

# Optical Properties of Heavily Al-Doped Single-Crystal Si<sub>3</sub>N<sub>4</sub> Nanobelts

Fengmei Gao,<sup>‡,§</sup> Yansong Wang,<sup>‡</sup> Ligong Zhang,<sup>‡</sup> Weiyu Yang,<sup>§</sup> and Linan An<sup>‡,¶</sup>

<sup>‡</sup>Laboratory of Excited State Process, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Science, Changchun 130032, China

<sup>§</sup>Institute of Materials, Ningbo University of Technology, Ningbo 315016, China

<sup>¶</sup>Advanced Materials Processing and Analysis Center, University of Central Florida, Orlando, Florida 32816

The optical properties of heavily Al-doped single-crystal Si<sub>3</sub>N<sub>4</sub> nanobelts are investigated by measuring their absorption, photoluminescence, and photoluminescence excitation spectra. The results suggest that the doped Si<sub>3</sub>N<sub>4</sub> exhibit two absorptions at 2.5 and 4.2 eV, instead of absorption at 5.0 eV in the pure Si<sub>3</sub>N<sub>4</sub>. The doped nanobelts show light emissions in a range of 1.4 to 3.6 eV, which is red-shifted as compared with that of pure Si<sub>3</sub>N<sub>4</sub> nanobelts. These results are ascribed to the unique doping mechanism of Al, which generates two types of defects.

## I. Introduction

SILICON nitride has been widely used as a structural material for high-temperature applications and as a dielectric material for microelectronic and optoelectronic applications. The material is also an important wide band gap semiconductor with the band gap of 5.0 eV.<sup>1</sup> Similar to III-N semiconductors (e.g., GaN and AlN), silicon nitride possesses outstanding thermomechanical properties, chemical inertness, and high-doping concentration potential,<sup>2,3</sup> and thus could be an excellent host material for applications in short wavelength optical devices. Green light emission at room temperature was achieved from Er-doped silicon nitride thin films.<sup>4</sup> Recent development in the synthesis of one-dimensional (1D) nanostructured silicon nitride demonstrates their potential applications for nanometer-scaled optoelectronic devices.<sup>5–10</sup>

Previous studies on the optical properties of silicon nitride have primarily focused on its amorphous form.<sup>11–18</sup> Less attention has been paid to its crystalline form and to doping effects in particular. Zhang *et al.*<sup>1</sup> reported the absorption, light emission, and photoluminescence excitation (PLE) behavior of pure single-crystal Si<sub>3</sub>N<sub>4</sub> nanobelts. They revealed that the optical behavior of the pure Si<sub>3</sub>N<sub>4</sub> is determined by its intrinsic defects. Munakata *et al.*<sup>2</sup> studied the absorption behavior of Al-doped Si<sub>3</sub>N<sub>4</sub>, and found that the Al doping can introduce a midgap impurity level of ~2.4 eV into the intrinsic indirect band gap, which suggested that the optical behavior of the Si<sub>3</sub>N<sub>4</sub> can be significantly affected by doping.

In this paper, we report a detailed study on the optical behavior of heavily Al-doped single-crystal Si<sub>3</sub>N<sub>4</sub> nanobelts synthesized via catalyst-assistant pyrolysis of polymeric precursors. We find that the heavy Al doping has a pronounced effect on the optical properties of the Si<sub>3</sub>N<sub>4</sub>. Based on the optical behavior observed, a qualitative model is proposed for the electronic structure of the Al-doped Si<sub>3</sub>N<sub>4</sub>.

## II. Experimental Procedure

The heavily Al-doped Si<sub>3</sub>N<sub>4</sub> nanobelts are synthesized using a procedure described previously.<sup>19</sup> A commercially available polysilazane is first reacted with 2 wt% of aluminum isopropoxide to form a polyaluminasilazane precursor.<sup>20</sup> The precursor is then crushed to a fine powder by high-energy ball milling, with 3 wt% FeCl<sub>2</sub> powder added as a catalyst. This powder mixture is then pyrolyzed in a tube furnace in flowing ultrahigh-purity nitrogen at 0.1 MPa at 1450°C for 2 h, followed by furnace cooling to room temperature.

The morphology and structure of the obtained nanobelts are characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray diffractometer (XRD). The photoluminescence spectra were measured using a micro-PL spectrometer (Lab-Ram infinity, JobinYvon, Ville-neuve D'ascq, France) with the excitation of He–Cd laser. Absorption spectra and PLE spectra were measured using a UV-3101 double-channel spectrometer (Shimadzu, Kyoto, Japan) and an F4500 spectrophotometer (Hitachi, Tokyo, Japan).

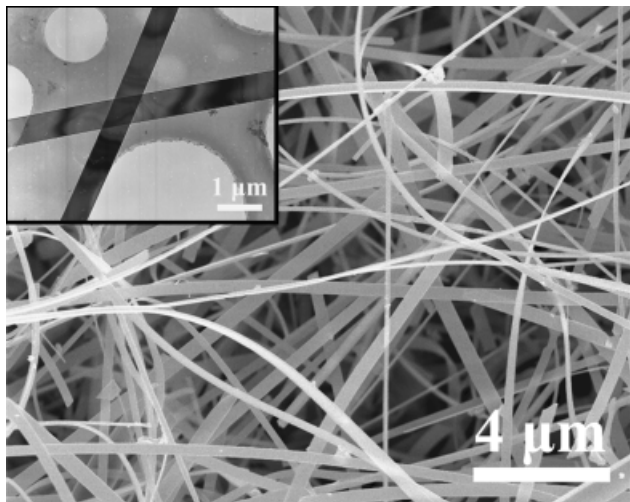
## III. Results and Discussion

Figure 1 is a typical SEM image of the nanobelts obtained, which are ~60 nm in thickness, ~500 nm wide, and up to a few micrometers long. The composition of the nanobelts is measured using energy-dispersive spectra (not shown) under TEM, revealing that the nanobelts contain 1.1 at.% of Al, suggesting that the nanobelts are heavily doped with Al. XRD analysis reveals that the nanobelts are  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>. The diffraction peaks (not shown) shift to a higher angle direction compared with the pure Si<sub>3</sub>N<sub>4</sub>, suggesting that the heavy Al doping causes the decreases in lattice parameters, similar to the previous study.<sup>19</sup>

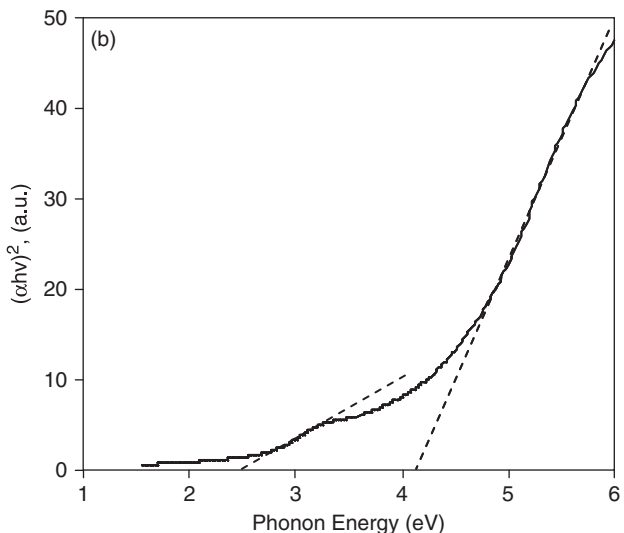
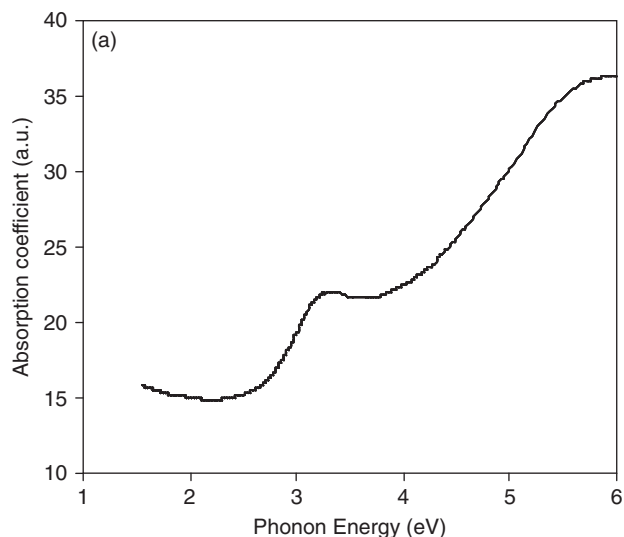
The effect of such heavy Al doping on the optical behavior of the nanobelt was first investigated by measuring its transmission optical absorption. Figure 2(a) shows the relationship between absorption coefficient ( $\alpha$ ) and photon energy ( $h\nu$ ). To further understand the nature of this absorption, Fig. 2(b) plots the  $(\alpha h\nu)^2$  versus  $h\nu$ . The result reveals that the spectrum exhibits two direct absorption regions, indicated by linear relationships between  $(\alpha h\nu)^2$  and  $h\nu$ .<sup>21</sup> The respective energy gaps are estimated to be 2.5 and 4.2 eV by extrapolation (dashed lines in Fig. 2(b)). This spectrum is fundamentally different from that of pure single-crystal  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> nanobelts, which show an indirect absorption with the band gap of 5.0 eV, ascribed to the transition between valence and conduction bands.<sup>1</sup> Our result is also different from a previous study of large-sized Al-doped Si<sub>3</sub>N<sub>4</sub> single crystals, which showed a single direct absorption with a mid-gap band at 2.4 eV.<sup>2</sup> This observed behavior of double absorptions, which has not been reported before, suggests that the heavy Al doping introduced two impurity mid levels into the wide band gap of pure Si<sub>3</sub>N<sub>4</sub>.

Figure 3(a) shows the typical room-temperature photoluminescence (PL) spectrum for the doped Si<sub>3</sub>N<sub>4</sub> nanobelt measured un-

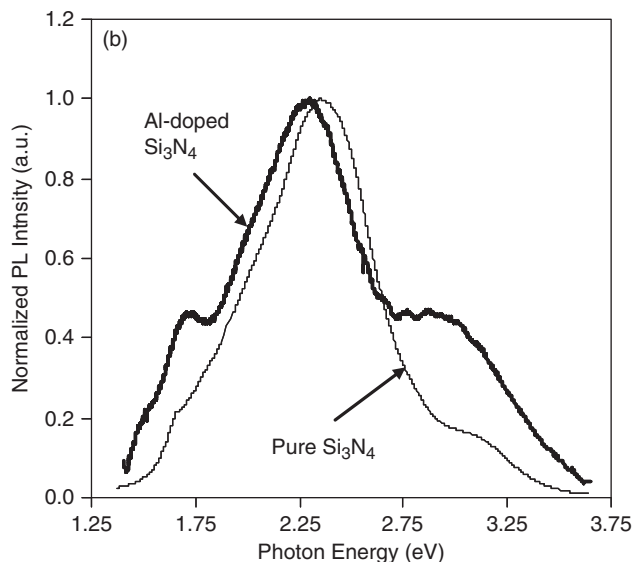
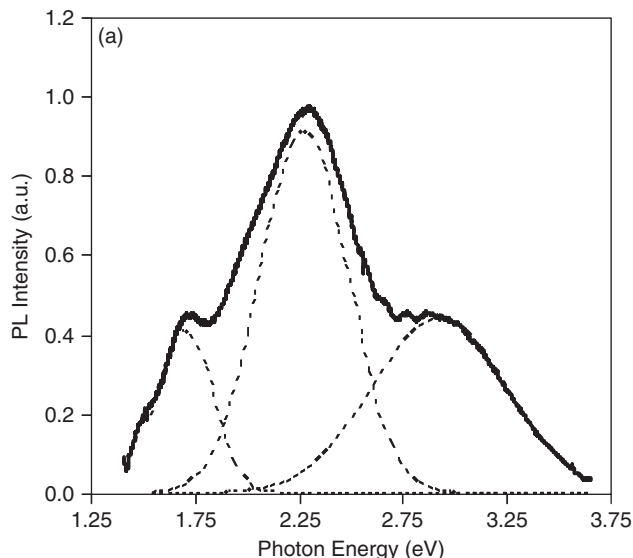
R. H. French—contributing editor



**Fig. 1.** Scanning electron microscopic image of the synthesized heavily Al-doped silicon nitride nanobelts. The inset is a transmission electron microscopic image of the nanobelts.



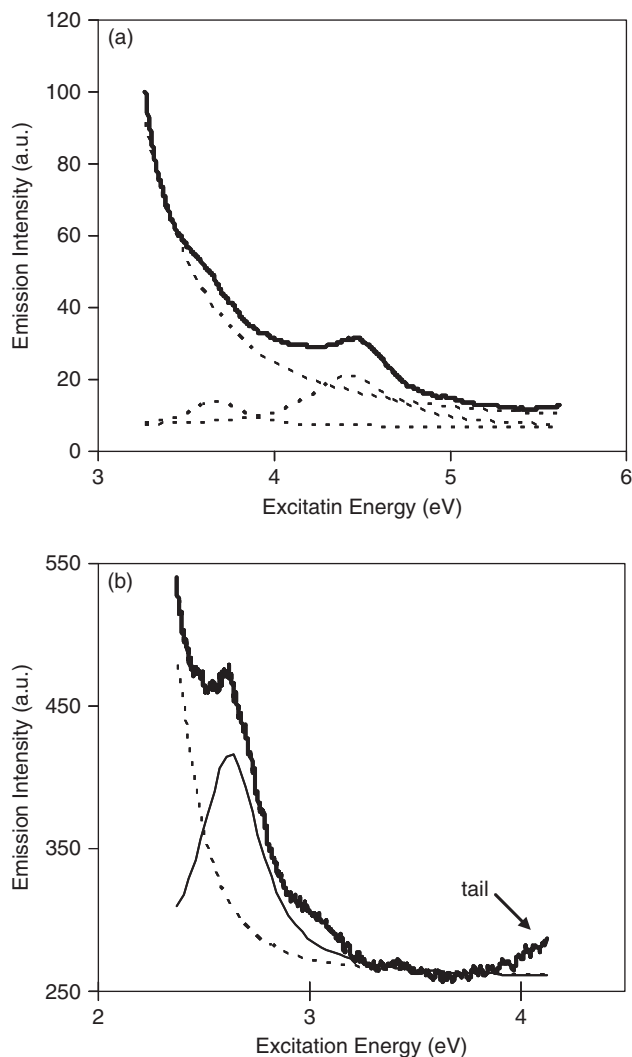
**Fig. 2.** Transmission optical absorption spectra of the heavily Al-doped  $\text{Si}_3\text{N}_4$  nanobelts: (a) the relationship between absorption coefficient,  $\alpha$  and phonon energy,  $h\nu$  and (b) the relationship between  $(\alpha h\nu)^2$  and  $h\nu$ .



**Fig. 3.** (a) Room temperature photoluminescence spectra of the heavily Al-doped  $\text{Si}_3\text{N}_4$  nanobelts. (b) Comparison of the PL spectra of the heavily Al-doped and pure  $\text{Si}_3\text{N}_4$  nanobelts measured under the same condition. Both of spectra are normalized with respect to the intensity of the major peaks.

der the excitation of 325 nm line of a HeCd laser ( $E_{\text{ex}} = 3.81$  eV). Intensive light emission for the nanobelts is even visible with the naked eye. Curve-fitting the spectrum reveals that it contains three peaks centered at 1.75, 2.27, and 3.02 eV, with the maximum emission occurring at  $\sim 2.27$  eV. Figure 2(b) compares the PL spectra of Al-doped and pure  $\text{Si}_3\text{N}_4$  measured under the same conditions. It is observed that the Al doping causes a red shift of the emission peaks by  $\sim 100$  meV. In addition, the relative intensities of the peaks centered at 1.75 and 3.02 eV are enhanced by  $\sim 3$  times.

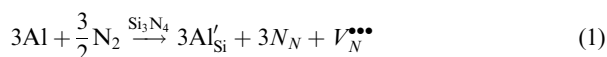
Further characterization of the light emission processes was performed by measuring the luminescence intensity of the nanobelts as a function of excitation energy at selective detection energies. Figure 4(a) shows the PLE spectrum of the heavily Al-doped nanobelts with detections at 3.1 eV. Curve fitting of the spectrum reveals that it contains two peaks with the onset energies at 4.2 and 3.2 eV, respectively. The major contribution is from the excitation energy of 4.2 eV, which corresponds to the higher energy absorption edge (Fig. 2(b)). It was reported previously that the major contribution for light emission at 3.0 eV from pure  $\text{Si}_3\text{N}_4$  nanobelts was from the transition between intrinsic band edges of 5.0 eV.<sup>1</sup> This transition is not observed



**Fig. 4.** The photoluminescence excitation spectra of the heavily Al-doped  $\text{Si}_3\text{N}_4$  nanobelts with detection at (a) 3.1 eV and (b) 2.2 eV.

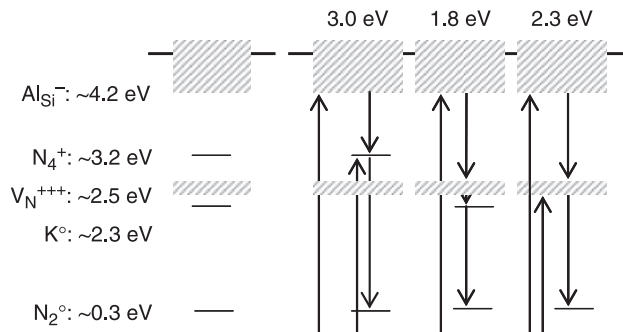
in the doped nanobelts, consistent with the disappearance of the intrinsic indirect absorption in the absorption spectrum of the doped  $\text{Si}_3\text{N}_4$  nanobelts (Fig. 2(b)). Previous studies have shown that the transition at 3.2 eV is due to  $\text{N}_4^+$  defects.<sup>1,22</sup> The current result suggests that this defect level is also present in the Al-doped  $\text{Si}_3\text{N}_4$  nanobelts. Figure 4(b) shows the PLE spectrum of the Al-doped nanobelts with detections at 2.2 eV. Curve-fitting the spectrum reveals that the major contribution to this emission is from an excitation energy of 2.5 eV, which corresponds to the lower energy absorption (Fig. 2(b)). It is seen that there is a tail at the high-energy end in Fig. 4(b), suggesting that the transition of the 4.2 eV also contributes to the light emission of 2.2 eV.

To understand the optical behavior of the heavily Al-doped  $\text{Si}_3\text{N}_4$  nanobelts better, it is instructive to explore the doping-induced defects in the material. A previous study revealed that the doping mechanism can be ascribed to the following reaction<sup>19</sup>:



The reaction suggests that Al doping introduces two types of defects: negatively charged misplaced Al ions,  $\text{Al}'_{\text{Si}}$  and positively charged nitrogen vacancies,  $V_N^{\bullet\bullet\bullet}$ . This is consistent with the two direct absorption bands observed.

Based on the above results and discussion, a simple qualitative model is proposed for the electronic structure of the heavily Al-doped  $\text{Si}_3\text{N}_4$  nanobelt (Fig. 5). The two types of Al-doping-



**Fig. 5.** Schematic showing a qualitative model for the electronic structure of the heavily Al-doped  $\alpha\text{-Si}_3\text{N}_4$  nanobelts; and light emission processes for emissions at 3.0, 1.8, and 2.3 eV.

induced defects form two defect energy levels in the intrinsic band gap of  $\text{Si}_3\text{N}_4$ , corresponding to the two direct absorptions (Fig. 2(b)). The disappearance of the original indirect absorption of undoped  $\text{Si}_3\text{N}_4$  is likely due to the overlap between the intrinsic conduction edge and the defect energy level of  $\text{Al}'_{\text{Si}}$ . According to Robertson,<sup>22</sup> there are four types of defects in pure silicon nitride: Si-Si and N-N bonds, and Si and N dangling bonds. Previous studies suggested that the Si-Si bond formed an anti-bonding orbital ( $\sigma^*$ ) that has an energy level of 4.6 eV<sup>1,13,16</sup>; the silicon dangling bond ( $\text{K}^\circ$  center) formed an energy level at  $\sim 2.3$  eV<sup>1,16,23,24</sup>; the N dangling bonds ( $\text{N}_2^\circ$  centers) formed an energy level at  $\sim 1.3$ – $1.5$  eV<sup>1,16,25</sup>; and the  $\text{N}_4^+$  defect with an energy level of 3.2 eV.<sup>1,22</sup> As suggested by the PLE spectrum (Fig. 4(a)), the Al-doped  $\text{Si}_3\text{N}_4$  should also contain  $\text{N}_4^+$  defects. It is seen that the  $\sigma^*$  level overlaps with the  $\text{Al}'_{\text{Si}}$  level, and thus cannot be seen from Fig. 5. There is no reason/evidence to show the effect of the Al doping on the silicon dangling bond; thus, we believed that the energy level associated with  $\text{K}^\circ$  centers should also exist in the doped  $\text{Si}_3\text{N}_4$ . The PLE spectra shown in Fig. 4 reveal that the 3.2 eV excitation generated an emission at 3.0 eV and 2.5 eV excitation generated an emission at 2.2 eV. These transition processes suggest that the  $\text{N}_2^\circ$  defect level should be  $\sim 0.3$  eV. It is seen that the energy level of the  $\text{N}_2^\circ$  center for the Al-doped  $\text{Si}_3\text{N}_4$  is significantly different from that for pure  $\text{Si}_3\text{N}_4$ . Such a difference is likely due to the formation of a large amount of N vacancies, which reduced the concentration of the N dangling bond.

The above model can be used to explain the observed optical behavior of the Al-doped  $\text{Si}_3\text{N}_4$  nanobelts (Fig. 5). The light emission at  $\sim 3.0$  eV arises from a transition from  $\text{N}_4^+$  level and  $\text{N}_2^\circ$  level. The major light emission at  $\sim 2.3$  eV arises from a recombination between the N vacancy level (2.5 eV) and  $\text{N}_2^\circ$  level. It is seen from Fig. 5 that in order to have the light emissions at 3.0 eV and 2.3 eV, the  $\text{N}_2^\circ$  level must be  $\sim 0.3$  eV. The PL peak at  $\sim 1.8$  eV has a contribution from the recombination process between the misplaced Al level and the N vacancy level, and possibly a recombination between the  $\text{K}^\circ$  level and the  $\text{N}_2^\circ$  level. It is seen that all emission processes involve the Al-induced defects. Because of the high doping concentration, increases in emission intensities are expected.

#### IV. Summary

We report a detailed study on the optical properties of the heavily Al-doped single-crystal  $\text{Si}_3\text{N}_4$  nanobelts. The results suggest that the Al doping, which introduces two types of defects in  $\text{Si}_3\text{N}_4$ , has a significant effect on its electronic structures and optical behaviors. The absorption spectrum shows that the Al doping introduces two impurity bands, which lead to two direct absorptions and cause the disappearance of the original indirect absorption of pure  $\text{Si}_3\text{N}_4$ . The doped nanobelt exhibits strong light emission with three emission peaks centered at 1.75, 2.27, and 3.02 eV. The emission peaks are red-shifted as compared with those for pure  $\text{Si}_3\text{N}_4$ . A simple model for the electronic

structure of the doped Si<sub>3</sub>N<sub>4</sub> has been proposed, which can satisfactorily explain the observed optical behavior.

### References

- <sup>1</sup>L. Zhang, H. Jin, W. Yang, Z. Xie, H. Miao, and L. An, "Optical Properties of Single-Crystalline  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> Nanobelts," *Appl. Phys. Lett.*, **86**, 061908 (2005).
- <sup>2</sup>F. Munakata, K. Matsuo, K. Furuya, Y. Akimune, J. Ye, and I. Ishikawa, "Optical Properties of  $\beta$ -Si<sub>3</sub>N<sub>4</sub> Single Crystals Grown from a Si Melt in N<sub>2</sub>," *Appl. Phys. Lett.*, **74**, 3498–500 (1999).
- <sup>3</sup>A. R. Zanatta and L. A. O. Nunes, "Green Photoluminescence from Er-Containing Amorphous SiN Thin Films," *Appl. Phys. Lett.*, **72**, 3127–9 (1998).
- <sup>4</sup>W. Han, S. Fan, Q. Li, B. Qu, and D. Yu, "Synthesis of Silicon Nitride Nanorods using Carbon Nanotube as a Template," *Appl. Phys. Lett.*, **71**, 2271–3 (1997).
- <sup>5</sup>Y. Zhang, N. Wang, R. He, J. Liu, X. Zhang, and J. Zhu, "A Simple Method to Synthesize Si<sub>3</sub>N<sub>4</sub> and SiO<sub>2</sub> Nanowires from Si or Si/SiO<sub>2</sub> Mixture," *J. Cryst. Growth*, **233**, 803–8 (2001).
- <sup>6</sup>H. Kim, J. Park, and H. Yang, "Synthesis of Silicon Nitride Nanowires Directly from the Silicon Substrates," *Chem. Phys. Lett.*, **372**, 269–74 (2003).
- <sup>7</sup>H. Chen, Y. Cao, X. Xiang, J. Li, and C. Ge, "Fabrication of  $\beta$ -Si<sub>3</sub>N<sub>4</sub> Nanofibers," *J. Cryst. Growth*, **325**, L1–3 (2001).
- <sup>8</sup>L. Yin, Y. Bando, Y. Zhu, and Y. Li, "Synthesis, Structure, and Photoluminescence of Very Thin and Wide Alpha Silicon Nitride  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> Single-Crystalline Nanobelts," *Appl. Phys. Lett.*, **83**, 3584–6 (2003).
- <sup>9</sup>W. Yang, Z. Xie, H. Miao, H. Ji, L. Zhang, and L. An, "Synthesis of Single-Crystalline Silicon Nitride Nanobelts via Catalyst-Assisted Pyrolysis of a Polysilazane," *J. Am. Ceram. Soc.*, **88** [2] 466–9 (2005).
- <sup>10</sup>W. Yang, Z. Xie, J. Li, H. Miao, L. Zhang, H. Ji, and L. An, "Ultra-Long Single-Crystalline  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> Nanowires: Derived from a Polymeric Precursor," *J. Am. Ceram. Soc.*, **88** [6] 1647–50 (2005).
- <sup>11</sup>H. R. Philipp, "Optical Properties of Silicon Nitride," *J. Electrochem. Soc.*, **120**, 295–300 (1973).
- <sup>12</sup>I. G. Austin, W. A. Jackson, T. M. Searle, P. K. Bhat, and R. A. Gibson, "Photoluminescence Properties of a-SiN<sub>x</sub>:H Alloys," *Philos. Mag.*, **B52**, 271–88 (1985).
- <sup>13</sup>P. A. Pundur, J. G. Shavalgin, and V. A. Gritsenko, "On the Nature of Deep Centers Responsible for the Memory Effect and Luminescence of a-SiN<sub>x</sub> with  $x \leq 4/3$ ," *Phys. Status Solidi A*, **94**, K107–12 (1986).
- <sup>14</sup>V. V. Vasilev, I. P. Mikhailovskii, and K. K. Svtashev, "Effect of Hydrogen on Photoluminescence Spectra of Silicon Nitride Amorphous Films," *Phys. Status Solidi A*, **95**, K37–42 (1986).
- <sup>15</sup>C. Savall, J. C. Bruyere, and J. Krautwurm, "Correlations Between ESR and Photoluminescence in Slightly Hydrogenated Silicon Nitride," *J. Phys. D: Appl. Phys.*, **28**, 565–70 (1995).
- <sup>16</sup>S. V. Deshpande, E. Gulari, S. W. Brown, and S. C. Rand, "Optical Properties of Silicon Nitride Films Deposited by Hot Filament Chemical Vapor Deposition," *J. Appl. Phys.*, **77**, 6534–41 (1995).
- <sup>17</sup>F. Giorgis, C. F. Pirri, C. Vinegoni, and L. Pavesi, "Luminescence Processes in Amorphous Hydrogenated Silicon-Nitride Nanometric Multilayers," *Phys. Rev.*, **B60**, 11572–6 (1999).
- <sup>18</sup>M. Molinari, H. Rinnert, and M. Vergnat, "Visible Photoluminescence in Amorphous SiN<sub>x</sub> Thin Films Prepared by Reactive Evaporation," *Appl. Phys. Lett.*, **77**, 3499–501 (2000).
- <sup>19</sup>W. Yang, H. Wang, S. Liu, Z. Xie, and L. An, "Controlled Al-Doped Single-Crystalline Silicon Nitride Nanowires Synthesized via Pyrolysis of Polymer Precursors," *J. Phys. Chem.*, **B111**, 4156–60 (2007).
- <sup>20</sup>A. Dhamne, W. Xu, B. Fookes, Y. Fan, L. Zhang, S. Burton, J. Hu, J. Ford, and L. An, "Polymer-Ceramic Conversion of Liquid Polyaluminasilazanes for Si-AlCN Ceramics," *J. Am. Ceram. Soc.*, **88** [9] 2415–19 (2005).
- <sup>21</sup>J. L. Pankove, *Optical Processes in Semiconductors*. Prentice-Hall, Englewood Cliffs, NJ, 1971.
- <sup>22</sup>J. Robertson, "Electronic Structure of Silicon Nitride," *Philos. Mag.*, **B63**, 47–77 (1991).
- <sup>23</sup>D. Chen, J. M. Viner, P. C. Taylor, and J. Kanicki, "Photoluminescence in Nitrogen-Rich a-SiN<sub>x</sub>:H," *Mater. Res. Soc. Symp. Proc.*, **258**, 661–6 (1992).
- <sup>24</sup>J. Robertson, "Electronic Structure of Defects in Amorphous Silicon Nitride," *Mater. Res. Soc. Symp. Proc.*, **284**, 65–76 (1993).
- <sup>25</sup>W. L. Warren, J. Robertson, and J. Kanicki, "Si and N Dangling Bond Creation in Silicon Nitride Thin Films," *Appl. Phys. Lett.*, **63**, 2686–7 (1993). □