# Manganese Doping of Germanium Nanowires Seeded from Gold Nanocrystals


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**Abstract:**

Reports of ferromagnetism in the semiconductor $Mn_XGe_{1-x}$ motivated the exploration of Mn doping of Ge nanowires grown by colloidal methods. The combination of semiconducting properties with ferromagnetism in these nanostructures would provide an ideal experimental system for fundamental studies of spin-dependent electron transport as well as a potential "building block" for new technological opportunities in information storage and computing.

The Ge nanowires were synthesized using the supercritical fluid-liquid-solid (SFLS) approach, in which Ge nanowire growth via thermal degradation of an organogermane precursor is seeded by alkanethiol-capped Au seed nanocrystals. Following nanowire synthesis, the nanowires were exposed to an Mn source, such as an organomanganese precursor, in the supercritical reactor. After Mn exposure, the Ge nanowires were characterized using HRSEM and TEM, EELS and EDS to determine the doping level in the nanowires.


**Introduction:**

The development of semiconductor nanowires has stemmed much research into the future miniaturization of electronic devices through higher device density [1]. Moreover, a new dimension has been added into these studies by the possibility of doping semiconductor nanowires with magnetic impurity atoms to yield ferromagnetism. At the bulk scale, successful synthesis of Mn doped Ge demonstrating ferromagnetism has already been reported [2, 3].

Synthesis of magnetic semiconductors nanowires would further benefit fundamental studies of their magnetic properties and point toward future applications in spin-dependent semiconductor technologies.

This paper reports attempts at the controlled synthesis of $Mn_XGe_{1-x}$. $(Cp^*)_2Mn$ (manganocene) was used as the Mn source and reacted with Ge nanowires under different reaction parameters. Using this approach, only trace amounts of Mn:Ge doping were achieved.

**Procedure:**

Ge nanowires were synthesized by Au nanocrystal-seeded growth in supercritical solvent, in a SFLS process developed at the University of Texas by Hanrath et al. [4].

The reaction injection precursor was prepared under inert atmosphere and consisted of 30 µl of 0.1M diphenylgermane (DPG, $(C_6H_5)_2H_2Ge$, Gelest, 95%) and 21 µl of size mono-disperse alkanethiol-coated Au nanocrystals (Ge:Au ratio 1000:1) in 2 ml hexane solvent. A second solution of 56 mg of Cp*Mn dispersed in 2 ml hexane served as the Mn precursor for doping (Ge:Mn ratio 500:1).

A flow-through reactor was created using a 1 ml titanium reactor cell connected to high-pressure tubing via LM-6 HIP reducers (High-Pressure Equipment Co.). A 4 x 10 mm silicon wafer was placed inside the titanium cell. The reactor cell and tubing was connected to a high-pressure liquid chromatography (HPLC) pump (Alcott) and enclosed in insulation and a heating block. A digital pressure gauge (Sensotech) monitored system pressure. Oxygen was purged by flowing deoxygenated, anhydrous hexane through the system several times. The system was heated to 385ºC, and system pressure ramped to 500 psi by increasing hexane flow.

After rinsing the injection loop with hexane, the injection solution was loaded into a 350 µl sample loop and delivered at a pressure of 1200 psi. The reaction was allowed to run approximately 10 minutes while the system cooled and pressure decreased. The loop was again rinsed with hexane, and the Mn precursor solution was then injected and delivered by repressurizing to 1200 psi.

The reactor was cooled and depressurized by ejecting the excess liquid reaction mixture. The sample was then rinsed with more hexane at a low flow rate to minimize impurities.

Nanowires were characterized by high-resolution scanning electron microscopy (HR-SEM, LEO 1530 at 10kV). High-resolution Transmission Electron Microscopy (HRTEM) samples were prepared by drop-casting a dilute solution of nanowires in hexane on carbon-coated 200 mesh Cu grids (Electron Microscope Sciences).

**Results and Conclusions:**

HRSEM images showed that the reaction product consisted of a dense mesh of long tangled nanowires (Figure 1). TEM images also revealed that nanowires were relatively clean and free of crystalline defects (Figure 2). The average nanowire diameter was ~ 20 nm and reached lengths of tens of micrometers. Although Ge nanowire growth was abundant, EDS revealed very little Mn present in nanowires. Mn doping was not effective using the approach of post-synthesis exposure and annealing in the presence of an organomanganese precursor. We speculate that the low, or in some cases nonexistent, doping results from poor Mn diffusivity from the nanowire surface into the nanowire core. The addition of the organo-manganese precursor during the nanowire synthesis may provide one route to effective Mn doping.

Preliminary results from Hanrath et al. have shown promise with substantial doping. The anticipated challenges with this method relate to the competitive decomposition of the Ge and Mn precursors with dissolution in the Au seed particles, which potentially could quench nanowire formation altogether.

In conclusion, Mn doping of Ge nanowires is anticipated to be possible based on previous research of bulk semiconductors, however, appropriate reaction conditions and doping strategy must be developed to achieve these goals. It appears that post-synthesis exposure of the nanowires to the dopant—at least in the solution-phase—and subsequent annealing may not prove to be an effective method.

**Future Work:**

Future efforts will focus on increasing the amount of Mn doping. With substantial doping, the Ge nanowires will then be used for fundamental studies of magnetism in nanowires. Magnetic properties may be measured using a superconducting quantum interference device (SQUID).

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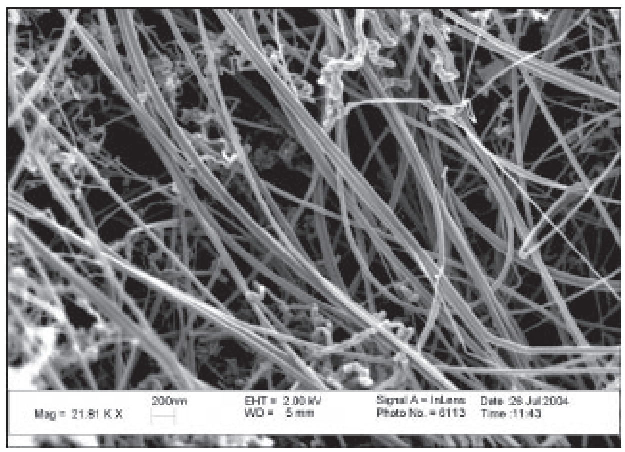


*Figure 1, above: SEM image of Ge nanowire.*

*Figure 2, below: TEM image of Ge nanowire.*