



In-situ transmission electron microscopy study of melting and diffusion processes at the nanoscale in ZnO nanotubes with Sn cores

Yanicet Ortega ^{a,*}, Maria L. Nó ^b, Paloma Fernández ^a, Javier Piqueras ^a, Jose M. San Juan ^c

^a Departamento de Física de Materiales, Facultad de Ciencias Físicas, Universidad Complutense de Madrid, Madrid, 28040, Spain

^b Departamento de Física Aplicada II, Facultad de Ciencia y Tecnología, Universidad del País Vasco, Leioa, 48940, Spain

^c Departamento de Física de la Materia Condensada, Facultad de Ciencia y Tecnología, Universidad del País Vasco, Leioa, 48940, Spain

ARTICLE INFO

Article history:

Received 5 August 2017

Received in revised form

20 November 2017

Accepted 11 February 2018

Available online 13 February 2018

Keywords:

Nanostructured materials

Diffusion

Thermal expansion

Transmission electron microscopy

TEM

ABSTRACT

The thermal behaviour of ZnO nanotubes partially filled with Sn cores, containing also Sn nanoclusters and nanovoids, has been investigated by *in-situ* heating treatments in a transmission electron microscope (TEM). The size effect on the melting temperature of Sn nanoclusters and nanorods, and diffusion of voids along the nanotube axis have been studied by directly recording the TEM images during heating treatments. Melting temperatures of 163 °C and 213 °C were found for a 10 nm diameter particle and a 30 nm diameter Sn core respectively. Different diffusion processes in the Sn-ZnO core/shell structure at 640 °C are described.

© 2018 Elsevier B.V. All rights reserved.

1. Introduction

Semiconductor nanotubes, as nanowires or other elongated nanostructures, have potential applications in nanoelectronics or nanophotonics, which in some cases are related to the formation of heterostructures, as for instance a metal-semiconductor nanostructure, by filling the tube with a suitable metallic element. Specific applications of nanotubes filled with low melting point metals such as Ga, Sn or In, heated to a liquid state, have been reported. Carbon nanotubes filled with Ga or In have been investigated [1,2], and in the case of Ga a carbon nanothermometer based on thermal expansion of Ga was demonstrated. Similar results have been reported for Ga filled MgO nanotubes [3]. Other potential applications of the expansion of a metal column inside a nanotube are nanoswitches or nanosolders [4,5]. Semiconductor oxide nanotubes with liquid metallic cores as In filled In₂O₃ [6], Sn filled ZnO [5–7], or Sn filled Ga₂O₃ [8] nanotubes have been reported. Studies of the thermal behaviour of a metallic core in nanotubes have been carried out by *in-situ* transmission electron microscopy experiments. In some cases thermal processes as melting and expansion were induced by heating with the focused electron beam

of the microscope [4–7], while in other cases a microscope with a heating device was used [1,2]. Besides melting and expansion, complex processes, such as diffusion involving core and shell materials or void formation, can take place during thermal treatments of metal filled nanotubes. Details of the growth procedure, morphology and different features of the nanowires and nanotubes have been previously reported in Refs. [5,7].

2. Experimental method

In the present work, melting and expansion of Sn core nanocolumns, melting point of the Sn core and of isolated Sn nanoclusters, Sn diffusion as well as formation, evolution and diffusion of nanovoids were studied by direct viewing and recording the samples evolution in TEM. TEM studies were carried out with a Philips CM200 equipped with a 652 Gatan double tilt heating holder. To study Sn melting temperature of nanoparticles or the expansion of a Sn nanocolumn inside a nanotube, the sample was heated at 20 or 10 °C/min up to about 250 °C. Moreover to investigate diffusion processes, heating at a rate of 5 °C/min was performed during observation in TEM to 640 °C.

3. Results and discussion

Fig. 1 shows typical arrangements of empty channels, Sn fillings,

* Corresponding author. Departamento de Física de Materiales, Universidad Complutense de Madrid, 28040, Madrid, Spain.

E-mail address: yanicet@fis.ucm.es (Y. Ortega).

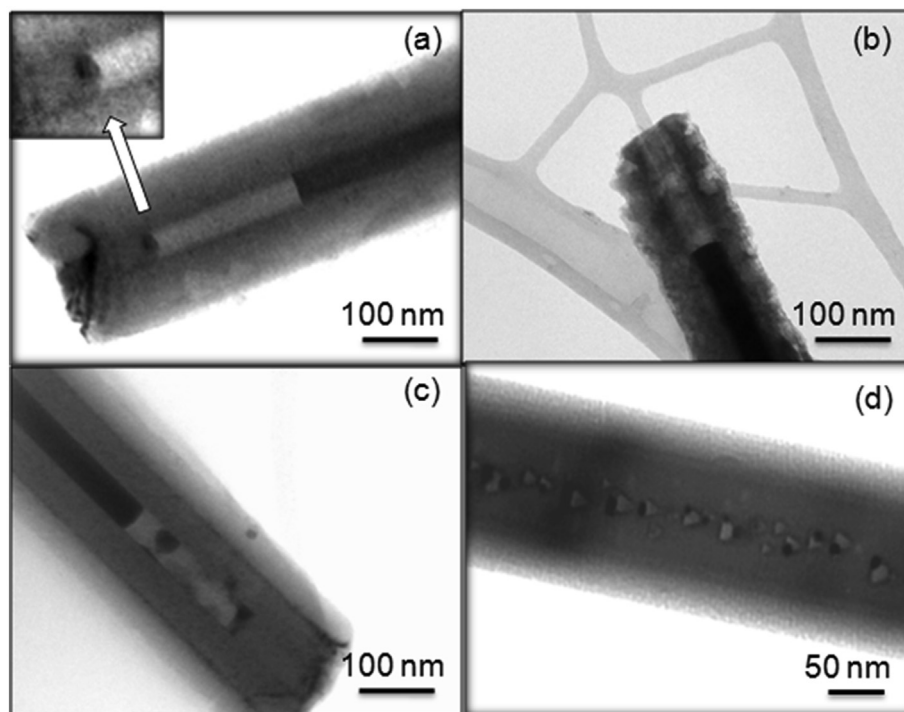


Fig. 1. TEM images of ZnO nanotubes showing (a) Sn core (dark column) partially filling the tube and a Sn nanoparticle marked with an arrow (b) partially filled nanotube with an open end (c) nanotube similar to that shown in (a) but with some Sn nanodrops at the tube wall and (d) row of triangular nanovoids aligned along the nanotube axis.

nanodrops and rows of voids in the investigated ZnO nanotubes. In our previous works [5–7], microdiffraction and EDX showed that the darker regions in the images correspond to Sn while light areas are empty ZnO nanotubes. This means that the wires with a dark elongated central part are Sn/ZnO core/shell structures while those containing channels, appearing as light areas in the images, are ZnO nanotubes. Partially filled nanotubes contain Sn cores with small diameters, typically of about 30 nm (Fig. 1(a) and (b)) and, in some cases, Sn nanodrops can be observed at the wall of the empty nanotube channel as well as isolated Sn nanoparticles or nanoclusters of about 10 nm diameter or less, as shown in Fig. 1(c). Moreover rows of triangular voids are observed along the nanotube axis (Fig. 1(d)). During the *in-situ* TEM thermal treatments, evolution or stability of these kinds of structures have been studied. The behaviour of such small dimensional Sn structures during the heating treatments below the bulk Sn melting point of 232 °C, enables to investigate the possible size dependence of melting temperature. The partially filled nanotube of Fig. 1(a), which contains a Sn cluster of about 10 nm, marked with an arrow in the image, was observed and video recorded during heating from room temperature at a rate of 20 °C/min. This is shown in the series of images of Fig. 2. At 163 °C a change in the shape of the Sn cluster took place by formation of a bulge, as observed in Fig. 2 (a). The cluster becomes rounded at 182 °C (Fig. 2(b)), the particle appears to move a little from left to right at 198 °C (Fig. 2(c)) and separates into two parts at 205 °C (Fig. 2(d)) which merge short after (not shown in the figure). At higher temperatures, up to 213 °C, the cluster was found to separate into two particles and merge again several times during the heating ramp.

Similar behaviour has been observed for other nanotubes containing Sn nanoclusters. We suggest that the formation of a bulge followed by the transformation of the cluster into a rounded particle shows that the melting of the Sn nanocluster starts at a temperature of 163 °C, which is significant lower than the bulk melting temperature (232 °C). Decrease of melting point with the size of

small particles has been often reported for different materials and thermodynamic models have been developed [9–11]. Some models are based on the thermodynamical treatment of Hansen [12], which assumes that the melting of a particle starts with a thin liquid surface overlayer and that the melting temperature is the equilibrium temperature between the solid particle core and the liquid layer. This model has been considered in several studies of the size dependence of melting point of Sn nanoparticles performed by electron diffraction [13], nanocalorimetry [14] and differential scanning calorimetry [15]. The relationship between particle radius r melting point T_m and thickness of the liquid overlayer t_0 , was given in Ref. [14] by Eq. (1)

$$T_m = 232 - 782 \left[\frac{\sigma_s}{15.8(r - t_0)} - \frac{1}{r} \right] \quad (1)$$

where T_m is in °C and r and t_0 are in Å. σ_s is the interfacial surface tension between the solid and liquid which was determined in ref. 14 to be 48 ± 8 mN/m and the best fit to the experimental data was obtained for $t_0 = 18$ Å. Comparable σ_s values were reported in Refs. [13,16] and [16]. Fig. 2(e) shows the dependence of melting temperature with the radius of Sn particles for $t_0 = 18$ Å - derived from the approaches of refs. [13,14,16].

For a particle of 5 nm radius the melting temperature ranges for the different models from 151 °C to 173 °C, which agrees with the above described start of melting at 163 °C for the 10 nm diameter particle of Fig. 2(a). In a recent work [17], size depending melting behaviour of colloidal Sn nanoparticles, investigated by differential scanning calorimetry, was reported. A melting temperature of about 185 °C was found in Ref. [17] for nanoparticles of 11 nm. This higher T_m value, as compared with the present results, is possibly related to the different kinds of samples investigated, colloidal system in Ref. [17] and single nanodrops in this work.

In the series shown in Fig. 2(a–d), no changes are observed, up to 205 °C in the Sn core. The core has a diameter of about 30 nm and

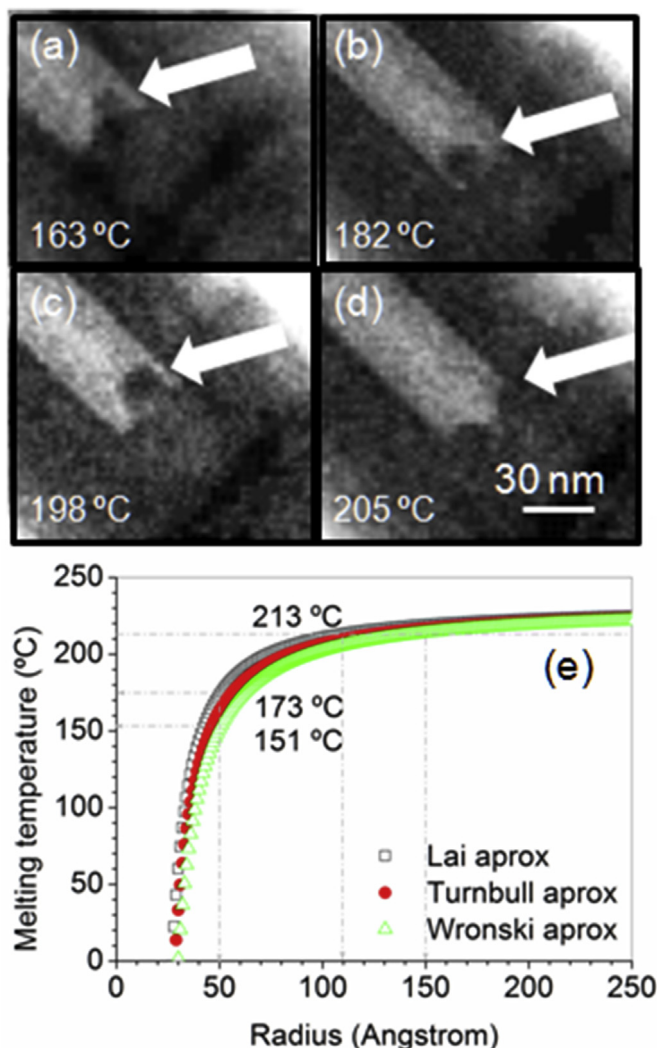


Fig. 2. Series of TEM images (a–d) showing the evolution of the Sn nanoparticle marked with an arrow in Fig. 1a, as a function of temperature (a) a shape change takes place at 163 °C, (b) (c) and (d) images at 182 °C, 198 °C and 205 °C respectively. (e) Dependence of melting temperature with radius of Sn nanoparticles, derived from approaches of refs 13, 14 and 16.

a length of about 1.4 μm and its melting temperature is expected to be closer to the bulk value of 232 °C. It is to be noticed that the size dependence of melting temperature shown in Fig. 2(e), applies to spherical particles and in principle not necessarily to rod shaped structures. At about 213 °C a sudden expansion of the Sn column takes place as shown in the images of Fig. 3(a) and Fig. 3(b), recorded at 213 °C and 213.3 °C respectively. The length of the empty part of the tube, marked with bars in both images, decreases from about 133 nm to 100 nm. The expansion of the Sn column is not related to the expansion of solid Sn, which takes place in a continuous manner by increasing temperature with a coefficient of $0.000023\text{ }^{\circ}\text{C}^{-1}$, but the sudden expansion is an evidence of the transition solid-liquid which is known to involve a volume expansion of 2.3% [18]. Assuming, as an approximation, that the diameter of the Sn filling is constant along the tube length, the observed expansion of 33 nm by melting, would correspond to the 2.3% expansion of a core of about 1.43 μm length. A lower magnification image of this rod (Fig. 3(c)) shows that the length of the Sn column is 1.49 μm in agreement with the observed expansion.

The melting temperature of the Sn core, 213 °C, is 8% lower than

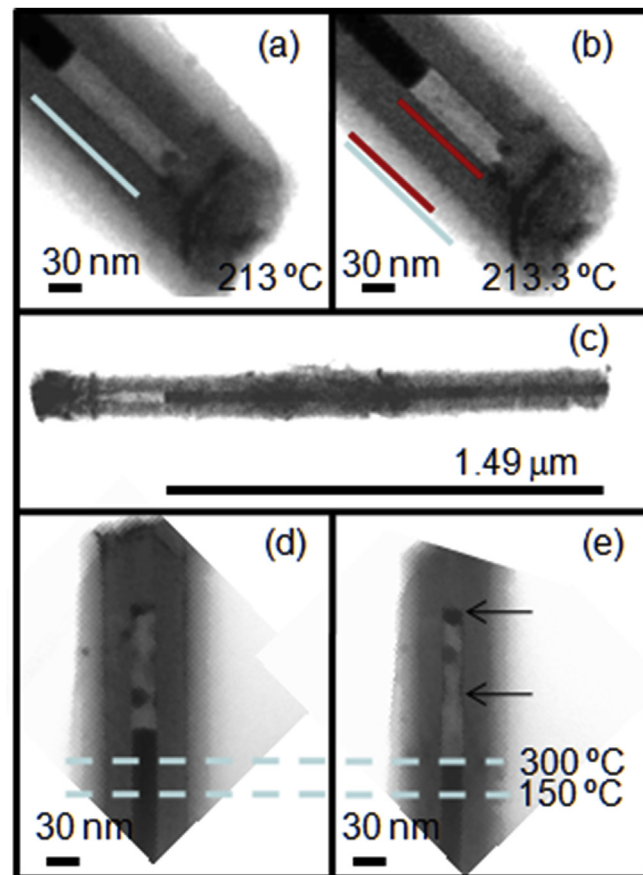


Fig. 3. TEM images of a nanotube at 213 °C (a) and 213.3 °C (b) showing the sudden expansion of the Sn core at 213 °C. (c) TEM image at lower magnification showing the whole nanotube. (d–e) TEM images of a nanotube after two (d) and four (e) thermal cycles between 150 °C and 300 °C respectively.

that of bulk Sn (232 °C). Although the curve of Fig. 2(e) was calculated for spherical particles, its validity was tentatively checked for the case of the nanorod. A T_m of 213 °C corresponds to a particle radius between 11 and 15 nm, depending on the approximation used, which is comparable to the 15 nm radius of the Sn core. This suggests that the melting temperature of cylindrical nanorods of radius r , in the size considered here, is similar to that estimated for spherical particles of the same radius. Above the melting temperature, expansion of the Sn cores along the rod axis into the empty space takes place as in the reported Ga filled carbon nanothermometer of Ref. [2].

In order to study the reversibility of the expansion process, the evolution of the rods during thermal cycles between 150 °C and 300 °C was recorded. Fig. 3(d–e) shows two images recorded at 300 °C of the same rod after two (image d) and four (image e) cycles respectively. The lower straight line in the figure marks the level of the Sn column at 150 °C and the upper line shows the level at 300 °C after four thermal cycles. The different lengths of the Sn column at 300 °C after two and four cycles are clearly appreciated. We suggest that this effect is due to changes in the core/shell structure during the thermal cycles. Comparison between Fig. 3(d) and (e), shows that in the upper end of the empty part of the tube of image (e), corresponding to a longer thermal treatment, Sn is accumulated forming a short core segment. In the same region of image (d), Sn is observed as a smaller and with an ill-defined shape cluster. On the other hand the empty tube of figure (e) shows a narrowing which seems to be related to Sn accumulation at the

tube walls, as the dark layer at the walls shows. Thermal stresses possibly also influence the deformation of the tube walls. The differences in Sn distribution as a function of the number of thermal cycles indicate the existence of thermal diffusion processes in the core/shell. In fact the presence of Sn clusters and precipitates associated with empty regions in these rods, has been proposed to be generated during growth by diffusion processes similar to the Kirkendall effect [7]. The post-growth treatments in this work lead

to diffusion induced changes in the empty region and Sn clusters of cores, as those shown in Fig. 3. The stronger interdiffusion processes could be behind the lack of the reproducibility in the amount of the Sn core expansion as a function of temperature, it prevents the development of this core/shell structure as a nanothermometer in the temperature range investigated.

The relationship between empty regions and Sn precipitates is especially evident in the case of rows of voids, as the triangular

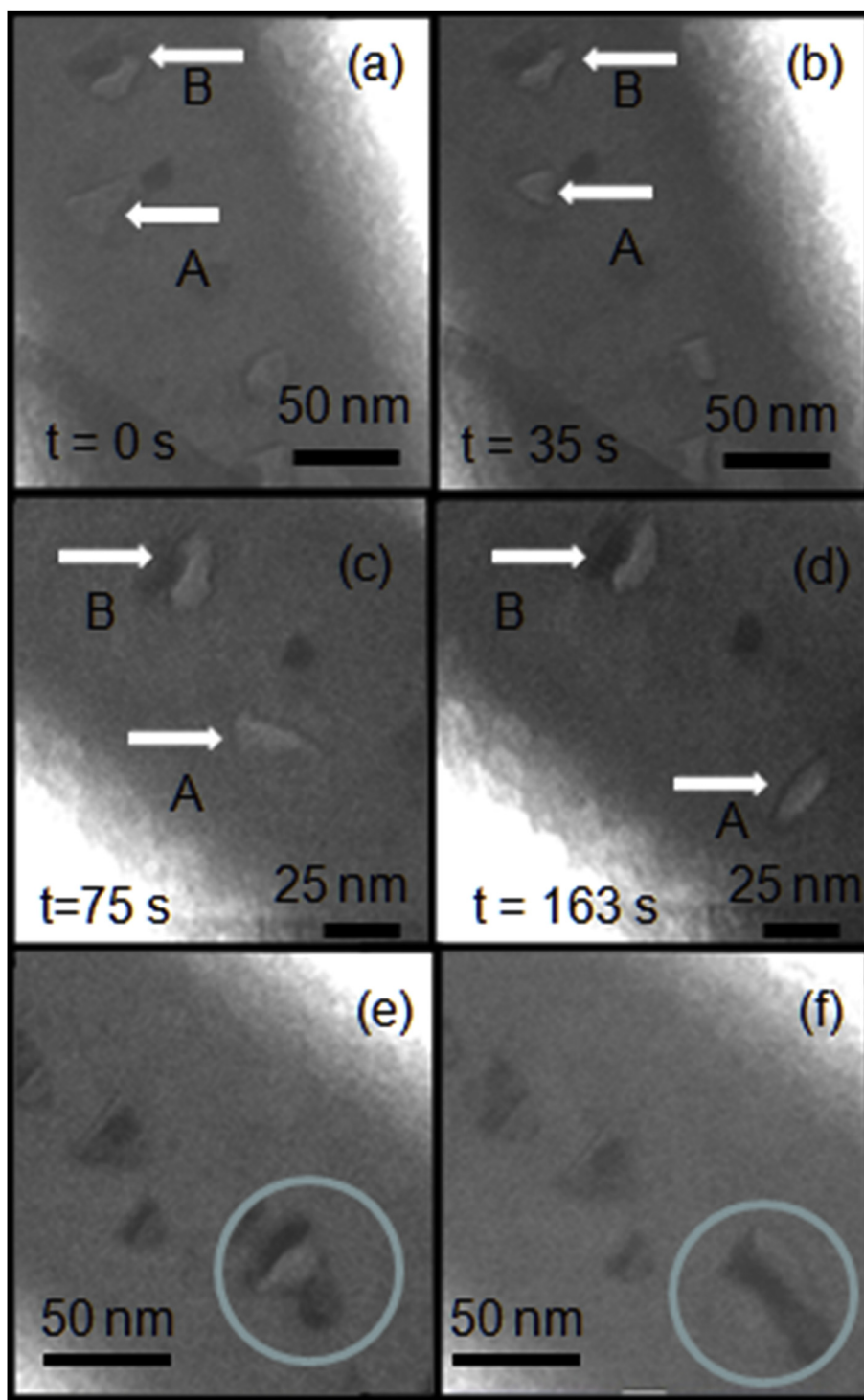


Fig. 4. TEM images showing diffusion of nanovoids along the axis of a nanotube at 640 °C. (a) at an arbitrary starting time (b) (c) and (d) after 35 s, 75 s and 163 s respectively. Arrows mark the positions of two voids during the diffusion process. (e–f) TEM images showing the rearrangement of pairs void-Sn cluster during the thermal treatment. In (e) two Sn clusters are separated by a void and appear merged (f) after 23 s.

voids of Fig. 1(d), which form part of void-precipitate pairs. In order to further investigate the diffusion related evolution of voids and Sn clusters, treatments at higher temperatures have been performed. A temperature of 640 °C has been found suitable to investigate diffusion processes in a relatively short time during observation and recording in TEM. The effect of this treatment is illustrated in Fig. 4 in the case of a row of voids. Fig. 4(a) shows the distribution of voids and clusters at a certain arbitrary instant, $t = 0$, when the sample has reached a stable temperature of 640 °C. Voids A and B marked with arrows, are associated with Sn clusters. In Fig. 4(b), recorded at $t = 35$ s, the void A appears separated from the cluster while void B is part of a more stable void-cluster pair. During this time interval interactions between void and cluster with small motions and shape changes of the void are observed till the situation shown in Fig. 4(b) is reached in which the void A, without the pinning effect of the cluster, starts to move along the rod axis. This is apparent in Fig. 4(c) and (d) corresponding to $t = 75$ s and $t = 163$ s respectively, where the displacement of void A is evident. Measurements of the void position as a function of time yielded a diffusion velocity of void A of about 0.7 nm s^{-1} . Video V1 of the Supporting Information shows the diffusion of void A.

Supplementary video related to this article can be found at <https://doi.org/10.1016/j.jallcom.2018.02.128>.

In the case of pinned voids, small rearrangements within the pairs void-cluster, have been observed to take place. An example of this is the aggregate of two clusters at opposite sides of a central void shown in the encircled area of Fig. 4(e–f). In Fig. 4(e) the two Sn clusters are not in contact and in Fig. 4(f) recorded after 23 s the clusters appear merged into a single elongated particle while the empty space is displaced to one side. This process is recorded in video V2 of the Supporting Information. One interesting result is that the diffusion of voids is not a random process but it takes place along the axis of the rod. In the case of voids with approximate triangular shape, the triangles are in general orientated with one side perpendicular to the rod axis so that the opposite vertex points to the axis direction, as the voids of Fig. 1(d) or the void A in Fig. 4(b). The displacement has been found to take place always in the direction pointed by the vertex, probably because the sharp diffusion front at the vertex involves less atomic rearrangements in each diffusion step. Triangular voids, as those observed in this work, are not typical features of ZnO, but they have been sometimes reported with the [0001] direction pointed to a flat side of the void [19].

4. Conclusions

ZnO nanotubes with partial Sn filling, containing also different kinds of nanovoids and Sn nanoclusters, have been investigated by

in-situ heating treatments in a transmission electron microscope. Melting, expansion and diffusion processes were directly recorded in TEM. The melting temperature of Sn nanoclusters and cylindrical nanocores has been found to be lower than the bulk melting temperature of Sn in agreement with previous theoretical estimation of several authors for nanoclusters. This behaviour has been demonstrated now for nanorods. Melting temperatures of 163 °C and 213 °C were measured for a 10 nm nanoparticle and a core of 30 nm diameter in a core/shell nanotube respectively. Thermal displacements of the Sn core during thermal cycles in the range 150 °C – 300 °C were not reproducible in different cycles due to Sn diffusion and slight changes in the shape of the tube during the treatment. This effect would prevent the use of these structures as nanothermometers. Nanovoids, often with triangular shape, diffuse along the nanorod axis at a temperature of 640 °C, while other voids appear to be pinned by associated Sn nanoclusters.

Acknowledgements

This work was supported by MINECO (Projects CSD 2009-00013, MAT 2012-31959 and Consolidated Research group IT-10-310 from Basque Government).

References

- [1] Y. Gao, Y. Bando, *Nature* 415 (2002) 599–600.
- [2] Y. Gao, Y. Bando, D. Goldberg, *Appl. Phys. Lett.* 81 (2002) 4133–4135.
- [3] Y.B. Li, Y. Bando, D. Goldberg, Z.W. Liu, *Appl. Phys. Lett.* 83 (2003) 999–1001.
- [4] X. Tao, L. Dong, W. Zhang, X. Zhang, J. Cheng, H. Huang, Y. Gan, *Carbon* 47 (2009) 3122–3127.
- [5] Y. Ortega, W. Jäger, J. Piqueras, D. Häussler, P. Fernández, *J. Phys. D Appl. Phys.* 46 (2013), 395301, 7pp.
- [6] M. Kumar, V.N. Singh, B.R. Mehta, J.P. Singh, *J. Phys. Chem. C* 114 (2010) 2891–2895.
- [7] Y. Ortega, Ch. Dieker, W. Jäger, J. Piqueras, P. Fernández, *Nanotechnology* 21 (2010), 225604, 7pp.
- [8] J. Hu, Q. Li, J. Zhan, Y. Jiao, Z. Liu, S.P. Ringer, Y. Bando, D. Goldberg, *ACS Nano* 2 (2008) 107–112.
- [9] P.R. Couchman, W.A. Jesser, *Nature* 269 (1997) 481–483.
- [10] K.K. Nanda, S.N. Sahu, S. Behera, *Phys. Rev. A* 66 (2012), 013208.
- [11] K.K. Nanda, *Pramana - J. Phys.* 72 (2009) 617–628.
- [12] K.J. Hanszen, *Z. Phys.* 157 (1960) 523–553.
- [13] C.R.M. Wronski, *Br. J. Appl. Phys.* 18 (1967) 1731–1737.
- [14] S.J. Lai, J.Y. Guo, V. Petrova, G. Ramanath, L.H. Allen, *Phys. Rev. Lett.* 77 (1996) 99–102.
- [15] H. Jiang, K. Moon, H. Dong, F. Hua, C.P. Wong, *Chem. Phys. Lett.* 429 (2006) 492–496.
- [16] D. Turnbull, *J. Appl. Phys.* 21 (1950) 1022–1028.
- [17] M. Liu, R.Y. Wang, *Sci. Rep.* 5 (2015) 16353.
- [18] P.G. Harrison, *Chemistry of Tin*, Blackie, Glasgow and London, Chapman and Hall, New York, 1989.
- [19] C. Cheng, R. Xin, Y. Leng, D. Yu, N. Wang, *Inorg. Chem.* 47 (2008) 7868–7873.