Clean superconducting In nanowires encapsulated within insulating ZnS nanotubes

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We have synthesized indium (In) nanowires in pure form and large scale, encapsulated within insulating ZnS nanotubes, and examined the intrinsic superconductivity in one-dimensional limit. We demonstrate that the property of the superconducting nanowires encapsulated within insulating nanotubes can be controlled down to diameters much smaller than the characteristic lengths. The critical temperature and critical magnetic field of the one-dimensional In nanowires are not affected down to a diameter of 40 nm, almost 10% of the coherence length of bulk In. This study further suggests that superconducting interconnects, with controlled physical properties, in nanocircuits could be achieved by such encapsulation. © 2009 American Institute of Physics.

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Superconductivity in low-dimensional systems is an outstanding issue from both fundamental and application points of view. Particularly, after application of superconducting nanowires have been demonstrated1 in building high precision bolometers possessing the ability to detect a single photon, the necessity to synthesize one-dimensional superconducting structures in the purest form has grown rapidly. The superconducting nanowires, if the diameter is less than the characteristic length scales, namely, the coherence length (\(\xi\)) and the magnetic penetration depth (\(\lambda\)), had shown dramatically different properties from the bulk.2–5 Such a difference was attributed to (i) the dimensional confinement, (ii) the enhanced contribution from the surface that is in proximity to the natural contaminations, and (iii) the role of grain boundaries and defects when the wires are not single crystalline. Depending on the strength of such effects, the superconducting properties of the nanowires are seen to vary uncontrollably. In nanowires of type I superconductors such as Al, Sn, and Pb, though the \(T_c\) has been seen to remain equal to the bulk value or increase slightly, the critical field enhancements by several orders of magnitude.2–5 Such observation and attribution have existed for varieties of superconductors. However, hitherto a conclusive experiment on clean crystalline samples has been lacking. One promising way to achieve superconducting nanowires in the clean limit is to encapsulate them within insulating nanotubes. Encapsulation of superconducting nanowires within carbon nanotubes was done in the past.6,7 However, gaining control over the electronic properties of carbon nanotube itself is an unattained goal. The reverse proximity effect from the carbon nanotube might further complicate the properties of the encapsulated superconducting nanowire. In Ref. 6, the superconducting tin nanowires encapsulated within carbon nanotubes show considerably enhanced critical field. This enhanced critical field can be attributed to the possible existence of magnetic impurities in the nanotubes grown using magnetic catalysts. In fact, in the same report, at high magnetic fields the tin nanowires showed positive moment indicating existence of magnetic impurities in the system. In this paper we demonstrate that the fundamental property of the superconducting nanowires can be preserved down to a very low diameter compared to the characteristic length scales of the superconductor by encapsulation within insulating nanotubes.

The synthesis of indium (In) nanowires within ZnS nanotubes was carried out in a high temperature vertical induction furnace. The furnace consists of a graphite cylinder inside a quartz tube, which is attached to a gas passing arrangement. The quartz cylinder is surrounded by a copper coil for generating induction current in the graphite cylinder. In a typical synthesis, the ingredients (0.10 g of InS3, 0.25 g of ZnS, and 0.05 g of activated carbon) were thoroughly mixed, put onto a graphite crucible, and placed inside the graphite cylinder. To provide an inert ambience for the reaction, the furnace was evacuated to \(10^{-5}\) Pa and then filled with 99.99% Argon. The reaction was carried out at a temperature of 1300 °C for 45 min while simultaneously maintaining Ar carrier gas flowing at a rate of 0.2 l/min. The details of the nanowires growth including the growth mechanism have been discussed elsewhere.8

The samples were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), x-ray diffraction (XRD), and energy dispersive x-ray spectroscopy (EDS). Figure 1(a) shows the SEM image of the as-synthesized product of In nanowires encapsulated in ZnS nanotubes. The typical length of a nanotube is found to be a few micrometers, and their diameter varies between 200 and 300 nm. SEM investigation further indicated the absence of any clusters of In and other materials. Figure 1(b) shows a low magnification TEM image of a single nanostructure. De-
tailed investigations revealed that these are core-shell structures where In nanowires constitute the core while ZnS forms the shell nanotubes. The diameter of In nanowires varied between 40 and 50 nm, which is almost 10% of the coherence length (364 nm) of bulk In. This confirms that the In nanowires are truly one-dimensional. The shell nanotube thickness is of the order of 75–100 nm.

The high temperature fabrication procedure of the nanowires (where it remains in the molten state and then slowly cooled down at 5 °C/h) helps the nanowires to exist in single crystalline form inside the ZnS nanotubes. The selected area electron diffraction (SAED) pattern obtained from an encapsulated nanowire is shown in the inset of Fig. 1(b).

The purity of the nanowires was checked by XRD on the as-synthesized sample. An XRD spectrum of the material is presented in Fig. 1(c). The pattern reveals a biphasic mixture of wurtzite ZnS [a=3.82 Å and c=6.25 Å (Ref. 9)] and tetragonal In [a=3.25 Å and c=4.95 Å (Ref. 10)] and are marked by red and blue dots, respectively, in the figure. We did not observe any additional peak indicating a presence of impurity.

The composition of the samples is further elucidated by the energy dispersive x-ray analysis of the heterostructures. Figure 2(a) shows a bright field TEM image of two nanostructures dispersed on a TEM grid. The corresponding elemental maps are displayed in Figs. 2(b)–2(d). As seen, the Zn K-edge and the S K-edge signals are evenly distributed throughout the shell structure with a depleting signal at the core, while there is strong In L-edge signal in the central region. These confirm that In constitutes the core nanowire, while ZnS forms the shell.

The magnetization measurements were performed in a superconducting quantum interference device magnetometer. 30 mg of the sample containing bundles of the encapsulated In nanowires was used for this measurement. The diamagnetic transition at $T_c=3.4$ K is clearly observed in the magnetization versus temperature ($M$--$T$) data in Fig. 3(a) acquired at 10 G. The $T_c$ is very close to the reported value (3.41 K) for bulk In. There is a broadening observed near the transition, which was observed in the past and was attributed to the effect of one-dimensional shapes of the material. In fact, the broadening suggests the existence of enhanced quantum fluctuations in the one-dimensional wires. To estimate the contribution of such fluctuations, however, the transport property of the nanowires should be investigated carefully. Also, this broadening might arise from the natural distribution in the nanowire diameter.

Figure 3(b) shows the magnetization versus external field ($M$--$H$) curves at different temperatures. The corresponding $H$--$T$ phase diagram is presented in Fig. 4. The red line in Fig. 4 is the behavior predicted within the Bardeen-Cooper-Schrieffer (BCS) theory and follows the relation $H_c(T)=H_{c0}(1-(T/T_c)^2)$, where, $H_{c0}$ is the critical field at zero temperature and $H_c(T)$ is the temperature dependent critical field of the superconductor. The critical field ($H_c$) at the low-
est measurement temperature (2 K) is found to be 270 Oe, which is nearly equal to the critical field (282 Oe) of pure bulk In. Further, the general shape of the $M$-$H$ curves, i.e., the sharpness of the curve close to $H_c$ indicates that the superconductor might be of type I. However, there is a hysteresis observed in the $M$-$H$ curves. In the past such hysteresis was observed\textsuperscript{14} in type I superconductors where it was attributed to the effect of impurities, grain boundaries, dislocations, and edge barriers. Since the In nanowires in the present case are trapped inside ZnS nanotubes, impurities arising from surface oxidation of the superconductors are eliminated, and the single crystallinity of the nanowires excludes the role of grain boundaries. The hysteresis might also be expected to arise due to the finite dimensionality of the type I superconductor where the intermediate state\textsuperscript{15} of the superconductor is expected to contribute strongly or form the surface superconductivity.\textsuperscript{16} Recently it has been proposed that in a quasi-one-dimensional superconducting wire, such hysteresis might appear due to splitting of the band of single electron states in a series of subbands.\textsuperscript{17} Detail discussion about the hysteresis in the light of the proposed theory is beyond the scope of this paper.

The coherence length of the nanowires was calculated following the relation\textsuperscript{18} $H_c(T) = \phi_0/2\pi\xi^2(T)$, where $\phi_0$ is the flux quantum. To examine if the superconducting nanowires still behave as type I superconductors in the confined state, we calculated the Ginzburg–Landau parameter $\kappa$, which is given by $\kappa = \lambda/\xi$. The critical value of this parameter is $1/\sqrt{2} = 0.707$, below which the superconductor behaves as type I and as type II otherwise. Since there is no report available on the penetration depth of In nanowires, we tried to get an approximate estimate of the same from the existing reports on thin films and nanoparticles of In. The penetration depth of a thin In film (of ~100 nm thickness) was reported\textsuperscript{19} to be 39 nm at absolute zero. This value is much larger than the bulk penetration depth (25 nm as determined by ultrasonic attenuation measurements\textsuperscript{20}) and the penetration depth reported for In nanoparticles (3.3 nm).\textsuperscript{21} Therefore, since our nanowires are clean, it would be rational to expect that the penetration depth of the nanowires would be in between these two values, and we may consider 39 nm as the upper limit of the penetration depth for the In nanowires.\textsuperscript{22,23} Taking the corresponding $\xi$ to be 89 nm at absolute zero, as obtained from the BCS analysis of our data, the upper limit of the $\kappa$ value for the encapsulated nanowires is found to be 0.438, which is much below the critical value. Hence, unlike almost all previous reports, the superconducting In nanowires encapsulated within insulating ZnS nanotubes are showing type I superconductivity.

In conclusion, we have been able to synthesize In nanowires encapsulated in ZnS nanotubes. From the magnetization measurements on these nanowires, it is observed that the pure and single crystalline nanowires almost retain the superconducting properties of the bulk. This observation further indicates that in future nanoscale electronic circuitry, to use superconducting interconnects, the superconductors might be encapsulated by insulating nanotubes to gain fine control of their properties.

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\textsuperscript{22} In fact, keeping in mind that the critical magnetic field of the In nanowires is not much different from the bulk value, the penetration depth should not be so large. The relation between the enhanced critical field in thin superconducting cylinders with the effective penetration depth is given by $h = \lambda_0/d$, where $h$ is the factor by which the critical field is enhanced in the cylinder, $\lambda_0$ is the effective penetration depth, and $d$ is the diameter of the cylinder (for more details see Ref. 18). This relation predicts an effective penetration depth of 7.4 nm only in this case.