Structural and optical properties of individual Zn$_2$GeO$_4$ particles embedded in ZnO

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Abstract

Functionalizing transparent conducting oxides (TCOs) is an intriguing approach to expand the tunability and operation of optoelectronic devices. For example, forming nanoparticles that act as quantum wells or barriers in zinc oxide (ZnO), one of the main TCOs today, may expand its optical and electronic tunability. In this work, 800 keV Ge ions have been implanted at a dose of $1 \times 10^{16}$ cm$^{-2}$ into crystalline ZnO. After annealing at 1000 °C embedded disk-shaped particles with diameters up to 100 nm are formed. Scanning transmission electron microscopy shows that these are particles of the trigonal Zn$_2$GeO$_4$ phase. The particles are terminated by atomically sharp facets of the type $\{11\overline{2}0\}$, and the interface between the matrix and particles is decorated with misfit dislocations in order to accommodate the lattice mismatch between the two crystals. Electron energy loss spectroscopy has been employed to measure the band gap of individual nanoparticles, showing an onset of band-to-band transitions at 5.03 ± 0.02 eV. This work illustrates the advantages of using STEM characterization methods, where information of structure, growth, and properties can be directly obtained.

Keywords: STEM-EELS, embedded nanoparticles, optical properties, ZnO

(Some figures may appear in colour only in the online journal)

1. Introduction

ZnO is an important semiconductor that has attracted considerable scientific and technological interest due to a wide range of applications, including its use as transparent conductive oxide (TCO) [1, 2]. For further enhancement of the functionality of ZnO as a TCO, one possibility is to embed nanoparticles that can act as quantum wells, barriers or even utilize the optoelectronic properties of the particles for detection, emission or storage applications.

Highly conductive ZnO films used as TCOs can be realized via doping by aluminum [3], and gallium [4–7], but also using group IV elements such as silicon and germanium (Ge) [8]. Ge is of particular interest, since embedded nanoparticles of elemental Ge and several of its oxide forms are semiconducting with a size-dependent tunability [9], while the unprecipitated Ge remains as donor on substitutional site in the ZnO matrix [10, 11]. For Ge concentrations below 14%–15%, trigonal Zn$_2$GeO$_4$ is in thermodynamic equilibrium with ZnO [12]. However, this semiconducting oxide has received little attention despite having a wide range of intriguing properties, and possible applications for batteries [13, 14] and photodetectors [15, 16] among others. It has a wide band gap, which is often quoted to be in the range of 4.5–4.7 eV [17–19]. Systems with nanosized precipitates often have particles with the shape of rods, ribbons or spheres, and the particle shape and size are seen to influence the properties. The interaction between nanosized particles of Zn$_2$GeO$_4$ and...
a matrix of ZnO has not previously been accounted for. More information is therefore needed in order to utilize Zn$_2$GeO$_4$ particles in ZnO.

In this work, ion implantation and post-implantation annealing have been used to create particles in the form of disks of Zn$_2$GeO$_4$ embedded in ZnO. The structure of the interface between the particles and matrix is investigated in detail using scanning transmission electron microscopy (STEM) and geometrical phase analysis (GPA). Furthermore, the optical properties of individual embedded Zn$_2$GeO$_4$ particles are measured using electron energy loss spectroscopy (EELS).

2. Experimental methods

A hydrothermal (0001)-oriented ZnO single crystal from Tokyo Denpa was implanted by 800 keV Ge with a fluence of $10^{16}$ cm$^{-2}$ along [0001] using a 1 MV NEC tandem accelerator. The maximum resulting Ge concentration was estimated to be approximately $10^{20}$ cm$^{-3}$ at the projected depth ($R_p$) of $\sim 325$ nm. Furthermore, annealing at 1000 °C was performed for 1 h, whereas reference samples of virgin ZnO and Ge-implanted ZnO without annealing were also prepared.

Secondary Ion Mass Spectrometry (SIMS) was conducted using a Cameca IMS7f microanalyzer with a 10 keV O$_2^-$ primary beam. Areas of $125 \times 125 \mu$m$^2$ were scanned, and the crater depths were measured with a Dektak 8 stylus profilometer. A constant erosion rate was assumed in the conversion between sputtering time and depth, and the as-implanted sample was used as reference for the concentration calibration. Furthermore,structural quality of the samples before and after the anneal was analyzed by Rutherford backscattering spectrometry (RBS) in channeling mode (RBS/C). 1.62 MeV $^4$He$^+$ ions were employed, which were backscattered into the detector placed at 165° relative to the incident beam direction. X-ray diffraction (XRD) measurements were performed with Cu K$_{α1}$ radiation ($\lambda = 1.5406$ Å) in a Bruker AXS D8 Discover system.

Electron transparent cross-sectional transmission electron microscopy (TEM) samples were prepared by mechanical grinding and polishing. Final thinning was performed by Ar ion milling with a Fischione Model 1010, and plasma cleaning with a Fischione Model 1020 was applied directly before the TEM investigations. A JEOL JEM-2100F at an acceleration voltage of 200 kV was used for initial sample investigation by TEM and STEM. High resolution STEM imaging, energy-dispersive x-ray spectroscopy (EDS) and EELS were conducted on an FEI Titan G2 60–300 equipped with a CEOS DCOR probe-corrector, a monochromator and Super-X EDX detectors. High resolution STEM imaging and EDS were performed at 300 kV with a probe convergence angle of 31 mrad, using a high angle annular dark field (HAADF) detector. The resulting spatial resolution was approximately 0.08 nm. Fast Fourier transform (FFT) analysis was used on high resolution HAADF STEM images, and lattice strain maps were made by geometric phase analysis (GPA) in the Gatan GMS software suite. EELS spectrum imaging was performed at 60 kV using a Gatan Quantum 965 imaging filter, a probe convergence angle of 31 mrad, and a collection angle of 21 mrad. The energy dispersion was 0.01 eV/channel. The energy resolution measured using the full width at half maximum (FWHM) of the zero-loss peak was 0.12 eV. Principle component analysis (PCA) [20] with 17 components was used to reduce spectral noise.

3. Results and discussions

Figure 1(a) shows the Ge concentration measured by SIMS as a function of depth for the as-implanted sample, and after annealing at 1000 °C. For the as-implanted sample, the Ge is broadly distributed with a maximum centered around 400 nm below the surface. Interestingly, after annealing at 1000 °C, a distinct increase in the Ge signal around $R_p$ is observed, despite the implantation fluence being the same as for the
as-implanted sample. This increased SIMS intensity implies a change in the local environment around Ge, for instance through the formation of a new phase containing Ge, giving rise to a higher signal (the so-called “matrix-effect” [21]). A similar effect has been observed previously in this system after annealing at 800 °C [22], where small Ge nanoparticles have been identified in the ZnO matrix. Hence, the SIMS results indicate that a secondary phase is formed in the ZnO matrix causing an increased ionization efficiency of Ge.

The channeling RBS spectra of as-implanted and annealed samples are shown in figure 1(b), where a spectrum from an unimplanted (virgin) sample and a randomly oriented ZnO sample are shown as references. The as-implanted spectrum is characterized by the low yield of backscattered ions near the surface region (corresponding to the channel 400), but with a rapid increase from approximately 200 nm depth. The spectrum is also characterized by high de-channeling yield beyond the maximum of Ge concentration (∼400 nm) without a well defined damage peak. Such spectrum shape is typical for channeling implantations [23], and indicates the presence of extended defects, such as dislocation loops and stacking faults [24]. Figure 1(b) also shows that annealing at 1000 °C is not enough to completely anneal out the Ge-induced defects and the spectrum is still above that for virgin crystal, indicating that defects still persist and higher temperatures or longer annealing times are needed to completely restore the crystal structure.

Figure 1(c) shows x-ray diffractograms from the as-implanted and 1000 °C annealed samples. Disregarding the peaks from the sample holder, marked with asterisks, the as-implanted sample only shows diffraction peaks corresponding to pure crystalline ZnO. However, the sample annealed at 1000 °C shows additional peaks, confirming that a new crystalline phase has formed. The most prominent peaks are at 2θ = 12°, 25° and 66°. These peaks can be indexed as (1 1 2 0), (2 2 4 0), and (5 5 1 0) from the trigonal phase Zn₃GeO₄. These peaks can also be seen as 1st, 2nd and 5th order reflections from (1 1 2 0), showing that the trigonal phase Zn₃GeO₄ has a preferred orientation with respect to ZnO.

Figure 2(a) shows a low angle annular dark field (ADF) STEM image of the 1000 °C annealed sample, with an overlay of the Ge concentration depth profile found by SIMS. This ADF STEM image provides strong diffraction contrast, e.g. strained areas such as defects and coherent or semi-coherent nanocrystals are standing out as bright features. In the present work, our focus is on the large particles at a depth of 350–750 nm below the sample surface.

Figures 2(b) and (c) show Zn and Ge EDS elemental maps of one of the large particles. The maps clearly demonstrate the presence of Ge and depletion of Zn in the particle compared to the surrounding matrix.

Figure 3(a) shows a high resolution high angle annular darkfield (HAAADF) STEM image of a particle, hereafter referred to as Particle A, showing excellent crystallinity. The corresponding FFT diffractograms verified the wurtzite structure of ZnO (Figure 3(b)) and the trigonal Zn₃GeO₄ phase (figure 3(c)), and also reveal a preferred orientation relationship between the particle and the matrix described by:

\[ \{11ar{2}0\}\langle 0001\rangle_{ZnO} [0001][11ar{2}0]_{Zn₃GeO₄} \]  

which is consistent with the XRD results.

Figure 4(a) shows Particle A together with a second Zn₂GeO₄ particle referred to as Particle B (figure 4(b)). Particles A and B are viewed along two different projections of ZnO, [1 1 2 0] and [1 0 0 1], respectively. These projections are perpendicular to each other. Thus, we are observing Zn₂GeO₄ both along and perpendicular to the c axis of the trigonal unit cell.

As seen in figure 4 the dominating interface is \((1 1 2 0)_{Zn₂GeO₄}||\langle 0001\rangle_{ZnO}\) which is atomically flat. In addition, the particles make facets at the two other crystallographically equivalent sets of planes \((\bar{1}210)_{Zn₂GeO₄}||\langle 1 1 0 1\rangle_{ZnO}\).
The dominating (1120)_{ZnO} interface was further studied using GPA for the nanoscale localization of strained regions and misfit dislocations (MDs). Along the projection direction ([1100]_{ZnO}) the in-plane matching takes place between the (0006)_{Zn_{2}GeO_{4}} and (11\overline{2}0)_{ZnO} planes that are vertical to the interface. Given that their nominal interplanar spacings are $d_{0}^{Zn_{2}GeO_{4}} = 0.1588$ nm and $d_{0}^{ZnO} = 0.1625$ nm, the misfit with respect to the ZnO matrix ($\varepsilon_{xx} = \frac{d_{p} - d_{m}}{d_{m}}$, where $p$ and $m$ denote the particle and matrix, respectively).
respectively) is approximately $-2.3\%$, and for the full strain accommodation MDs are expected every 6.9 nm. The GPA strain map in Figure 4(c) created from the corresponding HAADF-STEM image in Figure 4(b) displays a periodic array of MDs along and at the vicinity of the two interfaces. The extra half planes are localized at the Zn$_2$GeO$_4$ side, since the MDs compressive component (green/blue) is inside the particle and the tensile component (red/yellow) is inside the matrix. The experimentally measured misfit ($-2.8\% \pm 0.3\%$) shown by the GPA strain profile (Figure 4(c) inset), is in good agreement with the nominal lattice misfit between the particle and the matrix, indicating that the system is almost fully relaxed, with the lattice mismatch being accommodated by the MD introduction.

As seen in Figure 4(a), the interfaces involving the {1 1 0 1} planes of ZnO become stepped. If we assume that these steps are easily formed, we have a partial explanation for why the precipitates become disk shaped. The growth of particles can often be explained in terms of a Terrace-Ledge-Kink (TLK) model [25, 26]. This model points to the fact that growth is difficult on an atomically flat surface (a terrace). At the concave corners of a stepped surface there are more directions for a newly arrived atom to form bonds. An interface with ledges and kinks will therefore generally grow faster, leading to precipitates shaped as plates or rods. This would explain the shape as we see it for Particle A. Since the precipitates of Zn$_2$GeO$_4$ are shaped as plates and not rods, a similar mechanism for fast growth must also exist for the perpendicular direction, as we see in the picture of Particle B. These interfaces need not be faceted, as an incoherent hemispherical interface will also have high mobility [27].

Concerning the functional properties of the Zn$_2$GeO$_4$ particles, EELS in STEM (STEM-EELS) provides a unique way of measuring the optical properties of individual embedded particles, in contrast to optical spectroscopy methods that probe the average properties of a large sample volume. STEM-EELS from a large Zn$_2$GeO$_4$ particle and from the ZnO matrix are shown in Figure 5. Here, the background consisting of the tail from the Zero-Loss Peak (direct beam without significant energy loss) can be described by a decaying power function as is shown by the dashed line. In ZnO, the onset of energy-loss is known to be related to the band gap [28–31], and assuming parabolic conduction and valence bands separated by a direct gap $E_g$, the energy-loss edge can be described by [32]

$$I(E) = c\sqrt{E - E_g}. \quad (2)$$

For the spectra measured in the ZnO matrix after background-subtraction, applying a curve fit of this function to the energy-loss edge yields an onset of $3.28 \pm 0.01$ eV (average and standard deviation of $N = 10$ separate measurements). This is highly consistent with previously reported values for the energy loss onset and band gap of ZnO [7, 33, 34], as well as the range of results by optical absorption measurements [35].

Figure 5 shows that the energy loss edge corresponding to ZnO is present in the spectrum from the Zn$_2$GeO$_4$ region. We attribute this to two effects: first there may be ZnO above and below the particle along the beam path, and second, the inelastic delocalization of the EELS signal means that approximately 50% of the signal originates at distances larger than 6–7 nm from the point of measurement [36]. Therefore, contributions from both the particle and the matrix are expected.

An important feature observed is that the spectrum from the Zn$_2$GeO$_4$ particle in Figure 5 exhibits an increased energy loss intensity starting at around 5 eV. This feature is not present in the matrix, and is assigned to the onset of band-to-band transitions in Zn$_2$GeO$_4$. The band gap of the Zn$_2$GeO$_4$ particles was estimated by studying the spectra from 10 different particles. The background originating from the ZnO edge was subtracted by using a linear function, and equation (2) was subsequently fitted to the resulting isolated Zn$_2$GeO$_4$ edge. By this procedure an average value of $E_g = 5.03$ eV with a spread of $\sigma = 0.02$ eV was obtained. While this is somewhat higher than the band gap values often quoted elsewhere (4.5–4.7 eV) [17–19], it is noteworthy that STEM-EELS provides a method for optical characterization on individual particles embedded in a matrix. This provides a useful tool for further exploration of small-scale systems, and opens up for a range of possible experiments with superior spatial resolution. This includes investigations of complex particles, grains, films, and so on, perhaps also in systems where quantum effects may influence results.

4. Conclusions

Implantation of Ge in a ZnO single crystal with subsequent annealing at 1000 °C has been found to form embedded Zn$_2$GeO$_4$ particles in the ZnO matrix. By employing atomic-resolution STEM imaging, we have demonstrated that the
Nanotechnology 30 (2019) 225702
C S Granerød et al.

Zn$_2$GeO$_4$ nanoparticles have a preferred orientation with the ZnO matrix, as well as preferred growth direction. The STEM-EELS spectrum imaging method has been successfully applied to the analysis of individual Zn$_2$GeO$_4$ embedded particles, providing a direct measurement of the band gap of the nanoparticles. The findings from this work show that ZnO can be functionalized by Ge, while also illustrating the advantages of structural and optical characterization using sub-angstrom spatial and high energy resolution STEM and EELS methods.

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References

[1] Özgür Ü, Alivov Y I, Liu C, Teke A, Reshchikov M A, Doğan S, Avrutin V, Cho S-J and Markoš H 2005 J. Appl. Phys. 98 041401
[2] Jagadish C and Pearton S J 2011 Zinc Oxide Bulk, Thin Films and Nanostructures: Processing, Properties, and Applications (Amsterdam: Elsevier)
[3] Maldonado F and Shasthans A 2010 J. Phys. Chem. Solids 71 784
[4] Look D C, Leedy K D, Tomich D H and Bayraktaroglu B 2010 Appl. Phys. Lett. 96 062102
[5] Kim C E, Moon P, Kim S, Myoung J-M, Jang H W, Bang J and Yun I 2010 Thin Solid Films Proc. 2nd Int. Conf. on Microelectronics and Plasma Technology—ICMAP 2009 vol 518, p 6304
[6] Look D C, Heller E R, Yao Y-F and Yang C C 2015 Appl. Phys. Lett. 106 152102
[7] Granerød C S, Bilde N S, Aarholt T, Yao Y-F, Yang C C, Look D C, Vines L, Johansen K M and Prytz Ø 2018 Phys. Rev. B 98 115301
[8] Carolan D 2017 Prog. Mater. Sci. 90 128
[9] Kamata Y 2008 Mater. Today 11 30
[10] Lyons J L, Janotti A and de Walle C G V 2009 Phys. Rev. B 80 205113
[11] Lv Y, Dai Y, Yang K, Zhang Z, Wei W, Guo M and Huang B 2011 Physica B 406 3926
[12] Ustalova O N, Koryagina T I, Kosov A V, Kutvitskii V A and Shorikov V M 1977 J. Inorg. Chem. 22 430 translated from Zhurnal Neorganicheskoi Khimii (Russian)
[13] Feng J K, Lai M O and Lu L 2011 Electrochem. Commun. 13 287
[14] Yi R, Feng J, Lv D, Gordin M L, Chen S, Choi D and Wang D 2013 Nano Energy 2 498
[15] Yan C, Singh N and Lee P S 2010 Appl. Phys. Lett. 96 053108
[16] Li C, Bando Y, Liao M, Koide Y and Golberg D 2010 Appl. Phys. Lett. 97 161102
[17] Liang J, Xu J, Gu Q, Zhou Y, Huang C, Lin H and Wang X 2013 J. Mater. Chem. A 1 7798
[18] Yan S, Wang L, Li Z and Zou Z 2011 Chem. Commun. 47 5632
[19] Liu Q, Zhou Y, Kou J, Chen X, Tian Z, Gao J, Yan S and Zou Z 2010 J. Am. Chem. Soc. 132 14385
[20] Bosman M, Watanabe M, Alexander D and Keast V 2006 Proc. Int. Workshop on Enhanced Data Generated by Electrons: Ultramicroscopy 106 1024
[21] Deline V R, Katz W, Evans C A and Williams P 1978 Appl. Phys. Lett. 33 832
[22] Aarseth B L, Granerød C S, Galeckas A, Azarov A, Nguyen P D, Prytz Ø, Svensson B G and Vines L 2018 Nanoscale (submitted)
[23] Azarov A, Wendler E, Monakhov E and Svensson B G 2018 J. Appl. Phys. 123 105701
[24] Turos A, Nowicki L, Stonert A, Pagowska K, Jagielski J and Muecklich A 2010 Nucl. Instrum. Methods Phys. Res. B 268 1718
[25] Kossel W 1927 Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen, Mathematisch-Physikalische Klasse (Berlin: Weidmannsche Buchhandlung) pp 135 http://www.digitzeitschriften.de/dms/resolverppn/?PID=GDZPPN00250717X
[26] Nicholas J F 1993 Structure ed G Chiarotti vol 24a (Berlin: Springer) pp 37–9
[27] Porter D A and Easterling K E 1984 Phase Transformations in Metals and Alloys 4th edn (Molly Mills Lane, Wokingham, Berkshire: Van Nostrand Reinhold (UK) Co. Ltd.)
[28] Egerton R 2003 Micron 34 127
[29] Lazar S, Botton G, Wu M-Y, Tichelaar F and Zandbergen H 2003 Proc. Int. Workshop on Strategies and Advances in Atomic Level Spectroscopy and Analysis: Ultramicroscopy 96 535
[30] Erni R and Browning N D 2005 Ultramicroscopy 104 176
[31] Granerød C S, Zhan W and Prytz Ø 2018 Ultramicroscopy 184 39
[32] Rafferty B and Brown L M 1998 Phys. Rev. B 58 10326
[33] Bosman M, Tang L J, Ye J D, Tan S T, Zhang Y and Keast V J 2009 Appl. Phys. Lett. 95 101110
[34] Granerød C S, Galeckas A, Johansen K M, Vines L and Prytz Ø 2018 J. Appl. Phys. 123 145111
[35] Viezbicke B D, Patel S, Davis B E and Birnie D P 2015 Phys. Status Solidi b 252 1700
[36] Zhan W, Granerød C S, Venkatachalapathy V, Johansen K M H, Jensen J I T, Kuznetsov A Y and Prytz Ø 2017 Nanotechnology 28 105703