Journal of Crystal Growth 388 (2014) 5–11

Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/jcrysgro

Growth and FIB-SEM analyses of C_{60} microtubes vertically synthesized on porous alumina membranes

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ARTICLE INFO

Article history:
Received 30 July 2013
Received in revised form
8 November 2013
Accepted 10 November 2013
Communicated by K. Deppert
Available online 18 November 2013

Keywords:
C_{60} microtubes
Vertical growth
Diaphragm LLIP method
DLLIP
FIB-SEM

ABSTRACT

The vertical growth of C_{60} microtubes (C_{60}MTs) on anodic aluminum oxide (AAO) membranes was investigated. The C_{60}MT size dependence on isopropyl alcohol (IPA) injection rate, into C_{60}-saturated toluene solutions through AAO membranes, was measured. A longitudinal section of the interface between a vertically grown C_{60}MT (V-C_{60}MT) and a membrane was prepared by focused ion beam processing, and observed with scanning electron microscopy. No cracking was observed along the interface, suggesting good bonding. V-C_{60}MTs exhibited spiral growth. V-C_{60}MT planar density, wall thickness and aspect ratio all decreased with increasing IPA injection rate. The relationships among length, inner and outer diameters of V-C_{60}MTs were also investigated by varying IPA injection rate.

1. Introduction

C_{60} microtubes (C_{60}MTs) vertically grown on porous alumina membranes were first prepared in 2007 by our group [1]. The method slowly introduces isopropyl alcohol (IPA) into a C_{60}-saturated toluene solution through a porous alumina membrane (anodic aluminum oxide (AAO)), using an electric syringe-piston. This is known as the diaphragm liquid–liquid interfacial precipitation (DLLIP) method. DLLIP originated from the liquid–liquid interfacial precipitation (LLIP) method, used to synthesize fullerene nanowhiskers and fullerene nanotubes [2–4,20]. C_{60} nanotubes with polycrystalline structures were first synthesized using the holes of AAO membrane as the synthetic template [21]. Further, polycrystalline C_{60} nanowires were synthesized using AAO membranes under a direct current electric field [22].

These materials have applications in field-effect transistors, solar cells, chemical sensors and superconductors [5–8]. Vertically aligned C_{60} fullerene microtubes (V-C_{60}MTs) will further the applications of low-dimensional C_{60} crystals toward three-dimensional fullerene architectonics [9]. However, to effectively control the growth of V-C_{60}MTs, their growth mechanism must first be clarified.

The planar density and diameter of V-C_{60}MTs were shown to vary depending on growth conditions in our previous report [1]. Growth parameters included the IPA injection rate and the IPA: C_{60}-saturated toluene solution volume ratio. It was also shown that the formation of V-C_{60}MTs depends on the supersaturation of C_{60} that is controlled by the injection rate of IPA into C_{60}-saturated toluene solutions through the AAO membrane [19]. In the current study, V-C_{60}MT growth is further investigated in more detail, by measuring the crystal size (outer diameter, inner diameter, length) and morphology that were not revealed in our previous papers with varying IPA injection rate in order to know the growth mechanism of V-C_{60}MTs.

Longitudinal section images of V-C_{60}MTs and the V-C_{60}MT/AAO joint interface are used to reveal the V-C_{60}MT growth mechanism for the first time as well as scanning electron microscopy (SEM) observations of the initial C_{60}MT nucleation stage on AAO membranes. This paper will give useful knowledge for the controlled growth of V-C_{60}MTs.

2. Experimental

V-C_{60}MT growth was performed as previously reported [1], using a 30-mL syringe with an inner diameter of 22.4 mm. IPA (non-dehydrated, Wako Pure Chemical Industries, Ltd., Japan) was slowly injected into the upper C_{60}-saturated toluene solution (C_{60} powder 99.5%, MTR Ltd., USA; toluene 99.5% non-dehydrated, Wako), through a porous alumina membrane at 5 °C. The IPA

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0022-0248/$ - see front matter
http://dx.doi.org/10.1016/j.jcrysgro.2013.11.009

injection rate was varied from 0.01 mL min^{-1} to 0.08 mL min^{-1}, by varying the syringe injection speed from 25 mL min^{-1} to 203 μm min^{-1}. The average AAO membrane pore diameter (Whatman Anodisc, 25 mm diameter, USA) was 200 nm.

V-C_{60}MTs were machined using a SEM-focused ion beam (SEM-FIB) system (Hitachi NB5000) at an accelerating voltage of 40 kV using a Ga liquid metal ion source. SEM (JEOL JSM-6700 F) was performed at an accelerating voltage of 5 kV for measuring the length and diameter of V-C_{60}MTs.

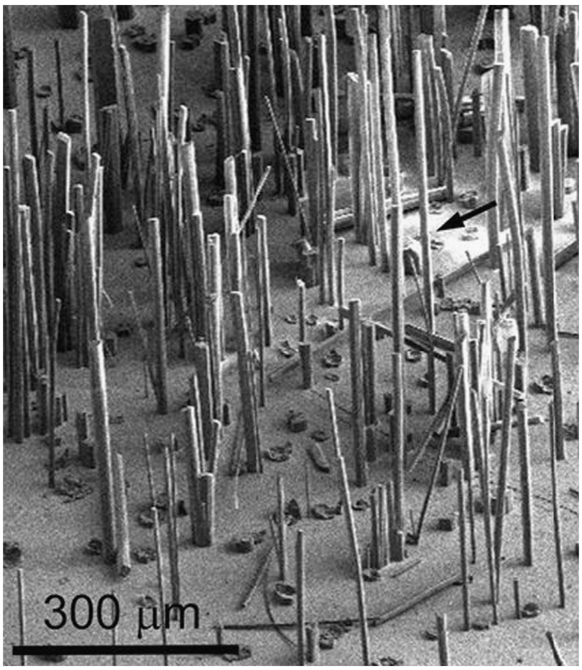

Fig. 1. SEM image of V-C_{60}MTs on an AAO membrane. The arrow points to a V-C_{60}MT with an apparent length of 465 μm.

3. Results and discussion

3.1. SEM observations of V-C_{60}MTs

Fig. 1 shows a SEM image of typical V-C_{60}MTs on an AAO membrane, whose lengths range from several tens of micrometers to > 400 μm. The apparent length of the V-C_{60}MT indicated by the arrow is 465 μm.

Fig. 2 shows SEM images of the preparation of a longitudinal section of a single V-C_{60}MT, using FIB processing. The original V-C_{60}MT wall in Fig. 2(a) was milled along the growth axis by the Ga ion beam, the result of which is shown in Fig. 2(b). V-C_{60}MT has a solid structure near the AAO membrane substrate during initial growth, which becomes tubular as growth proceeds. The tubular morphology is considered to form from a combined mechanism involving core dissolution and depletion of solute C_{60} molecules [10–12]. The hole has a steep cone-shaped morphology with a vertex angle (α) of $\sim 14°$. In Fig. 2(d), the various marked cavities are thought to have formed by non-uniform shrinkage of the C_{60}MT matrix during air drying [13]. The interface image in Fig. 2(d) shows good contact between the C_{60}MT and AAO membrane, without apparent cavities or cracking. C_{60} crystals are generally synthesized by solution growth processes involving solvent molecules. For example, C_{60} nanowhiskers synthesized by LLIP from IPA and C_{60}-saturated toluene solution exhibit a solvated hexagonal crystal structure, with lattice constants of a=2.405 nm and c=1.001 nm. Their structure transforms to a face-centered cubic (fcc) with a lattice constant of a= 1.420 nm upon matrix densification [14]. Matrix densification of ~13% upon transforming from hexagonal to fcc structures should be accompanied by stress generation at the interface. A relaxation mechanism must

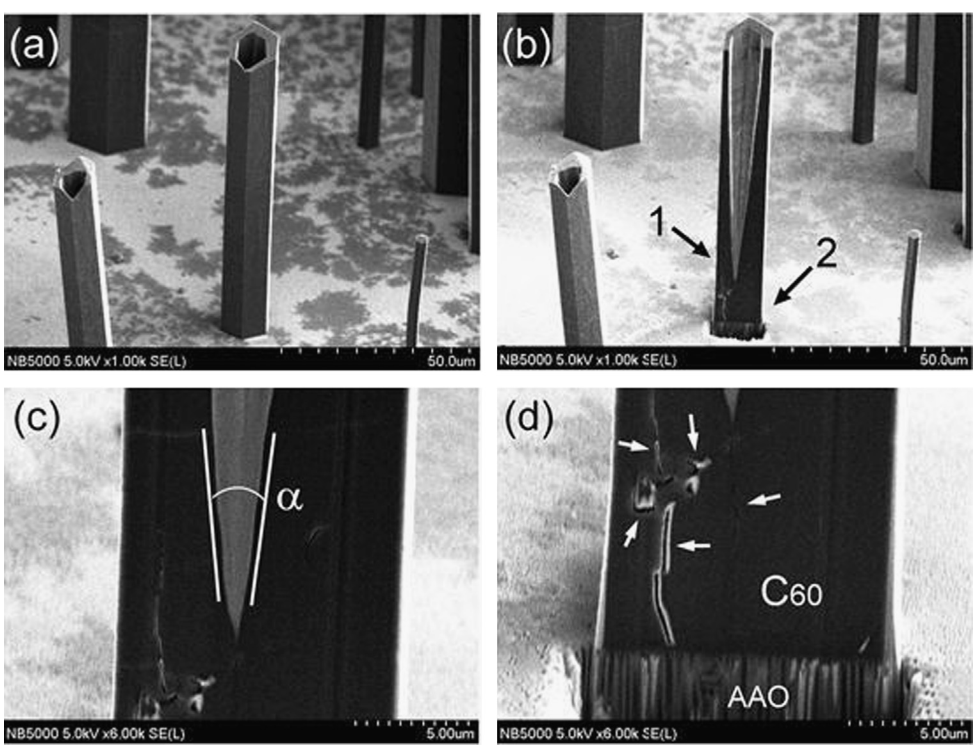

Fig. 2. SEM images showing preparation of the longitudinal section of a V-C_{60}MT on an AAO membrane. The V-C_{60}MT in (a) was vertically milled by FIB to give (b). (c) Magnified image for the region indicated by arrow 1 in (b). (d) Magnified image for the V-C_{60}MT-AAO membrane interface region indicated by arrow 2 in (b). The arrows point to cavities.