Journal of Alloys and Compounds 744 (2018) 421–425

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

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.

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 In_2O_3 [6], Sn filled ZnO [5–7], or Sn filled Ga_2O_3 [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).

https://doi.org/10.1016/j.jallcom.2018.02.128
0925-8388/

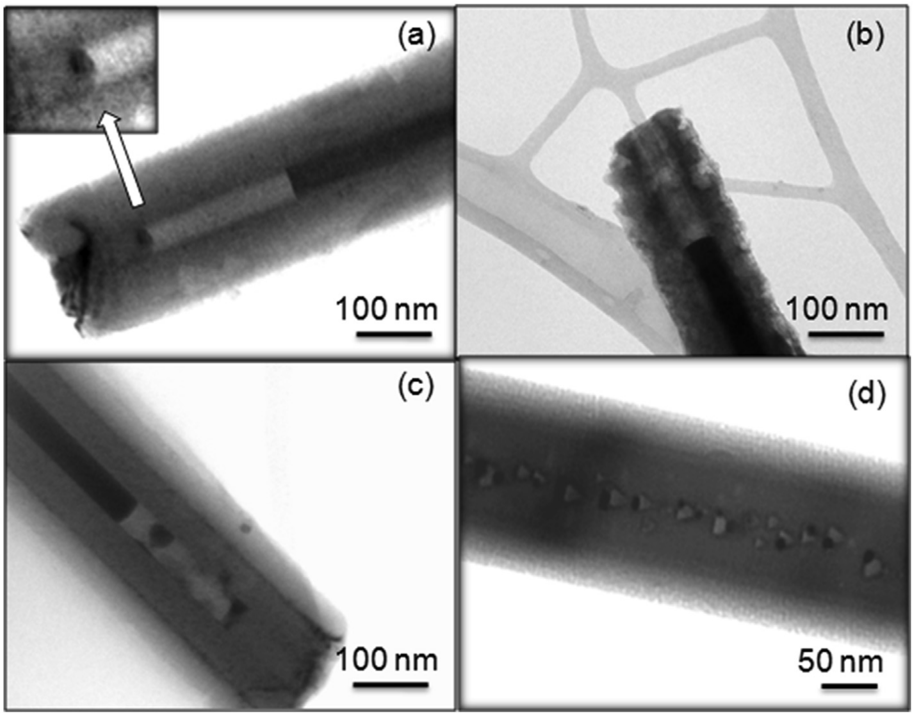

Fig. 1. TEM images of ZnO nanotubes showing (a) Sn core (dark column) partially filling the tube and a Sn nanoparticle marked with an arrow (b) partially filled nanotube with an open end (c) nanotube similar to that shown in (a) but with some Sn nanodrops at the tube wall and (d) row of triangular nanovoids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

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

where T_m is in ºC 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