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Device for rapid sample insertion and extraction in thermal chemical vapor deposition tube furnace

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In this article, a simple and inexpensive device to allow the rapid insertion and withdrawal of samples from a tube furnace is described. The device operates in an atmosphere that is separate from ambient. This device shortens sample insertion and extraction times, which allows the study of the short time kinetics of chemical vapor deposition processes, and may allow for the growth of structures that could not be achieved using the conventional sample insertion and extraction procedure. The use of magnets to provide actuation through the walls of a quartz tube furnace is entirely general to any procedure using a tube furnace.

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We have designed, built, and used a rapid sample insertion and withdrawal device in a thermal chemical vapor deposition (CVD) system. This device has been used with a Lindberg/Blue three-zone furnace equipped with a 1 in. diameter, and 66 in. long quartz tube (Quartz Scientific, No. 385T022CC66), which houses the sample insertion/extraction device; schematic, Fig. 1. Note the endcaps and gaskets that provide a separate nonambient atmosphere, in which rapid sample insertion and retraction occur. This device, shown schematically in Fig. 2, is made of a 0.5 in. outer diameter (o.d.) 16 in. long quartz tube that has been fused on one end to a rectangular plate of quartz attached at its end to a magnet. Note that the quartz tube is not closed off, in order to prevent gases from being trapped within it. The substrate holder is $3/8$ in. wide × 5 in. long × $1/16$ in. thick; it has a pattern of raised quartz "dots" that hold 1 cm square substrates in place during the insertion and removal procedure. On the other end of the tube is a $3/4$ in. diameter × $1/2$ in. thick cylindrical samarium cobalt magnet (Edmund Scientific, No. 30309-62) that has been fixed in place using high-temperature epoxy (McMaster-Carr, No. 7563A24) to which two more identical magnets are fastened (as shown in Fig. 3). The device resides inside the furnace tube and is manipulated from outside using a plastic coated ring-shaped cylindrical magnet (Edmund Scientific, strontium ferrite, No. 3037621). We chose to use samarium cobalt magnets due to the high temperatures this material can withstand before demagnetization. The magnet components with the high-temperature epoxy cost ∼\$130. The nominal price to get a glass blower to fuse your substrate holder of choice to a squared off quartz tube is ∼\$100. The 66 in. furnace tube is ∼\$75. The total cost of this device is ∼\$300; we mention this to emphasize that it is an inexpensive approach to achieving rapid insertion/extraction of samples in thermal CVD.

The insertion procedure is simple. First, the operator places the substrate on the substrate holder and gently inserts the insertion/retraction device into the furnace tube as shown in Fig. 4(a). The larger plastic-covered ring magnet is then placed on the index finger (like a ring) of the opposite hand. The operator slowly approaches the back of the insertion/retraction device with his ring-bearing index finger while making sure that the magnets are attracted to each other (if the magnets repel, then the plastic coated ring magnet is oriented incorrectly; flip it over). Figure 4(b) shows the contact of the tip of the index finger to the back of the cylindrical samarium cobalt magnet. Smoothly insert your index finger into the furnace tube as demonstrated in Fig. 4(c). The free hand that placed the insertion/retraction device into the furnace is now used to slide the ring magnet over the quartz furnace tube. The ring magnet may now be used to actuate the insertion/retraction device within the quartz tube by sliding the ring magnet along the quartz tube as shown in its final position in Fig. 4(b). The quick connect end cap is then placed upon the end of the quartz furnace tube that houses the rapid insertion and retraction device. The device may now be actuated and motion induced in a sealed tube with an atmosphere that is separate from ambient. For the smoothest actuation, the top of orifice of the ring magnet should be kept in contact with the top of the furnace tube [arrow, Fig. 4(c)]. Insertion velocities are typically 8–10 cm/s, which results in an insertion or withdrawal time of ∼5 s. This device thus allows for relatively rapid insertion and extraction of a sample with respect to the hot zone of the furnace, and can be contrasted with the alternative of moving the furnace back and forth along the tube on rails.[1] The latter method still exposes the sample to either a ramp-down time (for example, to return to room temperature), or a ramp-up time, that depends on the thermal inertia of the tube being used.

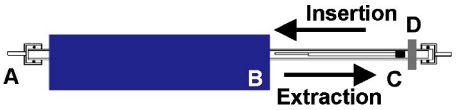

FIG. 1. (Color online) Schematic of: (A) 5.5 ft quartz tube (inner diameter: 22 mm o.d.: 25.8). Note endcaps and gaskets providing separate nonambient atmosphere. (B) Lindberg/Blue furnace box. (C) Rapid sample insertion and withdrawal apparatus. (D) Plastic coated ferrite ring magnet.

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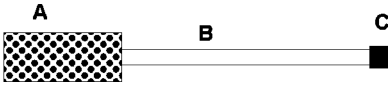

FIG. 2. Schematic of: Substrate holder and insertion/extraction device, top view/detail; (A) 3/8 in. wide by 5 in. long piece by 1/16 in. thick quartz decorated with quartz dots. (B) 16 in. long, 0.5 in. o.d. quartz tube. (C) Three 3/4 in. diameter, 1/2 in. thick cylindrical samarium cobalt magnets.

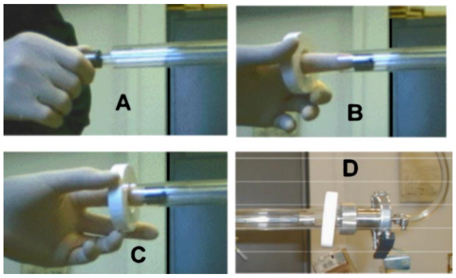

FIG. 4. (Color online) (a) Inserting the insertion/withdrawal device into the furnace tube. (b) Approaching the back of the rare-earth magnets with the ring magnet. (c) Placing the ring magnet outside the furnace tube to allow actuation (Note: contact between top of opening in the ring magnet and tip of tube furnace.) (d) The insertion/withdrawal device ready for use. Note that the device is completely enclosed prior to sample insertion.

Another commonly used sample loading device is known as an elephant. The elephant is a quartz tube that is approximately the same diameter as the furnace tube and has a d-shaped handle on the top of the cylinder. A quartz boat that holds wafer pieces rests inside the elephant. An elephant is typically used by positioning the opening of the elephant next to the opening of the furnace tube and pushing the boat into the furnace tube with a quartz rod. The insertion of the samples using the elephant differs from both the tube insertion method and the use of the rapid sample insertion and extraction device in that it breaks the atmosphere of the furnace (by removing an endcap). This procedure requires dumping the atmosphere of the furnace. With the elephant you can load samples rapidly, but not into a controlled atmosphere; i.e., an environment where chemical reactions will take place. Whereas, our device allows one to setup ready-to-do CVD, and then one may rapidly insert samples into a controlled atmosphere that is separate from that of the room. The rapid sample insertion device allows insertion, reaction, withdrawal, and cooling to all occur in an atmosphere that is separate from ambient. Elephant insertion cannot occur with a closed up tube that will allow insertion into the furnace in an atmosphere that is separate from ambient. The elephant necessitates breaching the integrity of the tube, inserting the tube, closing the tube, flushing the tube, flowing the reacting gases, and then breaching the tube to remove the samples from the hot zone of the furnace. A comparison between the rapid sample insertion and withdrawal device, and tube insertion will follow. The method of tube insertion is the most similar to the use of the rapid sample insertion device as both may be performed with a separate nonambient atmosphere.

The temperature versus time behavior of a 1 cm square piece of silicon wafer was measured by using a type-K thermocouple that was connected to an Agilent 34401A digital voltmeter interfaced to a computer via a general purpose interface bus interface. The substrate used for these experiments, and during the course of our thermal CVD experiments, is p-type silicon with a thickness of 475–525 μm with a 1 μm thick thermal oxide layer. A digital image of the thermocouple attached to the substrate holder using tungsten wire is shown in Fig. 5. Voltage and time data were gathered and are shown in a plot in Fig. 6. The substrate reaches a temperature of 860 °C after 66.5 s, which is the temperature at which we introduce the carbon precursor (e.g., methane) to initiate growth of single-walled carbon nanotubes (SWCNTs) while the furnace is ramping up to 900 °C. Thus, a little after 1 min, the substrate is at an appropriate temperature to grow SWCNTs. For the sake of comparison with our device, the time for sliding the tube into the furnace to arrive at the same temperature of 860 °C took 105 s. Note that the insertion device reaches synthesis temperatures almost twice as rapidly as sliding the furnace tube.

The most obvious advantage of this magnetic insertion device is that the amount of time required to perform a synthesis experiment is greatly reduced. CVD is a common technique that is used to synthesize SWCNTs and a variety of other materials. Tube furnaces typically have a large thermal inertia, which causes them to take several hours to cool to room temperature after having been heated to a temperature on the order of 800–900 °C. We compare, for our particular runs in synthesizing SWCNTs, the more standard insertion procedure without the magnetic insertion/extraction device, to that with use of the insertion device. Without the device, the steps are: (a) Insertion of a substrate into our furnace tube requires a few minutes. (b) A ramp from room temperature to 800 °C takes ~15 min. (c) A calcination step used in our experiments on SWCNT growth requires dwelling at this temperature for 5 min in air to drive off any residual organic material that may be present on the catalytic nanoparticles. (d) A further ramp to 900 °C takes 3 min. (e) A typical growth step involves maintaining this temperature for 10–15 min. (f) Cool down of the furnace from 900 °C to

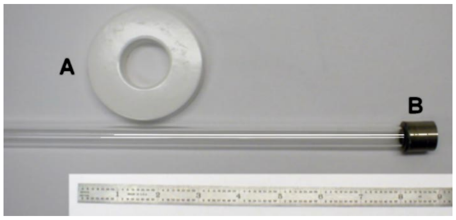

FIG. 3. Digital photo of: (A) plastic coated ferrite ring magnet, and (B) three 3/4 in. diameter, 1/2 in. thick cylindrical samarium cobalt magnets. The first is epoxied to the 0.5 in. diameter quartz transfer rod, and the other two magnets are stuck together by the magnetic force.

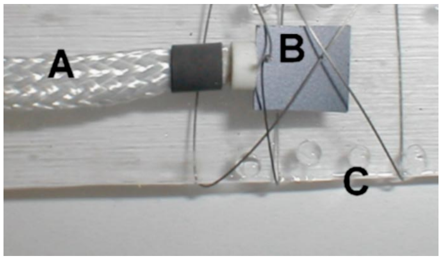

FIG. 5. (Color online) Digital photo of: (A) K-type thermocouple used to measure time to temperature of substrate, (B) 1 cm square of silicon wafer, and (C) tungsten wire used to maintain contact between thermocouple and silicon sample.

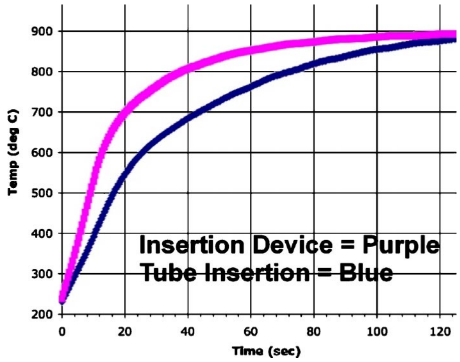

FIG. 6. (Color online) Plot of time in seconds vs temperature in degrees centigrade, which shows the time from 230 °C (temp in-tube preinsertion) to 900 °C (SWCNT synthesis temperature) for the silicon sample. Note that the time to reach 860 °C (the temperature at which growth is initiated by introducing methane into the chamber) is 66.5 s for the insertion device, and 105 s for the alternative approach of sliding the tube into the furnace.

room temperature takes ∼4 h. The steps preceding the cooling take ∼45 min. So, for this particular procedure for growing SWCNTs, the insertion and extraction device saves ∼3.5 h. An additional benefit is that one can extract the sample and holder to the part of the quartz tube that is outside the hot zone of the furnace, where it will relatively rapidly cool to room temperature. This allows one to not have to depress the furnace temperature while switching substrates, which saves one the ramping up time between experiments.

Besides increasing productivity, there are several other advantages, such as the exposure time of the metal catalyst particles to high temperature. Transition metal particles are typically used to catalyze the growth of SWCNTs. We have been using iron nanoparticles that are deposited on a silicon wafer having a 500 nm thick oxide.[2] At elevated temperatures (900–1100 °C) iron diffuses readily into silicon dioxide.[3] Exposure of small preformed metal particles to elevated temperatures for long time periods can also lead to a change in their size and spatial distribution due to surface diffusion and sintering. Because catalyst particle size has been shown to be proportional to SWCNT diameter,[4–6] minimizing changes in the catalyst particle morphology should give greater control over SWCNT diameter. It has recently been shown that rapid heating can grow particularly long (mm-scale) and well-aligned SWCNTs.[7] We suggest that a rapid insertion and extraction system will be useful for achieving certain types of growth that would otherwise not be achieved (due to long ramp-up and ramp-down exposures), and for studying the kinetics of growth processes. We draw analogy to the “temperature jump” experiments pioneered by Eigen.[8,9]

Automation and computer control of the insertion/extraction device are expected to be straightforward.

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[1] O. Toader (personal communication).
[2] H. C. Choi, S. Knudaria, D. Wang, A. Javey, Q. Wang, M. Rolandi, and H. Dai, Nano Lett. **3**, 2 (2003).
[3] D. A. Ramappa and W. B. Worth, J. Electrochem. Soc. **146**, 10 (1999).
[4] Y. Li, W. Kim, Y. Zhang, M. Rolandi, D. Wang, and H Dai, J. Phys. Chem. B **105**, 11424 (2001).
[5] C. L. Cheung, A. Kurtz, H. Park, and C. M. Lieber, J. Phys. Chem. B **106**, 2429 (2002).
[6] H. Dai, J. Kong, C. Zhou, N. Franklin, T. Tombler, A. Cassell, S. Fan, and M. Chapline, J. Phys. Chem. B **103**, 11246 (1999).
[7] L. An, J. M. Owens, L. E. McNeil, and J. Liu, J. Am. Chem. Soc. **124**, 46 (2002).
[8] M. Eigen and G. G. Hammes, J. Am. Chem. Soc. **83**, 2786 (1961).
[9] M. Eigen and G. G. Hammes, J. Am. Chem. Soc. **82**, 5951 (1961).