The formation of SiGaN/SiO$_x$N$_y$ nanocables and SiO$_x$N$_y$-based nanostructures using GaN as a resource of Ga

Congkang Xu, Misuk Kim, Sangyong Chung, Junghwan Chun, Dong Eon Kim *

*Department of Physics and Electron Spin Science Center, Pohang University of Science and Technology,
San 31, Hyoja-Dong, Namku, Kyungbuk 790-784, Republic of Korea*

Abstract

SiGaN/SiO$_x$N$_y$ nanocables and SiO$_x$N$_y$-based nanostructures on silicon and silica substrates, respectively, have been firstly synthesized via using GaN as a resource of Ga. The silica wafer is mainly responsible for the formation of SiO$_x$N$_y$-based nanostructures and the intermediate Ga plays an important role in the formation of diverse nanostructures. SEM, TEM, line scan and SAED were employed to characterize as-prepared samples. The growth mechanism of as-prepared samples is also discussed.
© 2004 Elsevier B.V. All rights reserved.

1. Introduction

Compared with SiO$_2$, silicon oxynitrides (SiO$_x$N$_y$) thin films are of interest for gate dielectrics and ultra-large scale intergrated (ULSI) circuits because of their improved reliability [1–3]. Hydrogenenated amorphous silicon oxynitride (a-SiO$_x$O$_y$:H) is also one of the most important insulating materials in microelectronics [4,5]. It can be applied to optical fibers and waveguide since its refractive can be continuously varied between wide limits by adjusting a proper composition of X/Y [6,7]. Similarly, silicon nitride is one of the most important dielectric materials for the microelectronic processing due to its remarkable electrical, optical and chemical properties [8–10]. With the emerging of nanoscience and nanotechnology, in the past a few years, Si$_3$N$_4$ and SiO$_2$ nanostructures (nanowires, nanowhiskers, nanobelts) have been synthesized via many approaches such as carbonthermal reduction and nitridation reaction [11,12], carbon nanotube template [13,14], hot filament chemical vapor deposition [15] and microwave plasma heating [16]. In addition, Kim et al. [17] and Ran et al. [18] have prepared silicon nitride nanowires directly from Si wafer with and without the presence of catalysts, Pan et al. [19] fabricated SiO$_2$ nanostructures on silicon wafer via using molten gallium as a catalyst. On the other hand, much attention is currently being paid to doping the element into nanowires, which allows one to tailor the properties and functions of nanowires. Ga-doped ZnO nanotips can for instance enhance the carrier concentration of ZnO [20], and Mn doped GaN nanowires have ferromagnetism above room temperature, which is expected to the manufacture of spintronic device [21]. However, to our knowledge, no literatures are available for elements doped silicon nitride nanowires and silicon oxynitride-based nanostructures. In fact, Ga is an effective catalyst for the preparation of Si compound because of both the solubility of Si in Ga at a wide range of temperature [22] and non-reactivity with Si. In addition, Si vacancies can easily be filled with Ga to form Ga doped Si [23] since the covalent radius for Ga (1.225 Å) is only 4.4% larger than that for Si (1.173 Å) [24]. In this Letter, an effort has been made to prepare Ga doped silicon nitrides nanowires and silicon oxynitrides-based nanostructures using

* Corresponding author.
E-mail address: kimd@postech.ac.kr (D.E. Kim).

GaN as source of Ga both catalyst and dopant. As a result, we have successfully fabricated Ga doped silicon nitride nanowires, SiGaN/SiO_xN_y nanocables and SiO_xN_y-based nanostructures on silicon and silica substrates by controlling reaction chamber pressure and flow rate of the ammonia gas. SEM and TEM were used to characterize as-prepared nanowires. The formation mechanism of as-prepared samples is also discussed.

2. Experimental procedure

Starting materials and substrates: GaN powders (99.99%, Sigma Aldrich) were used as a source for Ga, Ar 95% + H_2, and NH_3 were used as carrier gas and reacting gas. Substrates of silicon and silica wafers were ultrasonically cleaned in acetone for 30 min prior to use.

A quartz boat containing reagent grade GaN powder (Aldrich, 99.99%) was kept in the center of a quartz tube placed horizontally in a tubular furnace. The cleaned silicon and silica substrates were placed downstream from the boat, respectively. The distances between the boat and substrates were 150 mm. The base vacuum was kept at 95 mTorr. The powder was heated up to 900 °C at the rate of 15 °C/min with a flow of Ar 95% + H_2 5% at 60 sccm. Ar + H_2 gas was then turned off, and a pure ammonia gas (99.999%) was introduced at 50 sccm. The system was then heated up to 1050 °C at the rate of 10 °C/min and maintained for 300 min. The temperature of the substrates was around 950 °C; the reaction chamber pressure was kept at 300 mTorr. After the system was cooled down to ambient temperature with NH_3, the nanowires were obtained from the substrates.

Characterization: The morphology and size distribution of the nanowires were characterized using a scanning electronic microscope (SEM, HitachiH-8010) equipped with energy-dispersive X-ray (EDX) spectroscopy and transmission electronic microscope (TEM, Hitachi H-800). High-resolution TEM (HRTEM), EDX and selected area electron diffraction (SAED) analysis were performed with JEOL-2010.

3. Results and discussion

Fig. 1 shows the SEM morphologies of all as-prepared samples grown on silicon and silica substrates, respectively. The samples grown on the silicon substrate (Fig. 1a) are mainly composed of nanowires with spear-like droplets on their tips, and their cross-sections are circular. EDX results (the left lower inset) demonstrate that the nanowires consist of Si, N and Ga, and the content of Ga contents in the nanowires is about 3 at.%. The spear-like tips comprise Ga, Si and N, the atomic

ratio of Ga, Si to N being 31:7:62. Fig. 1b–f reveal the SEM image of as-fabricated sample on silica substrate. The products formed on the silica substrate have completely different morphology, size distribution and orientation. The morphologies include knotting-like nanowires, nanobundles, nanoflowers, and Chinese cabbage-like structures, EDX analyses indicate that the nanostructures comprise Si, O and N with the atomic ratio 39:41:20. As shown in Fig. 1b, the diameters of the knotting-like nanowires range from 50 to 120 nm, and the lengths reach up to a few microns. The node (as indicated by the arrow) comprises a minor proportion of Ga aside from Si, O and N. Fig. 1c demonstrates the SEM image of the nanobundles. It is interesting that one nanowire splits into two nanowires and subsequently newly grown nanowires proceed to split into another two nanowires (as indicated by the arrow); moreover, the diameter and growth direction are similar to that of original nanowires. The Ga tip on the top can simultaneously catalyze growth of many SiO_xN_y nanowires, differently from the conventional VLS in which one catalyst nanoparticle only catalyzed growth of one nanowire. On the other hand, the above-mentioned split growth made one nanowire extend to a larger volume of nanowires within short growth. These phenomena were also observed during the fabrication of SiO_2 nanowires via using Ga and Co as a catalyst [19,25]. Fig. 1d displays an array of the nanowires. The nanowires are well aligned, the diameter is approximately 50 nm and the length up to 15 μm. Fig. 1e shows the SEM image of a typical nanoflower. EDX analysis illustrates that it consists of Si, N and O. Fig. 1f demonstrates Chinese cabbage-like nanostructures, which grow separately from the surface of silica wafer. EDX analyses reveal that they are composed of Si, O and N, the tips are molten Ga covered with a thin oxide layer (for some cabbages, the molten balls are removed off and left a cavity on its top).

Fig. 2a, b show general and line scan analyses and a HRTEM image of a nanocable, respectively. Fig. 2a demonstrates a TEM image of a typical nanocable. The inset is line scan analysis as indicated by the line, which shows that Si and Ga have broad peaks and oxygen has a minimum at the central position. The nitrogen is distributed inside both sheath and core. Oxygen at the center position is the lowest. Ga is nearly uniform distribution across the nanowire. These results confirm that the nanocable has a good axial symmetry in composition and that the core is Ga doped silicon nitride, the sheath consists of Si, O and N rather than only Si and O. Fig. 2b shows a HRTEM image of another nanocable with an outer diameter of about 30 nm and inner diameter (core) of 15 nm. EDX (the right lower inset) indicates that the nanowires are composed of Si, N, O and Ga. The atomic ratio of Si, N, O to Ga is 52:37:10.5:0.5. The HRTEM clearly proves that the
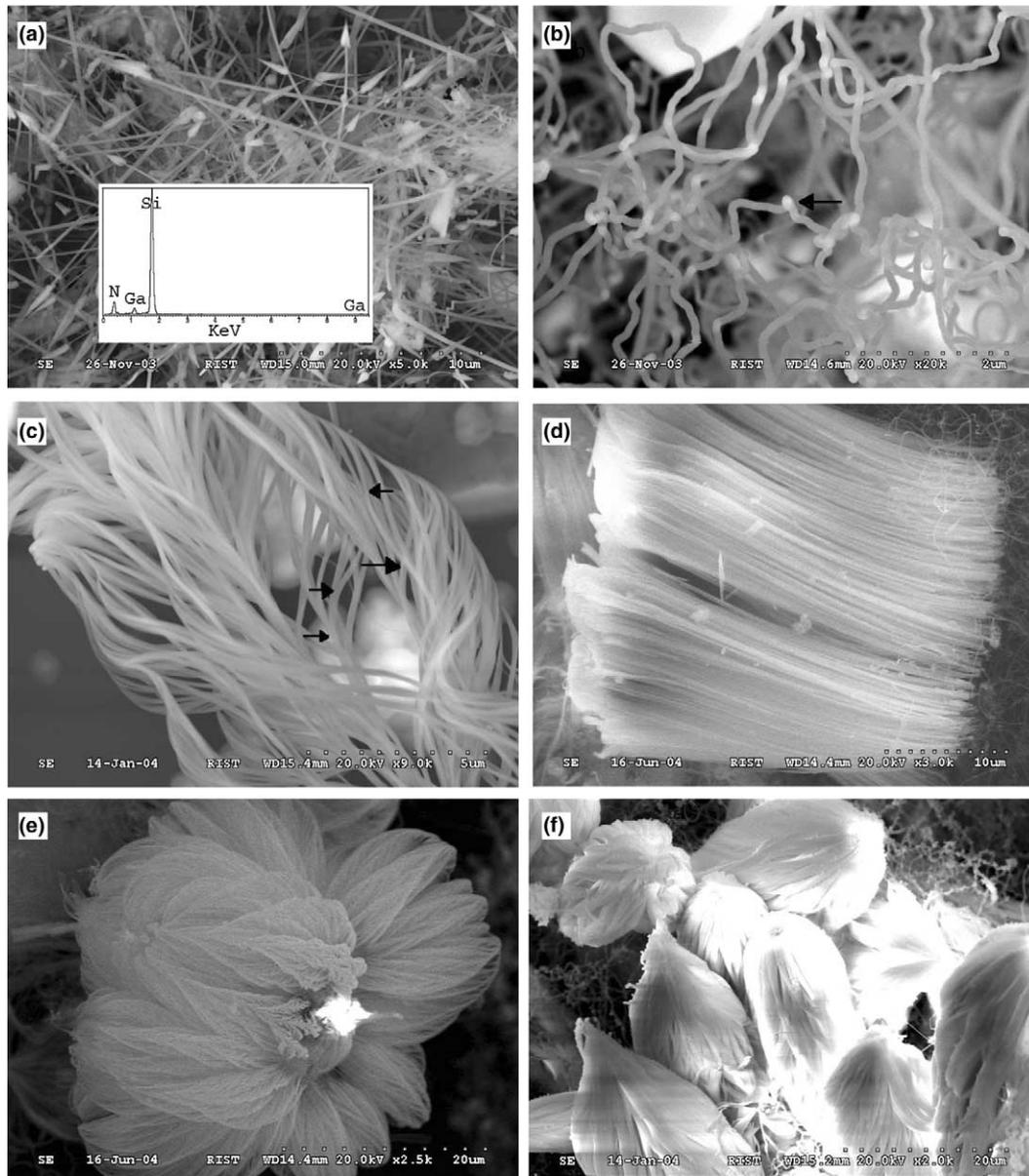
Fig. 1. (a) SEM image of the samples grown on the silicon substrate, the inset is EDX. (b) Knotting-like nanowires grown on silica substrate, (c) the nanobundles grown on silica substrate, and the arrows indicate the split growth of the nanowires, (d) the array of nanowires grown on silica substrate, (e) the nanoflowers grown on silica substrate and (f) Chinese cabbage-like nanostructures grown on silica substrate.

sheath is amorphous and the core of Ga doped silicon nitride is single crystal. The clear fringes demonstrate that the atomic layers of the nanowire are two-dimensional with a spacing of 0.66 nm corresponding to $(1\,0\,\bar{1}\,0)$ and $(0\,1\,\bar{1}\,0)$ plane of hexagonal α-Si_3N_4, respectively. The SAED (the left upper inset) further confirms that the core of the nanowire is single crystal with hexagonal structure α-Si_3N_4 and grows along $[1\,1\,\bar{2}\,0]$ direction. These results imply that the Ga doped Si_3N_4 nanowire form at first and then its outer layer is oxidized.

Fig. 3a shows TEM image of a nanowire grown on SiO_2 wafer. The nanowire has a diameter of about

80 nm and the length of a few microns as well as smooth and clean surface. EDX analyses (the left upper inset) indicate that the nanowire is composed of Si, O and N with the atomic ratio of Si, O to N about 50:38:12. EDX analysis (the right lower inset) on the node (as indicated by the arrow) indicates there exists Ga besides Si, O and N. Fig. 3b shows HRTEM image of a SiO_xN_y nanowire. It is amorphous and homogenous without crystalline Si or Si_3N_4 cores inside. SAED (the inset) further clarifies that the nanowire is amorphous.

In order to advance this approach, it is necessary to investigate the effect of the growth parameters (such as
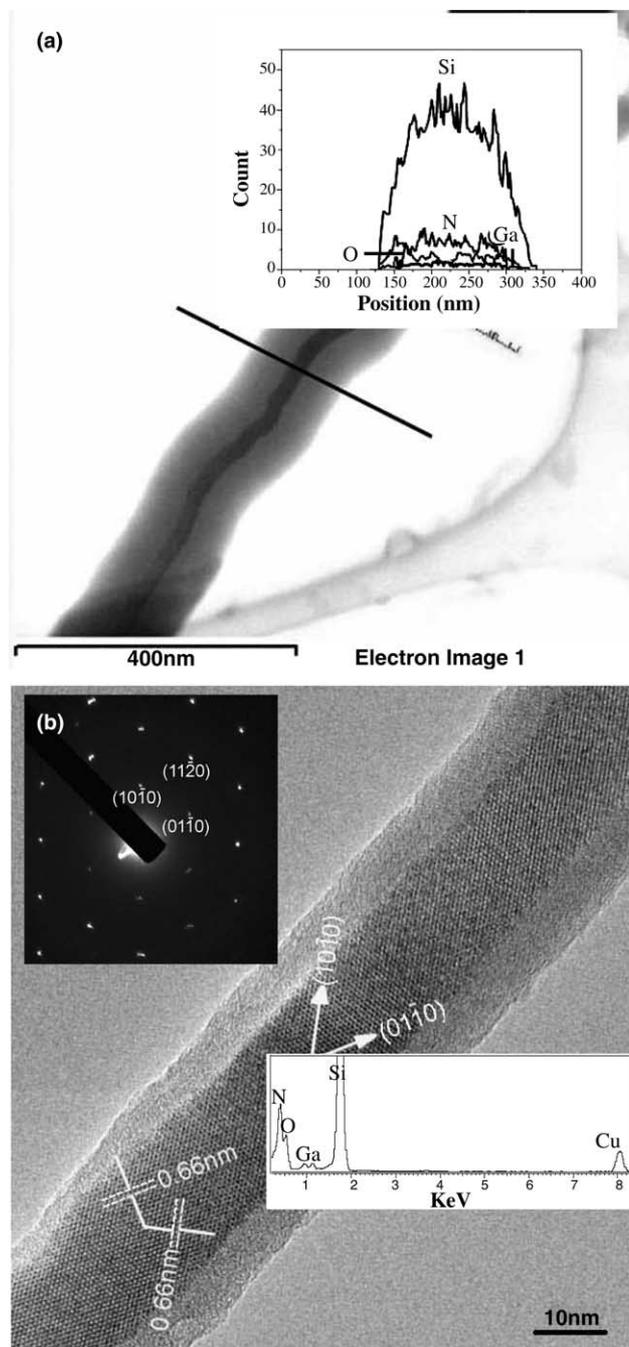
Fig. 2. (a) TEM of a typical nanocable grown on silicon substrate, and the inset is line scan analysis and (b) a high-resolution TEM image of another nanocable grown on silicon substrate, the left upper inset is SAED and right lower inset is EDX.
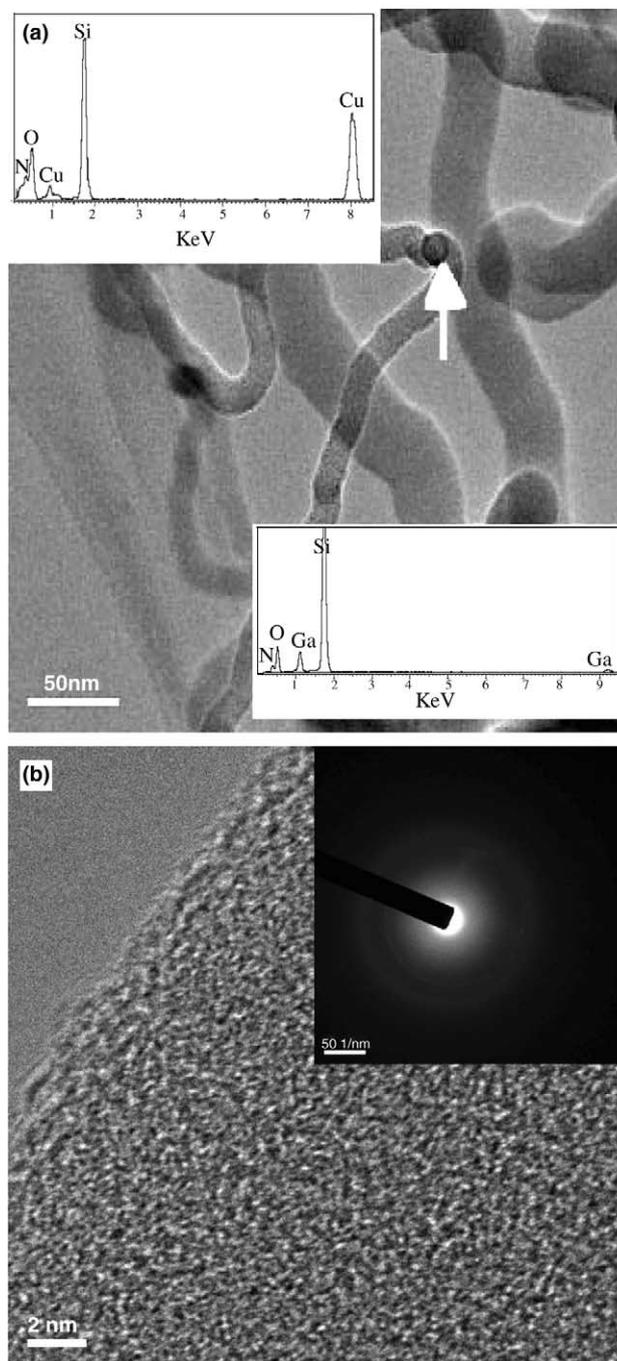

Fig. 3. (a) TEM image of SiO_xN_y nanowires grown on silica substrate, the left upper inset is EDX of a nanowire and right lower inset is EDX of a node and (b) a HRTEM of a SiO_xN_y nanowire and the inset is SAED.

flow rate of carrier gas and reaction chamber pressure) on the growth of nanostructures. Under the invariance of flow rate of the ammonia, Ga concentration in silicon nitride increases as the reaction chamber pressure increases, in the same way, under the constant of reaction chamber pressure, when the flow rate of the ammonia is less than 15 sccm, we only observed SiO_2 nanostructures rather than Si_3N_4 nanowires or SiO_xN_y nanostructures.

Accordingly, we suggest that reaction chamber pressure and the flow rate of ammonia play an important role on the doping of Ga into Si or Si compound and nitridation of Si or Si compound. The nitrogen in Ga doped Si_3N_4 nanowires and SiO_xN_y nanostructures are mainly from NH_3 instead of catalyst particles GaN. In addition, In order to clarify the function of Ar 95% + H_2 5%, we

put only silica wafer with the absence of GaN inside reaction chamber with a flow of Ar 95% + H$_2$ 5% at 60 sccm at 900 °C under the same condition of temperature, pressure, and base vacuum. As a result, we observed that some areas on the surface of silica were corroded severely and subsequently produce nanoparticles. EDX analyses indicated the oxygen in the corroded area is seriously deficient by comparison with non-corroded areas and nanoparticles are Si. Ar 95% + H$_2$ 5% gas is favorable to yield Si and delete the oxygen trace in reaction chamber.

When the temperature reaches up to 950 °C, GaN powders are decomposed into a dense, hot vapor of Ga and N$_2$. Hot Ga vapor rapidly condenses into small Ga cluster as Ga species cool through collision with the buffer gas. The formed Ga clusters are carried away to the downstream of quartz tube by the carrier gas and deposited onto a wafer. In the case of Si wafer, the Ga droplets etch silicon to form Ga–Si [22] alloy as an initial nucleation site and thus create a dense vapor of silicon species around the Si substrate, which acts as Si source for the growth of Si$_3$N$_4$ based nanowires. Meanwhile, Ga can easily doped into Si vacancies at a wide range of temperature to form Si$_{1-x}$Ga$_x$N, the Ga is mainly incorporated on Si lattice sites rather than on interstitial positions [23].

$$Si + NH_3 \xrightarrow{Ga} Si_3N_4/Ga + H_2 \qquad (1)$$
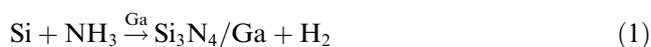
The molten metal Ga can serve as both an effective catalyst and dopants for the growth of Ga doped Si$_3$N$_4$ nanowires. Due to leakage of the system, the following reaction may occur:

$$Si_3N_4/Ga + O_2 \rightarrow SiO_xN_y/Ga \qquad (2)$$

As shown in Fig. 2a, it is most likely that the crystalline Si$_3$N$_4$ nanowires form firstly and subsequently outlayers are oxidized into amorphous silicon oxynitride to finally form nanocables.

In the case of silica wafer, firstly, at an elevated temperature,

$$2GaN \rightarrow 2Ga + N_2 \qquad (3)$$

The freshly formed gallium, having a higher activity and coalesces, was deposited on silica wafer by carrier gas and easily forms Ga–Si alloy, newly formed alloy Ga–Si as a nucleation site, and then:

$$SiO_2 + Si \xrightarrow{Ga} 2SiO/Ga(g) \qquad (4)$$

$$SiO(g)/Ga + NH_3 \rightarrow SiO_xN_y(s)/Ga + H_2O \qquad (5)$$

It is understood that final products are not SiO$_2$ but amorphous silicon oxynitride, which has been proven by previous numerous experiments with respect to the fabrication of silicon oxynitride films [26–29].

Therefore, the growth of SiO$_x$N$_y$ nanostructures can be summarized into the following three steps:

- At elevated temperature, GaN is partially decomposed into Ga and N$_2$. Si is dissolved in molten Ga to form Ga–Si alloy [30].
- The most important SiO gas is generated via the silicon reduction of silica. Due to the non-solubility of SiO in molten Ga, SiO segregates from molten Ga–Si and then diffuses on the surface of molten Ga–Si.
- At the introduction of NH$_3$ into reaction chamber, SiO reacts with ammonia to form many interesting SiO$_x$N$_y$ based nanostructures.

The intermediate Ga plays a key role on the formation of interesting SiO$_x$N$_y$ nanostructures, which are believed to be similar to that of SiO$_2$ nanowires [19]. The oxygen in silica wafer is mainly responsible for the formation of SiO$_x$N$_y$ nanowires.

4. Conclusion

The silica wafer is mainly responsible for the formation of SiO$_x$N$_y$-based nanowires and the intermediate Ga plays an important role in the formation of amazing growth phenomena. Ga has been successfully doped into α-Si$_3$N$_4$ nanowires on silicon substrates and the nanocable of SiGaN/SiO$_x$N$_y$ has also been attained via using GaN as a resource of Ga for catalyst and dopant. The growth mechanism of as-prepared samples is also discussed.

References

[1] T. Matsuoka, S. Taguchi, H. Ohtsuka, K. Taniguchi, C. Hamaguchi, S. Kakimoto, K. Uda, IEEE, Electron Device 43 (1996) 1364.
[2] M.Y. Hao, W.M. Chen, K. Lai, J.C. Lee, M. Gardner, J. Fulford, Appl. Phys. Lett. 66 (1995) 1126.
[3] Y. Okada, P.J. Tobin, P. Rushbrook, W.L. Dehart, IEEE, Trans. Electron Devices 41 (1994) 191.
[4] M. Murata, K. Yamauchi, H. Kojima, A. Yokoyama, T. Inoue, T. Iwamori, J. Electrochem. Soc. 140 (1993) 2346.
[5] M. Bhat, L.K. Han, D. Wristers, J. Yan, D.L. Kwong, Appl. Phys. Lett. 66 (1995) 1225.
[6] S. Wunderlich, J.P. Schmidt, J. Muller, Appl. Opt. 31 (1992) 4186.
[7] T.S. Larsen, O. Leistiko, J. Electrochem. Soc. 144 (1997) 1505.
[8] J.H. Kim, K.W. Chung, J. Appl. Phys. 83 (1998) 5831.
[9] W.T. Li, D.R. McKenzie, W.D. McFall, Q.C. Zhang, Thin Solid Films 384 (2001) 46.
[10] A.Y. Liu, M.L. Cohen, Phys. Rev. B 41 (1990) 10727.

[11] T. Hashishin, H. Iwanaga, J. Mater. Res. 18 (2003) 2760.

[12] L. Yin, Y. Bando, Y. Zhu, Y. Li, Appl. Phys. Lett. 83 (2003) 3584.

[13] W. Han, S. Fan, Q. Li, B. Gu, X. Zhang, D. Yu, Appl. Phys. Lett. 71 (1997) 2271.

[14] G. Gundiah, G.V. Madhav, A. Govindaraj, Md.M. Seikh, C.N.R. Rao, J. Mater. Chem 12 (2002) 1606.

[15] H. Cui, B.R. Stoner, J. Mater. Res. 16 (2001) 3111.

[16] Y. Chen, L. Guo, D.T. Shaw, J. Cryst. Growth 210 (2000) 527.

[17] H.Y. Kim, J. Park, H. Yang, Chem. Phys. Lett. 372 (2003) 269.

[18] G.Z. Ran, L.P. You, L. Dai, Y.L. Liu, Y. Lu, X.S. Chen, G.G. Qin, Chem. Phys. Lett. 384 (2004) 94.

[19] Z.W. Pan, Z.R. Dai, C. Ma, Z.L. Wang, J. Am. Chem. Soc. 124 (2002) 1817.

[20] J. Zhong, S. Muthukumar, Y. Chen, Y. Lu, H.M. Ng, W. Jiang, E.L. Garfunkel, Appl. Phys. Lett. 83 (2003) 3401.

[21] F.L. Deepak, P.V. Vanitha, A. Govindaraj, C.N.R. Rao, Chem. Phys. Lett. 374 (2003) 314.

[22] B. Girault, F. Chevrier, A. Joullie, G. Bougnot, J. Cryst. Growth 37 (1977) 169.

[23] R.N. Linnebach, J. Appl. Phys. 67 (1990) 6794.

[24] A. Van Vechten, J.C. Philips, Phys. Rev. B 2 (1970) 2160.

[25] Y.Q. Zhu, W.K. Hsu, M. Terrones, N. Grobert, H. Terrones, J.P. Hare, H.W. Kroto, D.R.M. Walton, J. Mater. Chem. 8 (1998) 1859.

[26] E.C. Carr, K.A. Ellis, R.A. Buhrman, Appl. Phys. Lett. 66 (1995) 1492.

[27] D.S. Park, H.J. Choi, B.D. Han, H.D. Kim, D.S. Lim, J. Mater. Res. 9 (2002) 2275.

[28] F.S.S Chien, J.W. Chang, S.W. Lin, Y.C. Chou, T.T. Chen, S. Gwo, T.S. Chao, W.F. Hsieh, Appl. Phys. Lett. 76 (2000) 360.

[29] S. Taguchi, S. Ribeiro, J. Mater. Process. Technol. 147 (2004) 336.

[30] B. Zheng, Y. Wu, P. Yang, J. Liu, Adv. Mater. 14 (2002) 122.