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Author(s)	Masubuchi, Yuji; Yamaoka, Ryohei; Motohashi, Teruki et al.
Citation	Journal of Crystal Growth, 337(1), 87-92 https://doi.org/10.1016/j.jcrysgr.2011.10.008
Issue Date	2011-12-15
Doc URL	https://hdl.handle.net/2115/48131
Type	journal article
File Information	JCG337-1_87-92.pdf



Crystal growth and characterization of gallium oxynitride nanowires grown on seed crystals

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Abstract

Nanowires of gallium oxynitride with wurtzite type structure were grown using seed crystals obtained by ammonia nitridation of an amorphous gallium oxide precursor containing 3 at% nickel additive. The seed crystals on a silica substrate were annealed with the amorphous gallium oxide precursor under ammonia flow to grow gallium oxynitride nanowires. The nanowires grew to lengths of about 150 μm along the seed crystal parallel to the hexagonal *c*-plane at 750 and 800 °C but they did not grow in the lateral direction. When the growth temperature was increased above 900 °C, the growth direction gradually changed to become parallel with the *c*-axis with a copresenting of gallium-nitride-like crystals. Room-temperature cathodoluminescence spectra of nanowires grown at 800 °C exhibited strong blue emission at 2.69 eV along with weak band-edge emission at 3.39 eV, similar to GaN. The latter emission was intense for nanowires grown at 1000 °C, which had an improved crystallinity and a higher nitride/oxide ion ratio. Nanowires grown at 750 and 900 °C exhibited persistent photoconductivity under UV irradiation at 393 nm.

Keywords: A2. Growth from vapor; A2. Seed crystals; B1. Gallium compounds; B1. Nanomaterials; B1. Oxynitride

1. Introduction

Gallium nitride is a wide band gap (~3.4 eV) semiconductor that is used in optoelectronic devices such as light emitting diodes and lasers with emission in the blue to ultraviolet wavelength region [1,2]. Gallium nitride nanowires are promising for use in a wide range of optical and electronic devices, including UV lasers, field effect transistors, and logic devices [3–5]. They have been grown by chemical vapor deposition (CVD), metal-organic CVD and vapor phase epitaxy using Au, Ni, Co, or Si as a catalyst for vapor–liquid–solid (VLS) growth at about 900 °C [6–9]. Most of the gallium nitride nanowires have been reported to grow in the VLS mechanism along the *c*-axis of the hexagonal wurtzite lattice to investigate their optical and electrical properties [10,11]. Yellow to blue cathodoluminescence (CL) and persistent photoconductivity (PPC) has been observed for undoped gallium nitride [12–15] due to unintentional defects such as gallium vacancies, gallium interstitials, and oxide ion impurities.

Spinel gallium oxynitride γ -Ga₃O₃N is theoretically predicted to either form at high pressures or to be stabilized by the introduction of gallium vacancies [16,17]. Gallium oxynitride (hereafter, GaON) with a hexagonal wurtzite related structure was first prepared by ammonia nitridation of NiGa₂O₄ [18]. Wurtzite GaON with cation vacancies (Ga_{0.89□0.11})(N_{0.66}O_{0.34}) was also prepared by ammonia nitridation of amorphous gallium

oxide obtained through the citrate route [19]. It was assumed to have a nonstoichiometric composition because its nitrogen/oxygen content was approximately 2. A similar method has been used to dope 3d transition metals into GaON [20–23]. GaON nanowires were grown with GaON particles in the ammonolysis of an amorphous gallium oxide precursor containing a few percent of Ni or Co additives [24]. GaON nanowires grown in the temperature range 750 to 850 °C were several micrometers long and several tens of nanometers wide. Their transmission electron microscopy (TEM) and electron diffraction (ED) pattern indicates that the growth direction was parallel to the *c*-plane and TEM energy-dispersive X-ray (EDX) measurements revealed that they had oxygen contents of 10–30% relative to the total amount of anions and that they did not contain any Ni and Co; these additives were only found in massive products. GaON nanowires are assumed to grow due to Ni or Co catalyzing one-dimensional growth in the hexagonal *c*-plane. They did not grow by the VLS mechanism. Optical and electrical measurements need to be performed on large GaON nanowires grown using seed crystals.

In this study, GaON nanowires were grown from seed crystals separated from an agglomerated product prepared by nitridation of amorphous gallium oxide with Ni 3 at% additives. TEM was used to investigate the dependence of the nanowire morphology and growth direction on the growth temperature. The CL and electrical conductivity were studied

for the wurtzite type structure with a nitride/oxide ion ratio of about 2 and gallium vacancies.

2. Experimental

Gallium oxynitride products consisting of nanowires and agglomerated grains were prepared by ammonolysis of an amorphous oxide precursor prepared from $\text{Ga}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ mixture in a molar ratio of Ga:Ni = 0.97:0.03 dissolved in 20 mL of distilled water with citric acid in an equimolar amounts to the total metal nitrates [24]. These reagents were purchased from Wako Pure Chemicals and had purities of 99.9%. The solution was heated on a hot plate while stirring to obtain gelatinous products. The gel was calcined in air at 350 °C for 1 h. The obtained amorphous oxide precursor was nitrided under flowing ammonia (flow rate: 50 mL/min) at 750 °C for 10 h. The nitrided product containing GaON nanowires and agglomerated grains were ultrasonically dispersed in acetone. The suspended solution was then dropped onto a silica substrate to use the GaON nanowires as seed crystals for subsequent nanowire growth. The seed crystals on the silica substrate were placed in a tube furnace with the gallium oxide precursor, which had been prepared by the above-mentioned route without a nickel additive. The seed crystals and the precursor were annealed at 750–1000 °C for 10 h under a NH_3 flow rate of 50 mL/min.

Crystalline phases in the as-grown products were characterized by powder X-ray

diffraction (XRD; Ultima IV, Rigaku) with monochromated Cu K α radiation. Their microstructures were observed by scanning electron microscopy (SEM; JSM-6390LV, JEOL) and scanning transmission electron microscopy (STEM; HD-2000, Hitachi) equipped with an energy-dispersive X-ray spectrometer (EDX). The samples were prepared by suspending the nanowires in 5 ml of carbon tetrachloride and then supporting them on a carbon-coated copper grid. Cathodoluminescence (CL) spectra of the nanowires were measured at room temperature using an accelerating voltage of 15 kV by field-emission scanning electron microscope (FE-SEM; S4300, Hitachi) attached to a CL system (MP32S/M, Horiba). The electrical transport properties were estimated by measuring the FET characteristics of the as-grown nanowires. They were dispersed into acetone again and then placed on a thermally oxidized Si wafer with a 500-nm-thick oxide layer (SiO₂). After drying the wafer and locating the nanowires by SEM observation, we formed Pt electrodes by electron-beam lithography. Current vs bias voltage (I - V) curve of an individual nanowire was measured using a semiconductor characterization system (Keithley 4200-SCS). The photoresponse of the current was measured under UV irradiation. Light emitting diode with a wavelength of 393 nm was used as a light source.

3. Results and discussion

3.1. Crystal growth on seed crystals

Pristine gallium oxynitride nanowires were obtained with agglomerated grains by ammonolysis of an amorphous gallium oxide precursor containing 3 at% of Ni (Fig. 1(a)). The nanowires had a maximum length of about 25 μm and were 30–150 nm wide. They were ultrasonically separated in acetone and then supported on a silica substrate (Fig. 1(b)). Even after ultrasonic treatment, they were slightly contaminated with small agglomerated grains. The nanowires on silica substrate were used as seed crystals. They were annealed with amorphous gallium oxide precursors under flowing NH_3 .

The morphologies of the products obtained by annealing under flowing NH_3 varied depending on the growth temperature. The nanowires grew to a maximum length of 150 μm but they did not grow laterally at 750 and 800 $^\circ\text{C}$ (Figs. 2(a) and (b)). A large amount of approximately 10 μm long GaON nanowires were observed together with long nanowires at 900 $^\circ\text{C}$ (Fig. 2(c)). The former were intertwined with each other and had similar widths as the seed crystals. Their morphology changed drastically at 1000 $^\circ\text{C}$. Needle-like crystals that were several micrometers wide and several tens of micrometers long grew together with thin nanowires with similar widths as the seed crystals. A different nucleation mechanism may be responsible for the growth of the large amount of nanowires at 900 $^\circ\text{C}$ and the needle-like crystals at 1000 $^\circ\text{C}$ independent from the seed crystals. Significant amounts of

gallium-containing vapors such as Ga_2O were reported to be generated from $\beta\text{-Ga}_2\text{O}_3$ above $900\text{ }^\circ\text{C}$ [25]. Excess supply of gallium vapor might increase GaON nucleation on the surface of seed crystals or small grains (Fig. 2(c)).

Figures 3(b)–(e) show the XRD patterns of as-grown nanowires (for comparison, Fig. 3(a) shows the XRD pattern of GaON containing nanowires and agglomerated grains prepared by nitridation of a Ga–Ni oxide precursor at $750\text{ }^\circ\text{C}$). GaON obtained by nitridation with Ni additives crystallizes with a highly disordered 2H wurtzite structure with some 3C zinc blende stacking faults [24]. XRD patterns for the GaON nanowires grown at 750 and $800\text{ }^\circ\text{C}$ exhibit remarkable preferred orientation (Figs. 3(b) and (c)). Their hexagonal *c*-planes are parallel to the substrate. The GaON nanowires have rectangular cross-sections (Fig. 4(a)) and hexagonal diffraction patterns when the electron beam is irradiated perpendicular to the nanowire (inset of Fig. 4(b)). At $750\text{ }^\circ\text{C}$, the nanowires grow parallel to the *c*-plane of the seed crystals [24]. The preferred orientation observed in the XRD patterns obtained from nanowires grown at 750 and $800\text{ }^\circ\text{C}$ is caused by long nanowires grown parallel to the *c*-plane lying on the substrate. GaON nanowires prepared at 900 and $1000\text{ }^\circ\text{C}$ have XRD patterns characteristic of wurtzite with sharp diffraction peaks with no remarkable orientation (Figs. 3(d) and (e)). These products contained nanowires that grew along the seed crystal, parallel to the *c*-plane, although some nanowires grew in different directions

(Figs. 4(c) and (d)). Similar growth has been reported for gallium nitride nanowires, which were grown by the VLS mechanism along the hexagonal *c*-axis [10,11]. The presence of nanowires that grew in different directions from the hexagonal *c*-plane and the absence of a preferred orientation in the XRD patterns at 900 and 1000 °C may indicate the coexistence of GaN-like nanowires. At temperatures below 800 °C, 150- μ m-long GaON nanowires grew parallel to the hexagonal *c*-plane of seed crystals.

3.2. Cathodoluminescence and electrical transport properties

CL spectra were obtained from GaON nanowires grown at 800 and 1000 °C (Figs. 5(a) and (b), respectively). Both spectra exhibit blue and band-edge emissions, although with different relative intensities. Blue emission was dominant in the CL spectrum obtained from the GaON nanowires grown at 800 °C. This spectrum also has very weak emission at about 3.39 eV, which has been assigned to band edge emission in GaN doped with oxide ions [26]. Blue emission from wurtzite GaN has been reported to be related to complex defects due to gallium vacancies formed by the substitution of nitrides with oxide ions [12]. In the present study, STEM-EDX revealed that about 20 at% of nitride ions were substituted by oxide ions in GaON nanowires grown below 800 °C. This amount is much less than that reported for wurtzite type GaON [19]. To preserve charge neutrality, some gallium sites

should be vacant, as mentioned in Ref. 19. Gallium vacancies and incorporated oxide ions form a complex defect $V_{\text{Ga}}\text{-O}_{\text{N}}$ (where the subscripts indicate the crystallographic sites in GaN). Similar defects in the present GaON may be related to the blue emission in the CL spectra of nanowires grown at 800 °C. When the growth temperature was increased to 1000 °C, the intensity of the band edge emission increased significantly, while the above-mentioned blue emission remained at around 2.9 eV. This increase in the band edge emission intensity may be due to the higher crystallinity of GaON nanowires grown at higher temperatures. The nanowires also exhibited weak blue emission. Decrease in oxygen content by increasing the growth temperature was expected as reported for GaON powders ($\text{Ga}_{0.89}\text{O}_{0.11}$)($\text{N}_{0.76}\text{O}_{0.34}$) nitrided without any additives [19,20]. The emission implies that the GaON nanowires grown at 1000 °C contain gallium vacancies, which may be due to the coexistence of residual oxide ions in the GaN-like lattice.

Figure 6(a) shows an SEM image of a GaON nanowire grown at 900 °C with microfabricated Pt electrodes. Figure 6(b) shows the I - V curve measured between two electrodes at room temperature. All the I - V curves are symmetric and linear, indicating ohmic contact between the nanowire and the Pt electrodes. In contrast, ohmic contact was not realized using Ti electrodes. The electrical conductivity was estimated by dc four-probe method. Nanowires grown at 900 °C had an n-type electrical conductivity of 76–116 $\text{S}\cdot\text{cm}^{-1}$

with an activation energy of about 1 meV in the temperature range 130 to 330 K. This is similar to the values obtained for nanowires grown at 750 °C. Figure 7 shows photoresponse spectra of GaON nanowires grown at 750 and 900 °C. The GaON nanowires were excited by 393 nm light (3.15 eV), which is a lower energy than the band gap observed in the CL spectra. For both nanowires, the photocurrent increased under UV light irradiation and it had a long decay time when the irradiation was turned off. PPC has been observed on n-type GaN; it was assigned to unintended Ga vacancies without elemental doping [27,28]. The present GaON nanowires have gallium vacancies that were intentionally induced by introducing oxide ions to the wurtzite type lattice. The observation of PPC in the nanowires suggests that the GaON nanowires grown in this study contain gallium vacancies formed by oxide ions introduced into the GaN lattice during high-temperature crystal growth.

4. Conclusion

Gallium oxynitride nanowires 150 μm long were grown along the short seed crystals parallel to the hexagonal *c*-plane at growth temperatures of 750 and 800 °C in 50 mL/min ammonia flow. At growth temperatures above 900 °C, simultaneous growth along the *c*-axis occurred in GaON nanowires containing less oxygen and having gallium-nitride-like crystal structures. Nanowires grown at 800 °C exhibited strong blue

emission related to gallium vacancies at 2.69 eV and weak band edge emission at 3.39 eV as reported for GaN. These peaks had opposite relative intensities for nanowires grown at 1000 °C (2.9 and 3.36 eV, respectively). The improved crystallinity at 1000 °C enhanced band edge emission in GaN and reduced the blue emission, which is related to gallium vacancies induced by the substitution of nitride ions with oxide ions, forming GaON. Nanowires grown at 750 and 900 °C exhibited photoconductivity with long decay times for 393-nm UV irradiation. This PPC is also related to gallium vacancies caused by oxide ion substitution. Nanowires grown at both temperatures contain gallium vacancies formed by oxide ion substitution more or less.

Acknowledgments

This research was partly supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 22015001) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan and for Exploratory Research (No. 236551388) from the Japan Society for the Promotion of Science (JSPS). Y.M. acknowledges financial support from the Global COE Program (Project No. B01: “Catalysis as the Basis for Innovation in Materials Science”) from MEXT of Japan.

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Figure captions

Figure 1 SEM images for gallium oxynitride nanowires: (a) as-nitrided gallium oxide precursor containing 3 at% Ni and (b) the separated gallium oxynitride nanowires for seed crystal on a silica substrate.

Figure 2 SEM images of gallium oxynitride nanowires grown at (a) 750, (b) 800, (c) 900, and (d) 1000 °C.

Figure 3 XRD patterns of gallium oxynitride nanowires a silica substrate grown at (b) 750, (c) 800, (d) 900, and (e) 1000 °C measured on the silica substrate. The reference XRD pattern (a) is of gallium oxynitride powder prepared by ammonolysis of a Ga–Ni oxide precursor, which contains nanowires and agglomerated grains. Open triangles indicate diffraction peaks of wurtzite. Peaks with asterisks are assigned to zinc blende. Filled diamonds indicate diffraction peaks of $\text{GaNi}_3\text{C}_{0.5}$.

Figure 4 STEM SE image of a GaON nanowire grown at (a) 750 °C and (b) its electron diffraction pattern. Diffraction patterns in (c) and (d) are for GaON nanowires grown at 900 °C. Insets show diffractions observed for GaON nanowires when the electron beam is

irradiated perpendicular to their longitudinal directions.

Figure 5 Room-temperature CL spectra of GaON nanowires grown at (a) 800 and (b) 1000 °C.

Figure 6 (a) SEM image of a GaON nanowire with Pt microelectrodes. (b) I - V curve of nanowire measured between two electrodes at room temperature. The I - V curve measured between electrodes 2 and 1 overlaps that obtained between electrodes 1 and 3.

Figure 7 Photoresponse spectra of GaON nanowires at biases of 10 and 50 mV for GaON grown at 750 and 900 °C, respectively. The spectra were excited by 393 nm (3.15 eV) UV light at room temperature. The observed photocurrents, I , were normalized by setting their dark currents, I_0 , to unity. UV irradiation was performed in the time periods indicated by the gray regions.

Figure 1

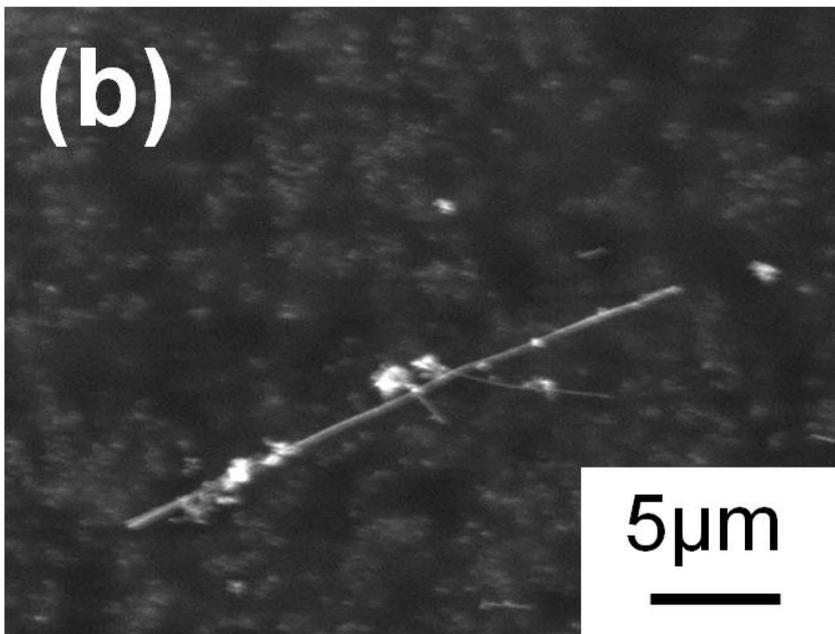
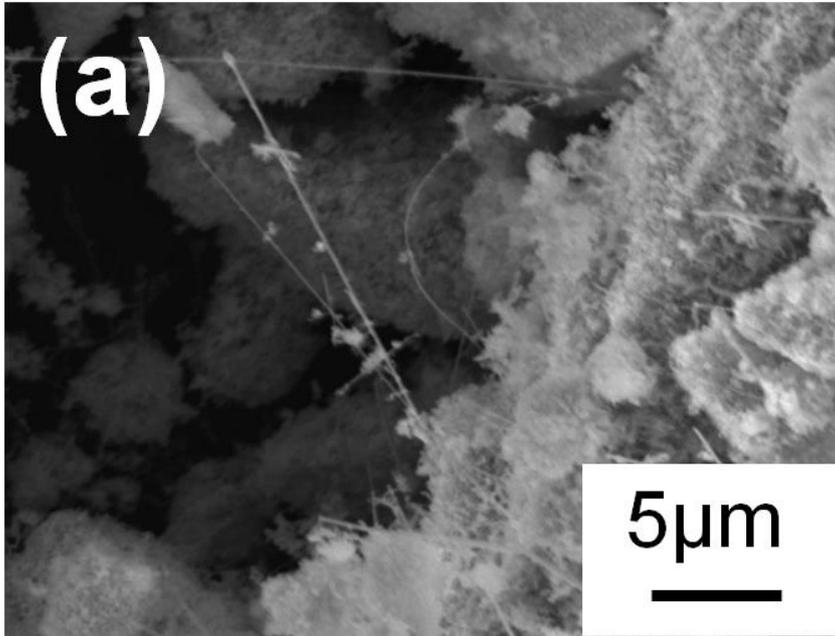


Figure 2

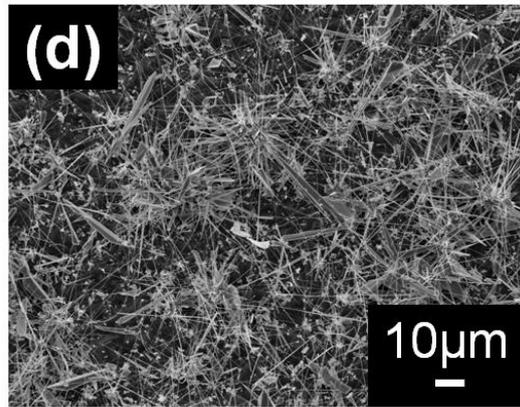
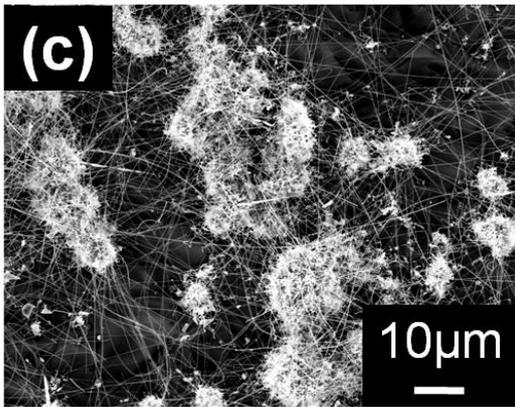
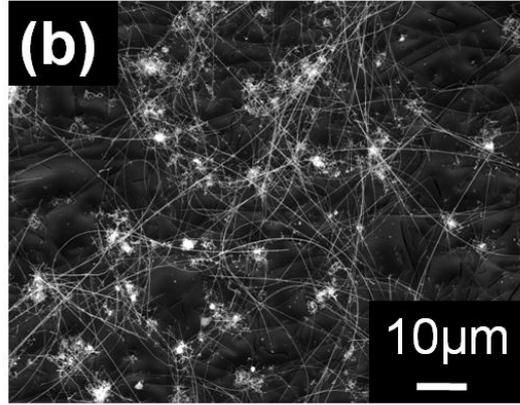
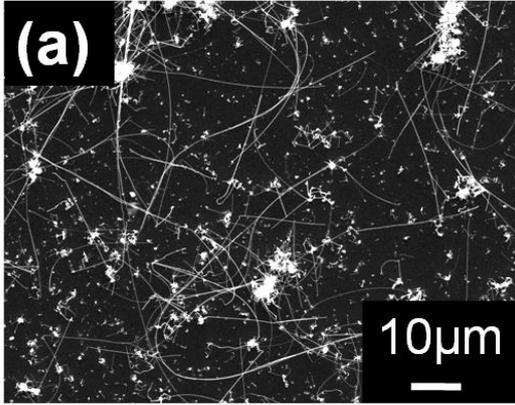


Figure 3

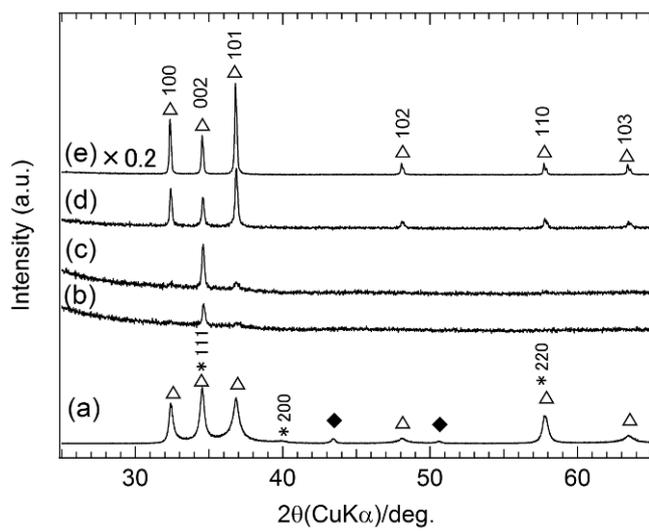


Figure 4

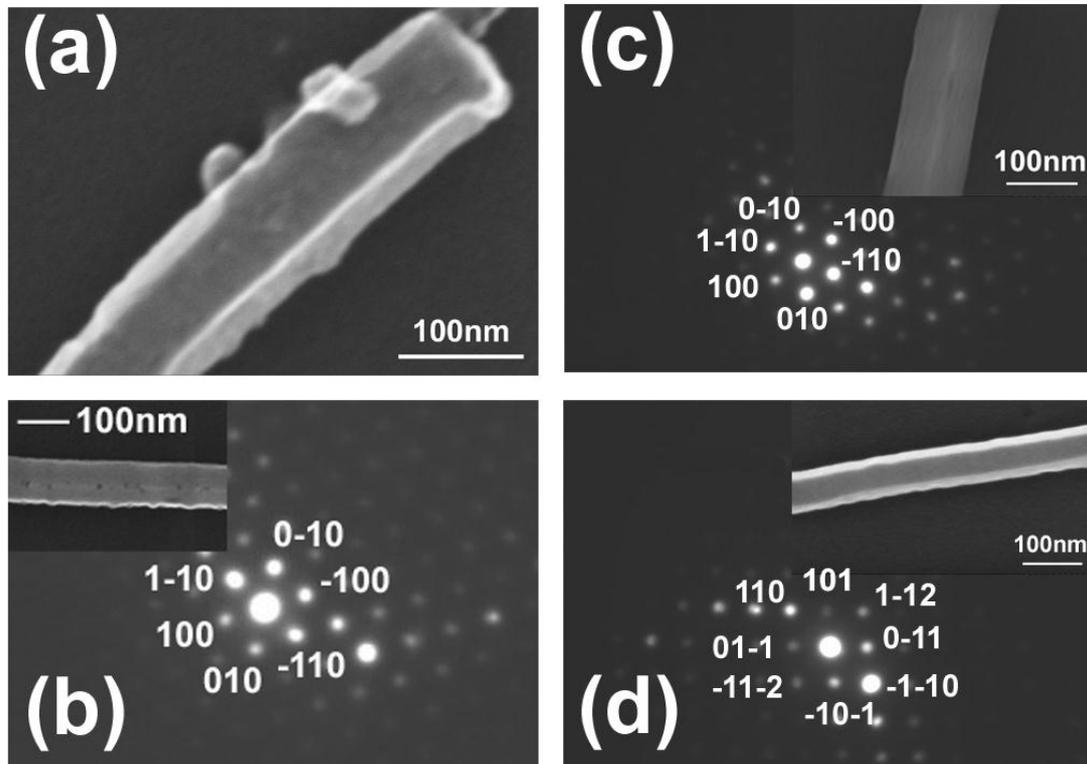


Figure 5

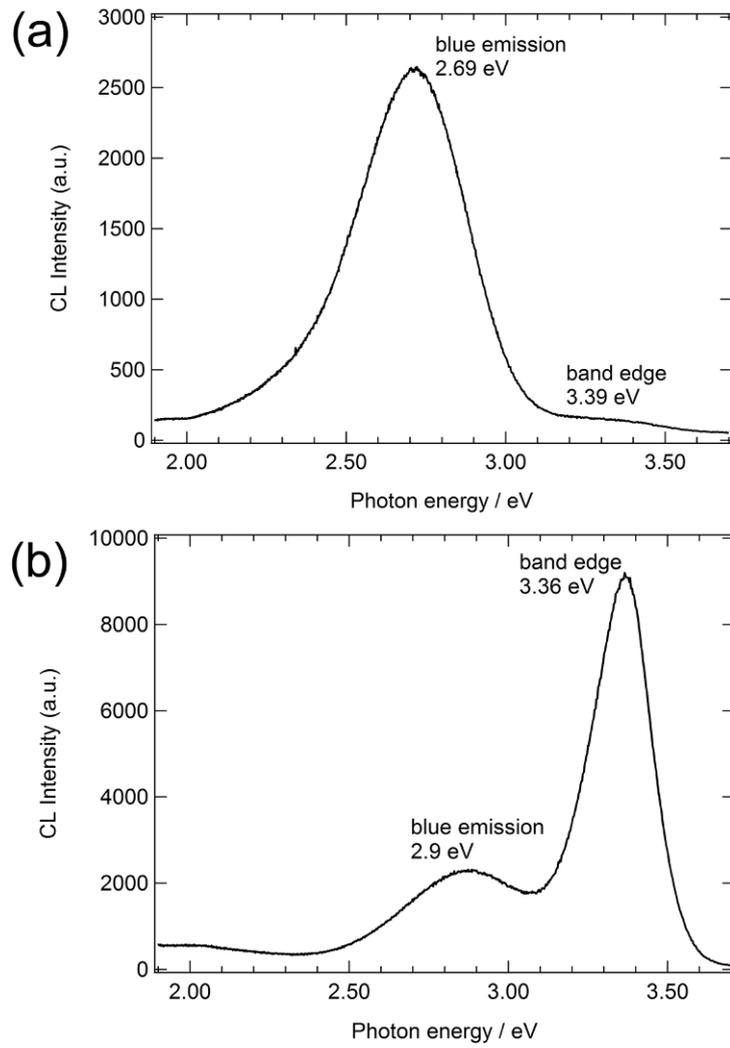


Figure 6

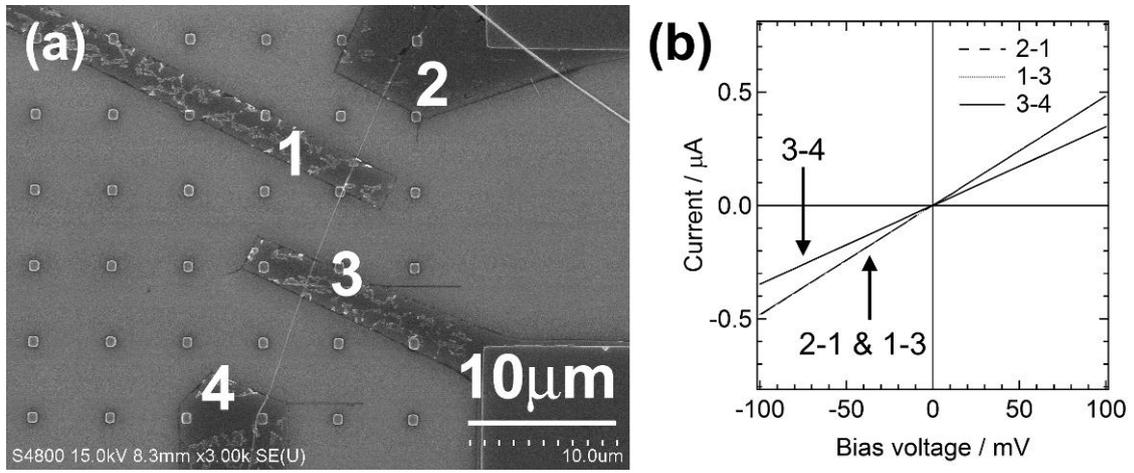


Figure 7

