Fe-catalytic growth of ZnSe nanowires on a ZnSe(001) surface at low temperatures by molecular-beam epitaxy

Yutaka Ohno,[a] Takeo Shirahama, and Seiji Takeda
Department of Physics, Graduate School of Science, Osaka University, 1-1, Machikane-yama, Toyonaka, Osaka 560-0043, Japan

Atsushi Ishizumi and Yoshihiko Kanemitsu[b]
Graduate School of Materials Science, Nara Institute of Science and Technology, Ikoma, Nara 630-0192, Japan

(Received 14 February 2005; accepted 2 June 2005; published online 19 July 2005)

We grew ZnSe needle-like nanowires on a ZnSe/GaAs epilayer using Fe catalysts by means of molecular-beam epitaxy operated at low temperatures of 250–350 °C, which are comparable to the usual temperatures for fabrication of ZnSe-based optoelectronic devices. The diameters at the tops of the nanowires ranged from 8 to 20 nm, and the typical length was about 200 nm. The number density of the nanowires was the order of 10^9 cm^{-2}. A nanowire was the zinc blende structure and the longitudinal direction was ⟨001⟩,⟨111⟩,⟨110⟩, or ⟨112⟩. Photoluminescence spectroscopy implied that the optical property of the nanowires differs from that of the bulk crystals. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1997275]

One-dimensional nanocrystals, such as nanowires (NWs), have attracted a great deal of interest for applications in electronics and optoelectronics, since they are potentially ideal building blocks of functional highly integrated nanoscale devices.[1–3] They have been frequently synthesized by the catalytic growth method based on the vapor-liquid-solid (VLS) mechanism.[4] By means of the method, we can obtain NWs with a variety of functional heterojunctions.[5–7] We can also grow NWs whose nucleation sites and sizes are precisely decided on a substrate by controlling those of catalysts,[8,9] at temperatures much lower than the usual growth temperatures. Their properties are of great advantage to integrating NW technology with current semiconductor component technology.

ZnSe, an important semiconductor with a wide band gap of 2.67 eV at room temperature, has been widely investigated for potential applications in short-wavelength optoelectronic devices such as blue laser diodes,[10] light emitting diodes (LEDs), and blue-ultraviolet photodetectors,[11] and white LEDs with low power consumption[12] have been commercialized. Since controlling the size and the dimension of ZnSe leads to special optical and photoelectronic properties,[13–16] much attention has been focused on the synthesis of ZnSe nanostructures. Recently, ZnSe NWs have been grown on substrates with gold[17–19] and silver[20] catalysts, by popular growth techniques such as molecular-beam epitaxy (MBE), chemical vapor deposition, etc. However, the growth temperatures (450–550 °C) were rather higher than the usual temperatures for fabrication of ZnSe-based devices (about 300–350 °C). In the present letter we demonstrate that ZnSe NWs on a substrate can be grown at low temperatures of 250–350 °C with proper catalysts, i.e., Fe nanoparticles, by means of MBE. We briefly discuss the formation mechanism. Also, we comment on the optical property of the NWs.

NWs were grown by using a VG-80 MBE chamber that is designed especially for growth of II-VI compound semiconductors.[21] A GaAs(001) wafer was installed into the chamber, and a ZnSe epilayer (about 90 nm thick) was grown on the wafer at the temperature of 300°C.[21] The wafer was cooled down to room temperature, and Fe atoms were evaporated on the epilayer, for fear that As and Ga atoms might mix with the Fe deposit. The thickness was estimated to be about 1 nm. The deposited wafer was heated up to a growth temperature T_g and maintained for a few min in order to generate Fe nanoparticles. Subsequently, NWs were grown at T_g by the exposition of Zn and Se fluxes (the flow ratio of 1:2) simultaneously for 1 h. No NW grew at T_g without the exposition. The structural nature was characterized by transmission electron microscopy (TEM) with a JEOL JEM-2010 microscope operated at 160 kV and scanning electron microscopy (SEM) with a FEI Sirion 400 microscope operated at 3 kV. The optical property was characterized with a photoluminescence (PL) spectroscopy system. NWs on an epilayer were illuminated with a 325 nm laser light, from a He–Cd laser (the output power of about 10 mW), at temperatures in the range 20–300 K. PL lights were corrected into a cooled charge-coupled device detector through a 32 cm monochromator. The spectral sensitivity of the system was calibrated using a tungsten standard lamp. The spectral resolution was about 3 meV.

A large amount of NWs grew at the optimum temperature of T_g=300 °C [Fig. 1(a)]. The number density n_{nw} was about 5×10^9 cm^{-2}. The lengths ranged from 80 to 360 nm, and the average length l_{nw} was about 200 nm. A NW tapered off to the top. The diameter at the top was in the range 8–20 nm, and it was about 14 nm on average. A nanoparticle existed on the top of a NW [Figs. 1(b) and 1(d)]. Energy-dispersive x-ray (EDX) analyses revealed that the nanoparticle contains Fe, Zn, and Se atoms, and the volume ratio of Fe:Zn:Se was about 9:1:1. No Fe atom was detected inside NWs. High-resolution TEM [e.g., Fig. 1(c)] revealed that a NW was the zinc blende structure with the lattice constant of 5.67 Å, which was the same as that of the bulk crystals

[a]Author to whom correspondence should be addressed: electronic mail: ohno@phys.sci.osaka-u.ac.jp
[b]Present adress: Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan.

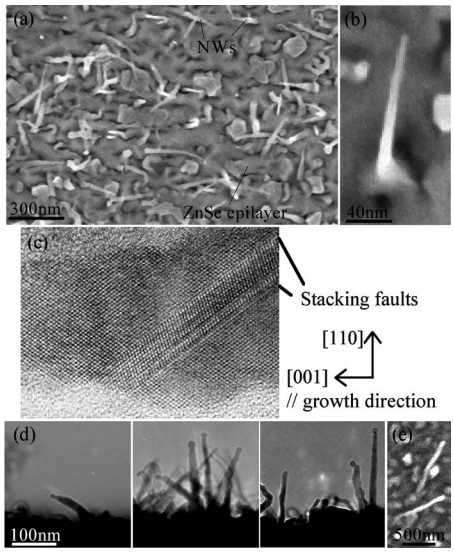

FIG. 1. (a) A SEM image of NWs and (b) a magnified image of a NW (T_g=300 °C). (c) A high resolution TEM image of a NW grown along [001] (T_g=300 °C). (d) TEM images of the cleaved specimens taken with the electron beam nearly parallel to the $[1\bar{1}0]$ direction of the substrates; T_g =250, 300, and 350 °C from left to right. (e) A SEM image of NWs on a silica glass grown using Fe catalysts at T_g=300 °C.

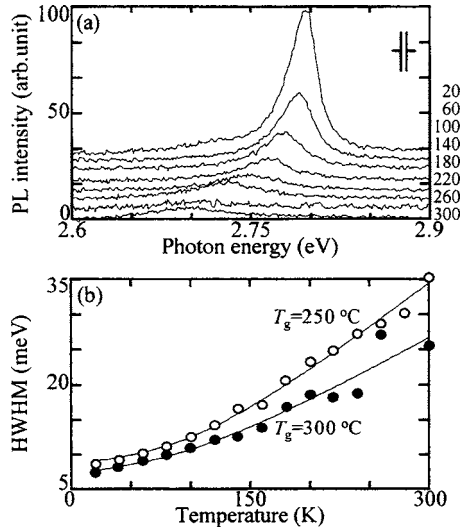

FIG. 2. (a) PL spectra of a specimen (T_g=300 °C) at different temperatures. (b) Temperature dependence of the linewidth of the I_2 luminescence for the specimen grown at T_g=250 or 300 °C. The solid lines are theoretical fits with Eq. (1).

within our experimental error, and the longitudinal direction was ⟨001⟩,⟨111⟩,⟨110⟩, or ⟨112⟩. Many NWs contained some stacking faults [e.g., Fig. 1(c)]. Cross sectional TEM revealed that growing NWs was accompanied by the growth of a ZnSe epilayer around the roots of the NWs (not shown). The thickness was estimated to be about 20 nm.

NWs of about 14 nm diameter, as well as a thin epilayer, also grew at T_g=250 or 350 °C [Fig. 1(d)], even though n_{nw} (4×10^8 cm^{-2} or 3×10^9 cm^{-2}, respectively) and l_{nw} (100 or 150 nm, respectively) were small in comparison with the NWs grown at T_g=300 °C. No NW, but a thin epilayer, grew at T_g=200 or 400 °C.

We discuss briefly the formation mechanism of the NWs. A nanoparticle containing Fe atoms on the top of a NW clearly shows that the NW grows via the VLS mechanism[4] or a similar growth mechanism.[22] NWs grew even on a silica glass by the same Fe-catalytic growth method [Fig. 1(e)]. Since the diffusion of Zn and Se atoms into Fe is negligible at temperatures below 380 °C,[23] it is very likely that Zn and Se atoms are preferentially deposited onto the surface of a Fe nanoparticle and they reach the growing nanowire by diffusing around the nanoparticle, similar to the Ti-catalytic growth of Si NWs.[22] NWs did not grow at T_g=200 °C presumably due to small mobility of Zn and Se atoms on Fe nanoparticles. It is expected that an Fe nanoparticle on a ZnSe/GaAs epilayer is converted into a Ga–Zn–Fe compound at temperatures above 380 °C, via the out-diffusion of Ga atoms through the ZnSe layer.[23] We speculate that the compound did not act as catalyst and so NWs did not grow at T_g=400 °C. So far, only straight NWs were obtained via the catalytic growth process at high temperatures above 450 °C.[17–20] A needle-like NW would be formed due to radial growth, via the vapor-solid mechanism which occurs without catalysts at low temperatures[24] and via the surface diffusion[25] of Zn and Se atoms from the epilayer, in addition to continuous growth along the longitudinal direction via the VLS mechanism.

We measured PL spectra of the specimens grown at T_g =250 and 300 °C. Both specimens emitted a strong near-band-edge PL light with the photon energy of about 2.795 eV at the temperature of 20 K, which is associated with the excitons bound on Zn vacancies (so-called I_2 luminescence)[26] [e.g., Fig. 2(a)]. The I_2 excitonic luminescence was obviously observed even at 300 K. We examined the temperature dependence of the linewidth $\Gamma(T)$, defined as a half width at the half maximum of the luminescence [Fig. 2(b)]. $\Gamma(T)$ is usually determined in terms of the strength of the exciton-acoustic phonon interaction α and that of the exciton-longitudinal optical (LO) phonon interaction β, and it is known that α and β in a nanostructure vary with the size of the nanostructure (e.g., Refs. 14 and 15). $\Gamma(T)$ can be fitted with a function

$$\Gamma(T) = \Gamma_0 + \alpha T + \beta/[\exp(\hbar\omega/kT) - 1], \quad (1)$$

where Γ_0 is a constant (e.g., Refs. 27 and 28). We assumed the optical phonon energy $\hbar\omega$=31 meV of the bulk crystals.[29] We also assumed that α and β in a NW grown at T_g=300 °C are, respectively, almost the same as those in a NW grown at 250 °C, since the NWs were of similar size.

The excitonic PL light would be emitted from both the total volume of the NWs excited by a laser beam V_{nw} and the volume of the epilayer excited by the same beam V_{epi}. The volume ratio $R=V_{nw}/(V_{nw}+V_{epi})$ for the sample grown at T_g=300 °C (about 20%) was much larger than that at T_g =250 °C (about 1%). When R was large, α was large and β was small in comparison with an epilayer (Table I). This result suggests that α and β in NWs were different from those in an epilayer. It is theoretically expected that α in a ZnSe nanocrystal is larger than that in the bulk crystals.[14] β in a ZnSe NW decreases with decreasing the diameter (e.g., β in a NW of 25 nm diameter is about 1/3 of β in the bulk crystals),[15] and the result is explained by a reduced polarity of the exciton wave function due to the wire confinement and due to a reduced number of final subband states that can be reached within the LO-phonon energy. We consider that we detected similar effects in NWs. A large Γ_0 was presumably

TABLE I. The fitting parameters of Eq. (1).

T_g (°C)	n_{nw} (cm^{-2})	R (%)	Γ_0 (meV)	α (μeV/K)	β (meV)
300	5×10^9	20±2	7±1	30±10	20±5
250	4×10^8	1±1	8±1	30±10	32±5
	ZnSe-epilayer[a]	0	6.5±2.5	7	30±7,24±8

[a]Reference 28.

due to structure inhomogeneity, such as strain, stacking faults, etc., in NWs.[27]

In conclusion, we grew ZnSe NWs on a ZnSe/GaAs epilayer at temperatures as low as the usual temperatures for fabrication of ZnSe-based optoelectronic devices, by using Fe catalysts. The sample emitted a strong and sharp excitonic PL light even at room temperature, due to high electronic quality, and this suggests possible application in optoelectronic devices. Also, since an Fe nanostructure on ZnSe has unique magnetic properties,[30] our growth technique is of interest for its potential applications to spintronics devices, etc.

This work was partially supported by the Ministry of Education, Science, Sports and Culture, Grant-in-Aid for Young Scientist (A)(2) No.15681006, 2003-2005. SEM images were taken at FEI Company Japan Ltd. Y.O. is indebted to Professor T. Yoshiie of Kyoto University for support for EDX measurements.

[1]J. Wang, M. S. Gudiksen, X. Duan, Y. Cui, and C. M. Lieber, Science **293**, 1455 (2001).
[2]X. Duan, Y. Huang, Y. Cui, J. Wang, and C. M. Lieber, Nature (London) **409**, 66 (2001).
[3]Y. Cui and C. M. Lieber, Science **291**, 851 (2001).
[4]R. S. Wagner and W. C. Ellis, Appl. Phys. Lett. **4**, 89 (1964).
[5]M. T. Biork, B. J. Ohlsson, T. Sass, A. I. Persson, C. Thelander, M. H. Magnusson, K. Deppert, L. R. Wallenberg, and L. Samuelson, Nano Lett. **2**, 87 (2002).
[6]J. Hu, M. Ouyang, P. Yang, and C. M. Lieber, Nature (London) **399**, 48 (1999).
[7]H. Kohno and S. Takeda, Appl. Phys. Lett. **73**, 3144 (1998).
[8]S. Takeda, K. Ueda, N. Ozaki, and Y. Ohno, Appl. Phys. Lett. **82**, 979 (2003).
[9]B. J. Ohlsson, M. T. Bjork, M. H. Magnusson, K. Deppert, L. Samuelson, and L. R. Wallenberg, Appl. Phys. Lett. **79**, 3335 (2001).
[10]K. Katayama, H. Yao, F. Nakanishi, H. Doi, A. Saegusa, and T. Shirakawa, Appl. Phys. Lett. **73**, 102 (1998).
[11]H. Ishikura, T. Abe, N. Fukuda, H. Kasada, and K. Ando, Appl. Phys. Lett. **76**, 1069 (2000).
[12]T. Shirakawa, Mater. Sci. Eng., B **91-92**, 470 (2002).
[13]N. Kouklin, L. Menon, A. Z. Wong, D. W. Thompson, J. A. Woollam, P. F. Williams, and S. Bandyopadhyay, Appl. Phys. Lett. **79**, 4423 (2001).
[14]S. Rudin and T. L. Reinecke, Phys. Status Solidi A **190**, 677 (2002).
[15]H. P. Wagner, H.-P. Tranitz, R. Schuuster, G. Bacher, and A. Forchel, Phys. Rev. B **63**, 155311 (2001).
[16]Y. Jiang, X.-M. Meng, W.-C. Yiu, J. Liu, J.-X. Ding, C.-S. Lee, and S.-T. Lee, J. Phys. Chem. B **108**, 2784 (2004).
[17]Y. F. Chan, X. F. Duan, S. K. Chan, I. K. Sou, X. X. Zhang, and N. Wang, Appl. Phys. Lett. **83**, 2665 (2003).
[18]B. Xiang, H. Z. Zhang, G. H. Li, F. H. Yang, F. H. Su, R. M. Wang, J. Xu, G. W. Lu, X. C. Sun, Q. Zhao, and D. P. Yu, Appl. Phys. Lett. **82**, 3330 (2003).
[19]R. Solanki, J. Huo, J. L. Freeout, and B. Miner, Appl. Phys. Lett. **81**, 3864 (2002).
[20]X. T. Zhang, Z. Liu, Y. P. Leung, Q. Li, and S. K. Hark, Appl. Phys. Lett. **83**, 5533 (2002).
[21]Y. Ohno, N. Adachi, and S. Takeda, Appl. Phys. Lett. **83**, 54 (2003).
[22]T. I. Kamins, R. S. Williams, D. P. Basile, T. Hasjedal, and S. Harris, J. Appl. Phys. **89**, 1008 (2001).
[23]D. H. Mosca, M. Abbate, W. H. Schreiner, V. H. Etgens, and M. Eddrief, J. Appl. Phys. **90**, 5973 (2004).
[24]K.-W. Chang and J.-J. Wu, Appl. Phys. A: Mater. Sci. Process. **77**, 769 (2003).
[25]L. Schubert, P. Werner, N. D. Zakharov, G. Gerth, F. M. Kolb, L. Long, U. Gosele, and T. Y. Tan, Appl. Phys. Lett. **84**, 4968 (2004).
[26]T. S. Jeong, P. Y. Yu, Y. J. Shin, C. J. Youn, H. K. Shin, T. S. Kim, H. Lee, T. S. Lee, and K. J. Hong, J. Cryst. Growth **172**, 89 (1997).
[27]Y. Kanemitsu, T. Nagai, Y. Yamada, and T. Taguchi, Appl. Phys. Lett. **82**, 388 (2003).
[28]L. Malikova, W. Krystek, F. H. Pollak, N. Dai, A. Cavus, and M. C. Tamargo, Phys. Rev. B **54**, 1819 (1996).
[29]It is known that $\hbar\omega$ of a ZnSe NW is about a few percent smaller than that of the bulk crystals (Ref. 16). We confirmed that the energy difference does not affect the fitting significantly.
[30]M. Marangolo, F. Gustavsson, M. Eddrief, Ph. Sainctavit, V. Cros, F. Petroff, J. M. George, P. Bencok, and N. B. Brookes, Phys. Rev. Lett. **88**, 217202 (2002).