Solution Phase Thermal Annealing Studies on the Activation Barrier to Ferromagnetism in Nanocrystalline Diluted Magnetic Semiconductor $Co^{2+}TiO_2$

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Abstract:

The paramagnetic to ferromagnetic transition occurring in the diluted magnetic semiconductor $Co^{2+}:TiO_2$ when processed from colloidal nanocrystals into nanocrystalline thin film at high temperatures, suggests a thermal activation barrier to ferromagnetism. Recent studies indicate cobalt migration within or even out of the titania host lattice during thermal treatment plays a pivotal role in ferromagnetic activation.

We report high temperature solution-phase annealing studies of colloidal $Co^{2+}:TiO_2$ nanorods and the effect on ferromagnetism. No Co^{2+} migration or increase in ferromagnetism was observed. A decrease in the paramagnetic moment with increasing annealing temperature was observed.

Introduction:

Diluted magnetic semiconductors (DMS) are envisioned as vital components of many spin-based semiconductor devices. If successfully produced, such devices may offer lower power consumption and greater operating speeds than conventional charge-based devices.

Recently, a novel wet-chemical approach has proven successful in yielding high quality colloidal suspensions of Co^{2+} doped Titania ($Co^{2+}:TiO_2$) nanocrystals [1]. Powders isolated from colloidal suspensions are weakly ferromagnetic when aggregated at room temperature, but thin films prepared from the colloids show strong room temperature ferromagnetism when spin coated at 350°C.

Several mechanisms are proposed to explain the ferromagnetic activation including: (1) aggregation or sintering of the nanocrystals increases the stability of the ferromagnetic domain against magnetization reversal [2] facilitating the proposed free-carrier-mediated magnetic ordering; and (2) an O^{2-} vacancy and/or a Co^{2+} dopant ion migration to a ferromagnetically active site. Because the Co^{2+} has a significantly smaller atomic radius than Ti^{4+} as well as charge mismatch, migration within and even expulsion from the lattice is likely. Cobalt migration has also been reported to activate ferromagnetism in thin films made by oxygen plasma assisted molecular beam epitaxy (MBE) (Chambers, S. A., et al, 2001).

If we are to study migration activated ferromagnetism, activation by aggregation must be eliminated. This is achieved by suspending the colloids in a high boiling coordinating solvent allowing temperature near that of the film preparation to be reached while retaining their isolated colloidal character.
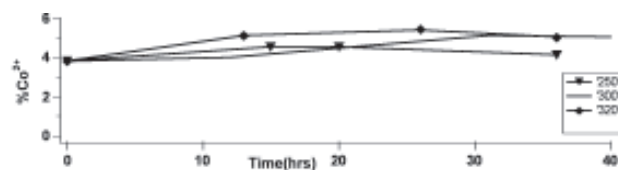

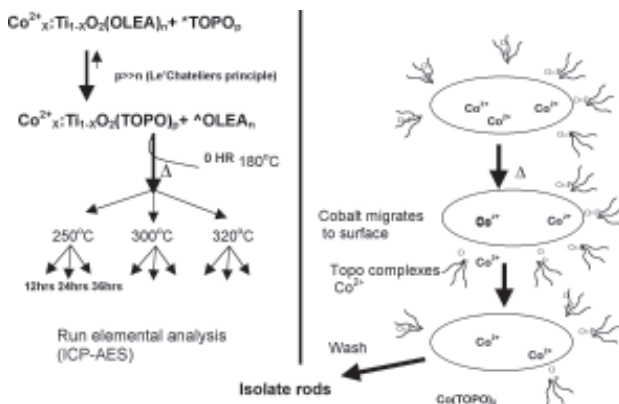*Figure 2: Mol fraction of Co^{2+} in TiO_2 versus time at various annealing temperatures.*

Methods:

A) Rod Synthesis: $Co^{2+}:TiO_2$ nanorods were synthesized by adapting a preparatory method for undoped TiO_2 nanorods [3] and will be reported elsewhere [4].

B) Annealing Studies: Five 1 ml aliquots of the colloidal $Co^{2+}:TiO_2$ nanorod/toluene solution were pipetted, precipitated with 2 ml of ethanol and separated by centrifugation. Two grams of trioctylphosphine oxide (TOPO) were added and the mixture was heated under nitrogen for 2 hours at 180°C. We will refer to this step as the ligand-exchange reaction (Figure 1a). The ligand-exchanged samples were then placed in a sand bath at a constant annealing temperature (250°C, 300°C, and 320°C). An aliquot was removed from the reaction every twelve hours (Figure 1a) providing a time profile of the annealing

Figure 1: (a) Ligand exchange and thermal annealing flow chart. (b) Schematic showing cobalt migration.

experiment. Colloidal processing then allowed any expelled Co^{2+}, now complexed by additional TOPO, to be separated from the nanorods by their markedly different solubilities.

C) Physical Methods: A Phillips 1830 powder diffractometer was used to deterimine crystallinity. Electronic absorption spectra were collected on a Cary 5E (Varian) spectrophotometer using 1 cm path-length quartz cuvette. Dopant ion concentrations were determined using an inductively coupled plasma emissions spectroscopy (ICP-AES, jarrel-Ash model 955). Magnetic susceptibility measurements were performed on powder samples using a Quantum Design MPMS SQUID magnetometer.

Results and Conclusions:

The data in Figure 2 show that no Co^{2+} migration out of the lattice was observed at any temperature within the error of the experiment. Room temperature magnetic saturation data were collected on a ligand-exchanged control sample and the 36 hour annealed samples from each time dependent annealing experiment. Though all the samples proved to be weakly ferromagnetic, the annealing steps show no increase on the ferromagnetic moment. On the contrary, a three fold higher magnetic moment per cobalt was observed in the un-annealed samples (Figure 3a).

One possibility for this decrease may be that the TOPO itself is withdrawing electron density from the nanorod, thereby reducing the ferromagnetic moment in a carrier mediated exchange model. An alternative explanation lies in the volume percentage of passivating ligand per sample. Thermal gravimetric analysis experiments (TGA) show less ligand for the 180°C ligand exchanged sample (19 wt%) than the annealed samples (36 wt%). A smaller fraction of capping ligand provides an opportunity for sintering in the dried powder used for magnetic measurements.

Figure 4 shows the paramagnetic component of the magnetic susceptibility data as a function of temperature. Though no increase in ferromagnetic component was observed, the paramagnetic moment decreases monotonically with increasing annealing temperature. Such a reduction would be expected if a portion of the

paramagnetic Co^{2+} were being converted into an exchange coupled antiferromagnetic species reducing the total paramagnetic moment. Co^{2+} (d^7) may also be undergoing a spin-crossover from high spin (S=3/2, μ_{eff}=4.2 μ_B) to a low spin (S=1/2, μ_{eff} = 1.8 μ_B) state, thus decreasing the overall paramagnetic moment.

Figure 4 also shows μ_{eff}/Co^{2+} for Co^{2+} decreasing from 4.2 to ~ 2.1 in agreement with a spin-crossover type event. Further experiments would be necessary to differentiate these two possibilities.

In conclusion, no thermal activation to ferromagnetism or Co^{2+} expulsion was observed under our experimental conditions. The results of this study support the idea that nanoparticles sintering and/or aggregation is essential to activation of ferromagnetism. Further studies focusing on the observed paramagnetic reduction are of great interest to the magnetic semiconductor community.

References:
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[3] Cozzoli, P. Davide; Kornowski, Andreas; Weller, Horst.J. Am. Chem. Soc. 2003. 125(47), 14539-14548.
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Figure 3, left: Ferromagnetic data of each annealed sample and the unannealed sample.

Figure 4, right: Effective magnetic moment per Co^{2+}.