Electron beam induced real time rocket-type propulsion effect in indium metal filled indium oxide nanotubes

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A B S T R A C T
In this work, reversible synthetic nano rocket-like behavior of indium-filled indium oxide nanotubes is reported once irradiated with high energy electron beam during transmission electron microscopy study. These rocket-like nanostructures were observed to be ignited by melting and vaporizing selectively low melting point indium metal encapsulated in high melting point indium oxide (~1910 °C) nanotubes. Based on the experimental results, it was proposed that the indium vapors escape through nanoscale openings in the rocket structure similar to a conventional rocket nozzle resulting in a reaction thrust force. The thrust generated per unit mass by the synthetic rocket was estimated to be ~5000 N/kg which is an order of magnitude superior to conventional thermal solid rockets.

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1. Introduction

The bottom-up approach to the growth of one-dimensional semiconductor nanostructures including transparent conducting oxides has stimulated immense interest. Recent advancement in nanotechnology have produced fascinating devices such as mass sensors with atomic-resolution based on tubular nanostructures and nanotube based nanoradios [1–3]. Nanotubes filled with low melting point metals were also used to develop novel nanofluidic devices including a nanothermometer, nanorobot spot welding and frictionless mass transport [4–8]. The metal filled inside the nanotube core can easily be manipulated via electron beam irradiation, external heating or external electric field [49–12]. For example, indium filled silica nanotubes have shown unusual behavior such as coalescence, birth and explosion of low temperature indium inside the nanotubes due to local heating induced by electron beam irradiation [10]. The development of oxide based nanotubes is also attracting considerable attention within the scientific community. Specifically indium oxide (IO) nanotubes which provide high oxidation resistance, wide band gap (~3.7 eV), good electrical conductivity (~10³ Ω−1 cm−1), high transparency (~80%) in visible region and high temperature stability (≥1900 °C) are attractive for a variety of nanoelectronic, optoelectronic and nanofluidic devices [13–17].

Herein, we report an electron beam driven synthetic nano rocket propulsion effect in a low melting point indium metal filled in thermally stable IO nanotubes.

2. Experimental

The details of the IO core-shell tubular nanostructures synthesis and their growth mechanism have been discussed elsewhere [17]. In short, the mixture of IO and carbon (1:1) powder was used as a precursor. The mixture was placed in an alumina boat and inserted into the central heating zone of the furnace. The system was heated to 1000 °C at a rate of 20 °C/min and maintained at this temperature for 1 hour. Bare Si(100) collector substrates were placed downstream at a temperature of 960 °C. A reservoir (5–10 ml) of ethanol was placed in the low temperature region (~65 °C) in the upstream direction during the growth. Constant flow of Ar gas at the rate of 200 ml/min was maintained during the growth process. The ethanol induced growth of In filled IO nanotubes can be explain as follows:

**Step 1.** carbthermal reduction of indium oxide

\[ \text{In}_2O_3(s) + C(s) \xrightarrow{1000^\circ C} \text{In}_2O(v) + CO_2(v) \]

**Step 2.** further reduction of reaction species into an In rich ambient

\[ \text{In}_2O(v) + C_2H_5OH(v) \xrightarrow{1000^\circ C} CO_2(v) + 3H_2(v) + 2In(v) \]
In$_2$O$_3$ gets reduced to In$_x$O ($x = 1, 2$) due to the presence of carbon in step 1. These species further get reduced to In or In$_2$O, step 2, in the presence of ethanol and result in an In rich growth ambient by the chemical reactions given below and results the growth of In filled IO nanotubes [17]. The yellowish powder was observed on silicon substrate. High resolution transmission electron microscopy (HRTEM) (Tecnai G20-Stwin at 200 kV) equipped with energy dispersive X-ray (EDX) is used to characterize the indium filled IO tubular nanostructures. For TEM measurement, the nanostructures were transferred on a carbon coated copper grid. The tubular nanorocket like structures were observed via TEM and the measurement was performed with different electron beam current density ranging from ~29 mA/cm$^2$ to ~58 mA/cm$^2$ by changing the illumination area of the electron beam on copper grid.

3. Results and discussion

The indium-filled core inside the IO shell was confirmed by HRTEM and EDX as shown in Fig. 1(a)–(d). Fig. 1(a) shows a TEM micrograph of an IO tubular nanostructure. The inset in Fig. 1(a) shows HRTEM of the nanotube tip region. Fig. 1(b) shows the cross section HRTEM image of the IO nanotube and reveals the presence of a cavity at the center of the structure. The interplanar spacing of IO shell planes is measured to be 0.506 nm which corresponds to (200) plane of cubic IO. The growth of tubular nanostructures occur along <$100>$ direction. The compositional analysis of Indium (In) and Oxygen (O) along the radial direction was determined using scanning transmission electron microscopy (STEM)-EDX as shown in Fig. 1(c) along with EDX spectra imposed on the structure. The result confirms the tubular nature (In metal encapsulated by IO shell) of the IO nanostructures. The spot EDX at the center of the tubular structure (Fig. 1(d)) further confirms that the IO nanotube is filled with In metal.

Fig. 1 (a–e) shows a schematic and TEM micrograph of a typical In-filled IO tubular nanostructure connected one end with a nanorocket like In-filled IO nanostucture and having the other end fixed. The mass of the nanorocket structure is roughly estimated of about 600 fg by measuring the physical dimension of nanorocket (1000 nm x 800 nm x 100 nm) and multiplied by density of the indium metal. The nanorocket connected with IO nanotube string forms a pendulum-like geometry and provides an elegant ultrasensitive force balance, since the bending deformation of the pendulum arm enables the estimation of the thrust force generated by the nanorocket. Such pendulum like structures may be the result of branched growth of IO nanostructures which have been reported earlier in the literature [18]. The mechanism for motion of tubular IO rocket like structure is proposed based on the electron beam induced melting and evaporation of In metal within the IO nanotube core and nanorocket structure. The In metal can be selectively melted because its melting point (~156 °C) is significantly lower than the encapsulating IO nanotube (~1910 °C). Note that electron beam irradiation elevates both temperature and pressure and a complex phase of In liquid...
and In vapor may co-exist within the IO nanotube and nanorocket structure. The In filled IO nanorocket geometry therefore acts as a miniaturized pressure vessel and when heated by electron beam irradiation under the high vacuum (~10^{-8} Torr) of TEM, the indium vapor pressure inside the IO rocket like structure will increase along with the release of gases (specifically hydrogen as mentioned in step 2 of the growth) dissolved in the liquid In during growth [19–20]. These pressurized gases can escape via openings/defects in the nanorocket structure similar to a rocket nozzle resulting in a reaction force (thrust) on the structure in the opposite direction, as shown in Fig. 2(b), (c–e). Note that the effect we report does not require the nanorocket to form a pendulum like structure. Even isolated In-filled IO tubular nanostructures were observed to move on the TEM grid on the application of similar electron beam current density under TEM imaging.

The charge accumulation-induced bending of carbon nanotubes and Si$_2$N$_3$ nanostructures has also been reported in the literature [21,22], in our case the IO nanostructures are situated on an electrically conducting carbon coated copper grid and hence the possibility of charge accumulation is ruled out. Fig. 2(a)–(b) shows the schematic

![Schematic and TEM images showing the rocket propulsion effect in In-filled IO nanostructure. (a) An In-filled IO nanotube structure, a string, is suspended at the end of an IO connecting arm. The other end of nanotube is connected with In-filled nanorocket like structure forming a pendulum-like geometry. (b) As the electron beam current density J is increased the nanorocket connected with In-filled IO nanotube deflected from \( \theta \) to \( \theta + \Delta \theta \). (c–e) TEM images of pendulum structure at different electron current density. The pendulum structure is propelled in an arc normal to the pendulum arm beyond electron current density of ~29 mA cm$^{-2}$. The corresponding TEM images at the mentioned electron beam current density are shown in (c), (d) and (e), respectively. Scale bar is 2 \( \mu \)m.](image)

![Fig. 3. (a) Deflection angle vs. electron beam current density. The first point in the graphs reveals the stationary state of the structure. (b) The deflection force (i.e. rocket thrust) is plotted as a function of the electron beam current density. The error bars in deflection force and deflection angle contain the measurement error in deflection of the structure and corresponding angle, error in electron beam illumination area and initial electron beam density calculation.](image)
of nanorocket propulsion effect. As the electron beam current density \(J\) is increased above the normal imaging value of 29 mA/cm\(^2\), the nanorocket is set in motion in a direction tangential to the nanopendulum arm as shown in Fig. 2(c)–(e). The nanorocket structure is opposed by the bending of the connecting arm of the pendulum. The force \(T\) required in deflecting the arm of the pendulum can be expressed in terms of the experimentally observed value \(\Delta x\) as \([24]\):

\[
T = \dot{m} v_c + (P_e - P_o)A_e
\]

(1)

where \(\dot{m}, v_c, P_e, A_e\) and \(P_o\) are the rate of change of mass, exit velocity of the jet, exit pressure, throat exit area and free steam pressure respectively. In the present case, increase in \(J\) from 29 to 58 mA/cm\(^2\) produces larger quantity of In vapors per unit time, thereby increasing \(\dot{m}, v_c, P_e, A_e\) and \(P_o\) which increases the amount of thrust \(T\). This thrust force on the nanorocket structure is opposed by the bending of the connecting arm of the pendulum. The force \(T\) required in deflecting the arm of the pendulum can be expressed in terms of the experimentally observed value \(\Delta x\) as \([24]\):

\[
T = K \times \Delta x, \quad k = \frac{3EI}{L^3}
\]

(2)

where \(K\) is the effective spring constant of the IO string that comprises the connecting arm of the pendulum, \(E, I\) and \(L\) are the Young’s modulus, second moment of inertia and length of the IO connecting arm, respectively. The spring constant \(K\) of the connecting IO string is estimated as \(1.53 \times 10^{-3}\) N/m by putting the value \(L = 5.59\) μm, \(I = 1.0510^{-36}\) m\(^4\) and \(E = 116\) GPa \([25]\). The thrust force generated by the nanorocket is plotted in Fig. 3(b) for different values of \(J\) while Fig. 3(a) quantifies the dependency of the deflection angle on \(J\). It is interesting to notice that the effect is reversible, i.e. by decreasing the value of \(J\), the nanorocket returns to the lower deflection angles. A real time video showing the motion of indium-metal filled IO rocket-like nanostructure by varying the electron beam current density is shown in the Supplementary information.

4. Conclusions

In summary, we have demonstrated for the first time rocket-like propulsion effect at nanoscale in IO nanotubes that encapsulate In metal in its core. Electron beam irradiation selectively vaporizes the In metal, with In vapors acting as the propellant. The thrust produced per unit mass of the nanorocket at electron beam intensity of 58 mA/cm\(^2\) is calculated to be \(\sim 5 \times 10^3\) N/kg which is an order of magnitude superior to conventional solid rockets \([23]\). These metal-filled nanostructures may find applications in thermally driven motion nanomechanics.

References