AIP | Applied Physics Letters

Cathodoluminescence from βGa2O3 nanowires

E. Nogales, B. Méndez, and J. Piqueras

Citation: Appl. Phys. Lett. **86**, 113112 (2005); doi: 10.1063/1.1883713
View online: http://dx.doi.org/10.1063/1.1883713
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v86/i11
Published by the American Institute of Physics.

Cathodoluminescence from β-Ga_2O_3 nanowires

E. Nogales, B. Méndez,[a] and J. Piqueras
Departamento de Física de Materiales, Facultad de Ciencias Físicas, Universidad Complutense de Madrid, 28040 Madrid, Spain

(Received 13 September 2004; accepted 25 January 2005; published online 10 March 2005)

β-Ga_2O_3 nano- and microwires with diameters ranging from tens of nanometers to about one micron and lengths of up to tens of microns, have been obtained by sintering Ga_2O_3 powder under argon flow. The structures have been investigated by cathodoluminescence in the scanning electron microscope. The samples showed the violet-blue emission characteristic of Ga_2O_3 and a red emission at 1.73 eV dominant in the nanowires and other nano- and microstructures formed during the sintering treatment. At temperatures below 210 K, this band exhibits sharp peaks separated by 20 meV. This observation suggests the exchange of phonons in the recombination process. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1883713]

The investigation of nanostructured low-dimensional semiconductor oxides has been of great interest in the very recent years in order to develop optoelectronic nanodevices.[1] In particular, the monoclinic phase of gallium oxide (β-Ga_2O_3) is a very good candidate for these purposes because of the wide band gap of 4.8 eV, which provides the possibility of light emission in the infrared, visible, and ultraviolet regions of the spectrum.[2–4] Furthermore, gallium oxide exhibits good conduction properties due to the donor band related to oxygen vacancies. Deposition processes have been employed to obtain nanoscale-sized gallium oxide using as starting materials either metallic gallium,[3–5] GaN,[6] GaAs,[7] or gallium oxide.[1,8] The studies on the optical properties of crystalline β-Ga_2O_3 have been centered until very recently in the ultraviolet-green range.[2,4] These emissions were assigned to recombinations due to donor-acceptor-pairs (DAP).[2] Oxygen vacancies act as donors with an ionization energy $E_d \sim 0.03-0.05$ eV and acceptors would be formed by a gallium-oxygen vacancy pair with ionization energy of $\sim$0.4 eV.[2] On the other hand, little information is available in the literature on luminescence properties of gallium oxide nanowires. Very recently, a red emission was reported in β-Ga_2O_3 nanowires doped with nitrogen.[3] The authors reported that the photoluminescence (PL) features of this emission as a function of temperature were in accordance with the DAP model,[9] in which the oxygen vacancies act as donors and the nitrogen dopant as deep acceptor.

In this work, we have obtained β-Ga_2O_3 nanowires and microcrystals during sintering Ga_2O_3 under Ar flow. The morphology and the luminescence of the samples were characterized by scanning electron microscopy (SEM) and by cathodoluminescence (CL) in SEM respectively.

The starting material was 99.999% purity Ga_2O_3 powder. Samples were prepared by compacting the powders under a compresive load to form disks of about 7 mm diameter and 2 mm thickness. They were then annealed under an Ar flow at 1500 °C for times of 8 or 24 h. Samples were labeled G8 (8 h) and G24 (24 h). Another sample was annealed in N_2 atmosphere for 8 h for comparison. One sample was prepared from powder which had been ball milled for 30 h in a centrifugal ball mill and then annealed for 24 h in Argon at 1500 °C. This sample was labeled GM24. Milling was performed at room temperature in air in a centrifugal ball mill (Retsch S100) equipped with hardened steel vial and 20-mm-diam agate balls. The obtained samples were characterized by x-ray diffraction to confirm their crystalline structure. SEM investigations were carried out either in a Leica 440 or a Hitachi S-2500 scanning electron microscopes. CL measurements were performed in the visible range between 88 and 370 K using acceleration voltages of 15 or 20 kV. CL spectra were acquired with a Hamamatsu PMA-11 charge-coupled-device.

Figure 1(a) shows nanowires with sizes from tens to hundreds of nanometers grown in sample G8. A detail of the wires is shown in Fig. 1(b). By increasing the annealing time, sample G24, the formation of regular sheets arranged in terraces of decreasing size terminating in micro- or nanoneedless is observed [Fig. 1(c)]. A similar structure has been reported for CdSe sintered under Ar flow.[10] In sample GM24, prepared from milled powder, the presence of wires with sizes in the range of 10–100 nanometers forming a comblike structure can also be observed. A representative SEM image of sample GM24 is shown in Fig. 2.

Room-temperature CL spectra corresponding to Ga_2O_3 powders and to sample G24, representative of all the annealed samples, are shown in Fig. 3(a). The starting oxide shows a blue-green CL emission composed of two peaks centered around 2.9 and 2.5 eV. After annealing, the green component disappears while a broadband centered at 3.3 eV rises along with an intense red emission around 1.73 eV. The bands in the blue-green region are characteristic of Ga_2O_3 and have been previously reported in photoluminescence (PL) studies.[2,4] The red emission appears in all the annealed samples and presents very sharp peaks (full width at half maximum $\sim$6 meV) centered at 1.805, 1.785, and 1.745 eV. Spatially resolved CL spectra show that the relative intensity of the red band is stronger in the nanowires and comblike structures than in the surface background of the samples. The behavior of the red emission has been found to show a strong temperature dependence. Figure 3(b) shows the trend of this emission with increasing the temperature. At 88 K, only the sharp peaks separated 20 meV intervals between 1.695 and 1.805 eV are obtained. The most intense peaks, centered at 1.805, 1.785, and 1.745 eV, can be observed up to at least a temperature of 370 K. At about 210 K, along with these

[a]Electronic mail: bianchi@fis.ucm.es

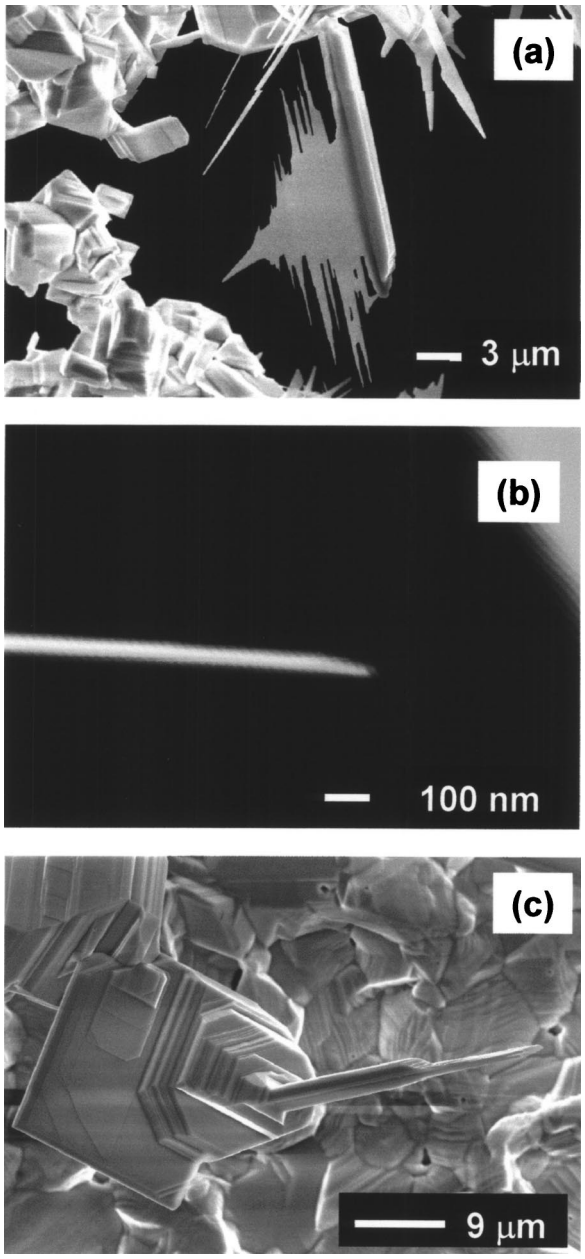

FIG. 1. (a) SEM micrograph from nanowires in sample G8. (b) Detail of a nanowire with a width of tens of nanometers. (c) SEM micrograph from sample G24. By increasing the annealing time needle-like structures are formed.

peaks an intense broadband emerges. The sharp peaks show a 5 meV redshift when the temperature raises from 88 to 295 K.

A PL red band has been recently reported in nitrogen doped β-Ga_2O_3 nanowires[3] synthesized via vapor phase growth. The properties of this emission were found to agree with a DAP transition model, with oxygen vacancies acting as donors and nitrogen impurities as deep acceptor levels. In Ref. 3, the red band was centered at 1.71 eV at a temperature of 10 K for nitrogen doped samples, and at 1.76 eV for an as-grown sample, where the red emission was explained by the presence of impurities. In order to study the possible influence of nitrogen atmosphere, a sample was prepared, as described above, under nitrogen flow. In this case the CL spectra were found to be similar to those of samples annealed in argon, shown in Fig. 3. This indicates that intrinsic defects

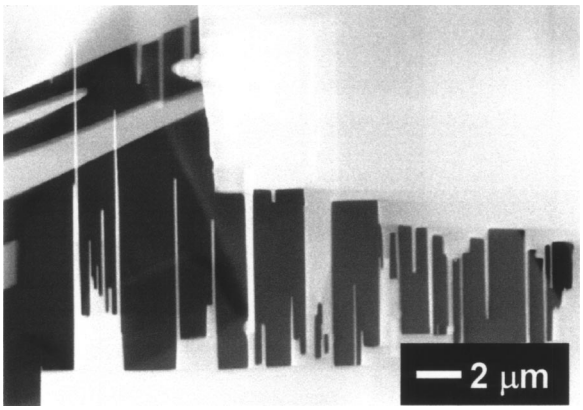

FIG. 2. SEM micrograph from sample GM24. A milling process before annealing leads to a higher density of low-dimensional structures as sheets and comblike crystals.

or impurities in the nanowires are the origin of the red luminescence in our samples. The different growing conditions of β-Ga_2O_3 nanowires in Ref. 3, possibly leading to different intrinsic or impurity defect levels than in this work, could

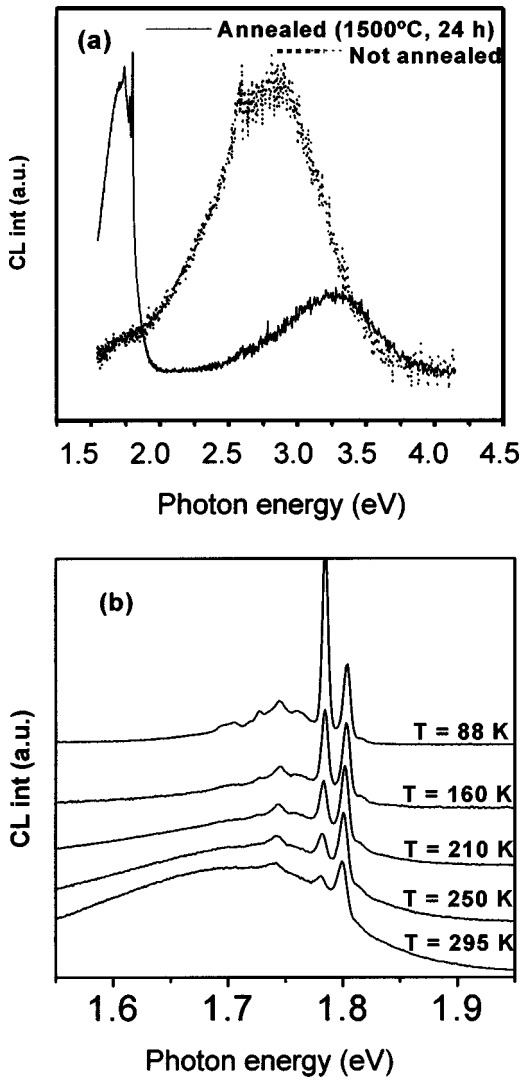

FIG. 3. (a) Room-temperature CL spectra from Ga_2O_3 powders (dot line) and sample G24 (continous line). The red band with sharp peaks is dominant in the last case. (b) Red peaks evolution with the temperature. Above 210 K, a broad red band emerges and only three sharp peaks remain.

explain that the sharp red peaks were not observed. Besides, Ref. 3 refers to PL measurements and it is well known that, due to the differences in the excitation energies and densities, CL and PL can give different information.[11] PL has a more selective character and a lower excitation energy as compared with CL.

In addition to the three intense peaks centered at 1.805, 1.785, and 1.745 eV observed even at room temperature [Fig. 3(b)] a richer peak structure is observed at 88 K. The peaks appear at 1.805, 1.785, 1.765, 1.745, 1.725, and 1.705 eV. These peaks could be regarded as three main peaks and their phonon replicas. Their constant separation may support the phonon assisted transition explanation of the less intense peaks. Raman scattering spectra of Ga_2O_3 nanorods and Ga_2O_3 powder have been recently reported. The dominant peaks were 167 cm^{-1} (20.7 meV) and 198 cm^{-1} (24.5 meV) for pure Ga_2O_3 powder, while for nanorods these peaks shifted to 160 cm^{-1} (19.8 meV) and 194 cm^{-1} (24 meV), respectively.[12] The shift was explained in terms of the presence of twins and edge dislocations presented in the nanorods. The energy values of phonons in the nanowires would be then close to the 20 meV separation of the CL peaks.

A peculiar peak structure was also observed by Binet and Gourier[13] in the optical absorption edge of crystalline β-Ga_2O_3, which consists of several peaks with energy differences of 0.06, 0.07, or 0.12 eV. They explained this structure as due to the presence of one-dimensional acceptor clusters with a size of $\sim 30-40$ nm acting as quantum wells and giving rise to acceptor discrete levels in the energy interval of 0.5 eV above the valence band. The transmission electron microscopy (TEM) (Ref. 14) observation of <5 nm clusters in crystalline β-Ga_2O_3 supported this interpretation. In our CL spectra, the main two sharp peaks at 295 K, placed at 1.805 and 1.745 eV, are separated at 0.06 eV. This value agrees well with the energy interval observed between three peaks of the absorption spectra.[13] In the framework of this model, these two emissions could be considered as radiative transitions from a deep level to two of the discrete levels described in Ref. 13. The presence of sharp peaks suggests a discrete level to discrete level transitions. It is known that the annealing of this kind of oxide, unless it is done in oxidizing atmosphere, creates a high density of oxygen vacancies. Thus, a high density of oxygen vacancies can be considered to be present in our samples that could be related to the sharp red peaks. However, further experiments will be performed in order to elucidate this point and the possible connections between the sharp peaks and the broad red band.

In conclusion, β-Ga_2O_3 nanowires and other low-dimensional structures have been obtained by sintering gallium oxide under argon flow. The nanowires show intense red emission at room temperature, composed of a broadband and sharp peaks. At low temperatures, the sharp peaks appear as the most intense red luminescence. DAP transitions from oxygen donor levels to impurity acceptor levels would be related to the broadband. Although the origin of the sharp peaks is yet unclear, our results suggest that phonon assisted transitions may take place and the possibility of transitions from a deep level to discrete acceptor levels generated by acceptor clusters cannot be ruled out.

This work was supported by the MEC project (MAT2003-00455).

[1] Z. W. Pan, Z. R. Dai, and Z. L. Wang, Science **291**, 1947 (2001).
[2] L. Binet and D. Gourier, J. Phys. Chem. Solids **59**, 1241 (1998).
[3] Y. P. Song, H. Z. Zhang, C. Lin, Y. W. Zhu, G. H. Li, F. H. Yang, and D. P. Yu, Phys. Rev. B **69**, 075304 (2004).
[4] D. P. Yu, J.-L. Bubendorff, J. F. Zhou, Y. Leprince-Wang, and M. Troyon, Solid State Commun. **124**, 417 (2002).
[5] S. Sharma, M. K. Sunkara, U. M. Graham, and B. H. Davis, Mater. Res. Soc. Symp. Proc. **755**, DD9.4.1 (2003).
[6] B. C. Kim, K. T. Sun, K. S. Park, K. J. Im, T. Noh, M. Y. Sung, S. Kim, S. Nahm, Y. N. Choi, and S. S. Park, Appl. Phys. Lett. **80**, 479 (2002).
[7] C. H. Liang, G. W. Meng, G. Z. Wang, Y. W. Wang, L. D. Zhang, and S. Y. Zhang, Appl. Phys. Lett. **78**, 3202 (2001).
[8] X. C. Wu, W. H. Song, W. D. Huang, M. H. Pu, B. Zhao, Y. P. Sun, and J. J. Du, Chem. Phys. Lett. **328**, 5 (2000).
[9] D. G. Thomas, J. J. Hopfield, and W. M. Augustyniak, Phys. Rev. **140**, A202 (1965).
[10] A. Urbieta, P. Fernández, and J. Piqueras, Appl. Phys. Lett. **85**, 5968 (2004).
[11] B. G. Yacobi and D. B. Holt, *Cathodoluminescence Microscopy of Inorganic Solids* (Plenum, New York, 1990).
[12] Y. H. Gao, Y. Bando, T. Sato, Y. F. Zhang, and X. Q. Gao, Appl. Phys. Lett. **81**, 2267 (2002).
[13] L. Binet and D. Gourier, Appl. Phys. Lett. **77**, 1138 (2000).
[14] E. G. Villora, Y. Murakami, T. Sugawara, T. Atou, M. Kikuchi, D. Shindo, and T. Fukuda, Mater. Res. Bull. **37**, 769 (2002).