 eV. Three broad peaks centered at 1.8, 2.3, and 3.0 eV were observed from the room-temperature PL spectrum of the nanobelts. The PLE spectra suggested the existence of multifold energy levels within the gap. A qualitative model was proposed to explain the observed absorption, PL and PLE spectra. © *2005 American Institute of Physics.* [DOI: 10.1063/1.1862753]

Silicon nitride is widely used for microelectronic and optoelectronic applications.[1–3] Similar to III-N semiconductors (e.g., GaN and AlN), crystalline silicon nitrides possess wide-band-gap semiconducting behavior and could be an excellent host material due to their excellent thermo-mechanical properties, chemical inertness and high dopant concentration.[4,5] Recently, the synthesis of one-dimensional nanostructured silicon nitrides opened potential applications in electronic/optic nanodevices.[6–14] Therefore, understanding of electronic/optic properties of silicon nitride is of a great interest. Previous studies on the optical properties of silicon nitride were primarily focused on its amorphous form.[15–24] While the optical properties of crystalline silicon nitrides were reported in a few previous studies,[13,25] no detailed study on the subject has been reported, particularly on nanostructured silicon nitride.

In this letter we report a detailed study on the optical properties of single crystal α-Si$_3$N$_4$ nanobelts synthesized via catalyst-assistant crystallization of amorphous silicon carbonitride (a-SiCN).[14] In this process, the polysilazane precursor was first decomposed to a-SiCN at 1000 °C under a flow of N$_2$. The a-SiCN powders were then reacted with catalyst (FeCl$_2$ in this study) to form Si–C–Fe liquid alloy droplets. The nanobelts were precipitated and grew from the liquid droplets at 1250 °C under a flow of N$_2$. The obtained nanobelts, which are 20–40 nm in thickness, 400–1000 nm in width and a few hundreds of micrometers to several millimeters in length, are single crystalline and α-Si$_3$N$_4$ phase.[26]

Optical absorption of the nanobelts was measured using a UV-3101 double channel spectrometer. Figure 1(a) shows the relationship between absorption coefficient α versus photon energy $h\nu$. In order to further understand the nature of the absorption, Fig. 1(b) plots the relationship between $\alpha^{1/2}$ and $h\nu$. A linear relationship observed in Fig. 1(b) suggests

that the transition of the absorption is indirect.[27] The band gap is estimated to be 5.0 eV by extrapolation (the linear dependence is extrapolated to the base line caused by equipment error, as indicated by the dashed line). This value is closely consistent with theoretical study,[28] where the extrapolated optical band gap of α-Si$_3$N$_4$ was calculated to be 5.0–5.2 eV. Previous studies revealed that the absorption
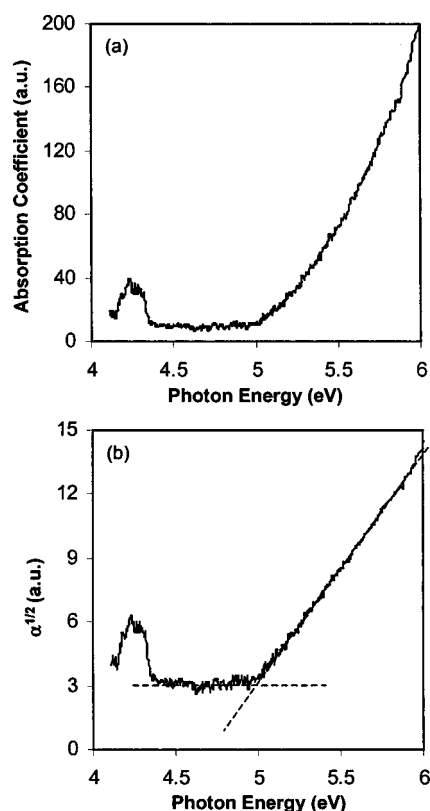

FIG. 1. Transmission optical absorption spectra of the α-Si$_3$N$_4$ nanobelts: (a) the relationship between the absorption coefficient α and photon energy $h\nu$, and (b) relationship between $\alpha^{1/2}$ and photon energy $h\nu$.

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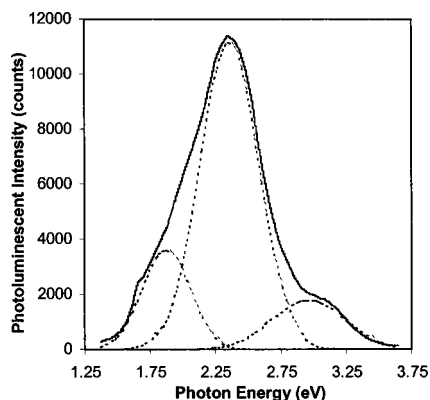
FIG. 2. Photoluminescence of the Si_3N_4 nanobelts under excitation of 325 nm at room temperature. Dotted line shows the Gauss-fit peaks, centered at 1.8, 2.3, and 3.0 eV, respectively.

FIG. 3. The photoluminescence excitation spectra of the α-Si_3N_4 nanobelts with detection at (a) 3.3 eV and (b) 1.8 eV.

edge for stoichiometric amorphous silicon nitride (Si/N =1.33) was ~4.6 eV,[15,19–21] and was ascribed to Si–Si defects.[19–21] Current result suggests that the nanobelts likely contain a lower amount of Si–Si defects than their amorphous counterparts, thus the intrinsic absorption can be revealed. In addition, a weak absorption peak centered at 4.2 eV, which was not observed previously, can also be seen from Fig. 1, suggesting the existence of a new absorption process.

Figure 2 shows a typical photoluminescence (PL) spectrum of the nanobelts measured under the excitation of HeCd laser 325 nm line (E_{ex}=3.81 eV). Intensive light emission of the nanobelts was observed even with the naked eye. The spectrum shows a broad emission band with the maximum at ~2.3 eV. This broadband can be further split into three peaks, centered at 1.8, 2.3 and 3.0 eV, respectively. The similar PL behavior was observed for amorphous silicon nitride,[16,19–22,29] suggesting that it is likely that the same defects were involved in the light emission processes for the nanobelts as for amorphous silicon nitride.

Further understanding of the light emission processes was carried out by measuring the luminescence intensity of the nanobelts as a function of excitation energy at selective detection energies. Figures 3(a) and 3(b) show the photoluminescence excitation (PLE) spectra with detections at 3.3 eV (e_1) and 1.8 eV (e_2), respectively. It can be seen that for both detections the positions of maximum luminescence intensity occur at the similar excitation energy; the onset energy is ~5.0 eV. This result suggests that the major contribution for the photoluminescence of the nanobelts is the transition between the intrinsic band edges. Previous study[22] revealed that the photoluminescence of amorphous silicon nitrides was dominated by the transition between Si–Si defect states. Again, it is likely that the amount of Si–Si defects in the crystalline nanobelts is much less than that in amorphous Si_3N_4. Both PLE spectra appear to have a contribution from a peak at ~4.2 eV, which is consistent with the weak peak observed in the absorption spectrum (Fig. 1). This result further suggests the existence of the transition. The PLE spectrum for e_1 also contains a peak at ~4.6 eV, which is not observed in the PLE spectrum for e_2. The 4.6 eV transition could arise from Si–Si defect.[19,22] The spectrum for e_2 shows an additional peak at ~2.6 eV, but the emission intensity at this peak is much weaker than that at excitation energies of 4.2 and 5.0 eV.
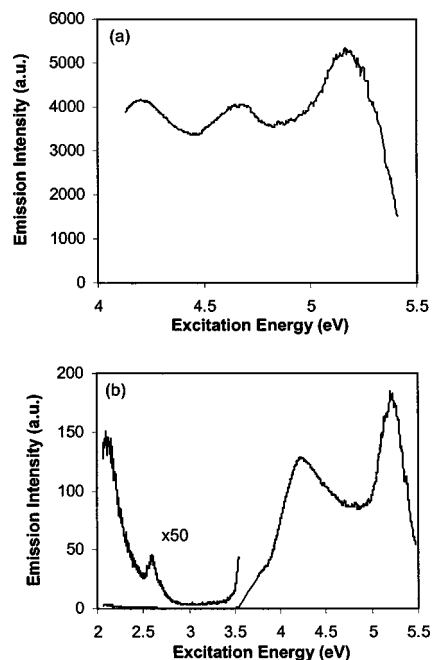
Robertson[30] has defined defects in silicon nitride to be of four types: Si–Si and N–N bonds, and Si and N dangling bonds. The Si–Si bond forms a bonding σ orbital and antibonding σ^* orbital that are separated by 4.6 eV for stoichiometric silicon nitride.[19,22] The silicon dangling bond (K^o center) forms a defects state about the midgap between σ and σ^*.[22,30,31] The silicon dangling bond forms a dominant trap and recombination center in silicon nitride and participates in the radiative transition giving rise to the luminescence.[22,32] According to Robertson,[30] besides the nitrogen dangling bond (N_2^0, N center), another type of nitrogen defect state can also give rise to a level within the Si–Si gap: namely N_4^+. The N_4^+ can be formed by reaction between positively charged silicon dangle bond and a bulk nitrogen ($Si_3^+ + N_3^0 = N_4^+ + Si_4^0$). Previous studies[22,33] suggested that the N_4^+ and N_2^0 defects form energy levels with the trap depth of 1.3–1.5 eV from the Si–Si band edges, respectively. The existence of silicon dangling bonds and nitrogen dangling bonds has been conclusively proved by analysis of ^{29}Si and ^{14}N hyperfine spectra, respectively.[34,35]

Based on these previous works, a simple qualitative model is proposed here to explain the optical behavior observed in the nanobelts, as shown in Fig. 4. In this model, the main broad PL peak at 2.3 eV arises from recombination processes at the silicon dangling bonds, similar as for amorphous silicon nitride. The peak at 3.0 eV has a contribution from the recombination between the Si–Si σ^* level and the
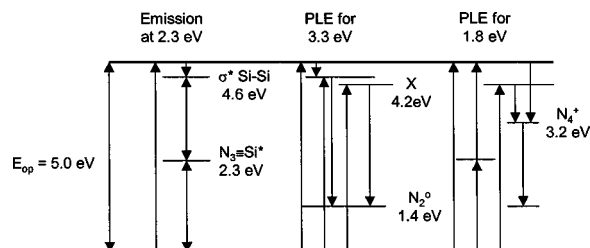

FIG. 4. Model for photoluminescence in the α-Si_3N_4 nanobelts.

N_2^0 level or between the N_4^+ and intrinsic valence band edge. The PL peak at 1.8 eV can be attributed to the following recombination processes: between conduction edge of the intrinsic band and N_4^+ level, and between the N_4^+ and N_2^0 states. In these processes, the following recombination shows irradiative processes: from intrinsic conduction edge to Si–Si σ^* level; and from the 4.2 eV state to the N_4^+; level. The PLE peak at 2.6 eV for e_2 is possibly due to double photons-absorption excitation from intrinsic valence edge to K^o center and then to the intrinsic conduction edge. Since the probability for such double excitation is low, the contribution from 2.5 eV peak is much lower than others. The absorption (Fig. 1) and PLE (Fig. 3) spectra suggest the existence of the excitation at energy of 4.2 eV. This excitation has not been observed before for stoichiometric amorphous silicon nitride. While a previous study[22] suggested that the σ-σ^* gap varied in a wide range, depending on the composition of silicon nitrides, we believed that the existence of the 4.2 eV in the nanobelts is not due to the variation in the σ-σ^* gap since the PL and PLE spectra clearly suggest the coexistence of both 4.6 (arises from σ-σ^* gap) and 4.2 eV. The original of the 4.2 eV trap is not clear at present. It is possible that the energy level is related to N-related defect(s) since a previous study[22] revealed that both emissions at 1.8 and 3.0 eV were associated with nitrogen defects.

In summary, we report a detailed characterization on the optical behavior of the single crystal α-Si_3N_4 nanobelts. The absorption spectrum reveals that the nanobelts shows intrinsic indirect absorption behavior with the optical gap of 5.0 eV. The PL spectrum of the nanobelts closely resembles that for stoichiometric amorphous silicon nitride. The PLE spectra reveal that both intrinsic and defect energy levels were involved in light emission processes with the intrinsic one as dominant transition. A transition process at 4.2 eV has been observed. A simple model is proposed to count for the observed absorption, PL and PLE behavior.

[1] H. Ono, T. Ikarashi, Y. Miura, E. Hasegawa, K. Ando, and T. Kitano, Appl. Phys. Lett. **74**, 203 (1999).
[2] F. Giorgis, C. F. Pirri, C. Vinegoni, and L. Pavesi, J. Lumin. **80**, 423 (1999).
[3] F. Giorgis, Appl. Phys. Lett. **77**, 522 (2000).
[4] F. Munakata, K. Matsuo, K. Furuya, Y. Akimune, J. Ye, and I. Ishikawa, Appl. Phys. Lett. **74**, 3498 (1999).
[5] A. R. Zanatta and L. A. O. Nunes, Appl. Phys. Lett. **72**, 3127 (1998).
[6] W. Han, S. Fan, Q. Li, B. Qu, and D. Yu, Appl. Phys. Lett. **71**, 2271 (1997).
[7] X. Wu, W. Song, B. Zhao, W. Huang, M. Pu, Y. Sun, and J. Du, Solid State Commun. **115**, 683 (2000).
[8] Y. Zhang, N. Wang, R. He, J. Liu, X. Zhang, and J. Zhu, J. Cryst. Growth **233**, 803 (2001).
[9] H. Kim, J. Park, and H. Yang, Chem. Phys. Lett. **372**, 269 (2003).
[10] H. Chen, Y. Cao, X. Xiang, J. Li, and C. Ge, J. Cryst. Growth **325**, L1 (2001).
[11] Y. Zhang, N. Wang, R. He, Q. Zhang, J. Zhu, and Y. Yan, J. Mater. Res. **15**, 1048 (2000).
[12] Y. Chen, L. Guo, and D. T. Shaw, J. Cryst. Growth **210**, 527 (2000).
[13] L. Yin, Y. Bando, Y. Zhu, and Y. Li, Appl. Phys. Lett. **83**, 3584 (2003).
[14] W. Yang, Z. Xie, H. Miao, H. Ji, L. Zhang, and L. An, J. Am. Ceram. Soc. (accepted for publication).
[15] H. R. Philipp, J. Electrochem. Soc. **120**, 295 (1973).
[16] I. G. Austin, W. A. Jackson, T. M. Searle, P. K. Bhat, and R. A. Gibson, Philos. Mag. B **52**, 271 (1985).
[17] V. V. Vasilev and I. P. Mikhailovskii, Phys. Status Solidi A **90**, 355 (1985).
[18] W. A. Jackson, T. M. Searle, I. G. Austin, and R. A. Gibson, J. Non-Cryst. Solids **77–78**, 909 (1985).
[19] P. A. Pundur, J. G. Shavalgin, and V. A. Gritsenko, Phys. Status Solidi A **94**, K107 (1986).
[20] V. V. Vasilev, I. P. Mikhailovskii, and K. K. Svitashev, Phys. Status Solidi A **95**, K37 (1986).
[21] C. Savall, J. C. Bruyere, and J. Krautwurm, J. Polym. Sci., Polym. Symp. **28**, 565 (1995).
[22] S. V. Deshpande, E. Gulari, S. W. Brown, and S. C. Rand, J. Appl. Phys. **77**, 6534 (1995).
[23] F. Giorgis, C. F. Pirri, C. Vinegoni, and L. Pavesi, Phys. Rev. B **60**, 11572 (1999).
[24] M. Molinari, H. Rinnert, and M. Vergnat, Appl. Phys. Lett. **77**, 3499 (2000).
[25] F. Munakata, K. Matsuo, K. Furuya, Y. Akimune, J. Ye, and I. Ishikawa, Appl. Phys. Lett. **74**, 3498 (1999).
[26] W. Yang, L. Zhang, Z. Xie, H. Miao, and L. An, Appl. Phys. A: Mater. Sci. Process. (accepted for publication).
[27] J. L. Pankove, *Optical Processes in Semiconductors* (Prentice–Hall, Englewood, Cliffs, NJ, 1971).
[28] Y. Xu and W. Ching, Phys. Rev. B **51**, 17379 (1995).
[29] V. A. Nadolinnyi, V. V. Vasilev, and I. P. Mikhailovskii, Phys. Status Solidi A **116**, K105 (1989).
[30] J. Robertson, Philos. Mag. B **63**, 47 (1991).
[31] J. Robertson, Mater. Res. Soc. Symp. Proc. **284**, 65 (1993).
[32] D. Chen, J. M. Viner, P. C. Taylor, and J. Kanicki, Mater. Res. Soc. Symp. Proc. **258**, 661 (1992).
[33] W. L. Warren, J. Robertson, and J. Kanicki, Appl. Phys. Lett. **63**, 2685 (1993).
[34] P. M. Lenahan and S. E. Curry, Appl. Phys. Lett. **56**, 157 (1990).
[35] W. L. Warren, P. M. Lenahan, and S. E. Curry, Phys. Rev. Lett. **65**, 207 (1990).