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Synthesis of High-Curie-Temperature $Fe_{0.02}Ge_{0.98}$ Quantum Dots

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Abstract: Self-assembled $Fe_{0.02}Ge_{0.98}$ dilute magnetic quantum dots show a high Curie temperature above 400 K. Such extraordinary magnetic properties can potentially resolve the critical problem of power dissipation in today's integrated circuits and lead to the realization of a new class of spintronics devices.

Dilute magnetic semiconductor (DMS) quantum structures have attracted great interest because the quantum confinement effect on the nanoscale can constructively enhance their magnetic properties.[1−4] Among various DMS materials, transition-metal-doped Ge ferromagnetic semiconductor nanostructures have drawn particular attention because of their enormous potential in spintronics applications and excellent compatibility with today's CMOS technology.[5] Indeed, the use of DMS materials could create and inspire exciting applications in low-power-consumption and nonvolatile spin logics as a result of the fact that spin-device operation is based upon the manipulation of the spin degrees of freedom in addition to the charge properties.[6]

In recent years, there has been a surge in efforts to increase the ferromagnetic transition temperature, i.e., the Curie temperature (T_c), in order to make practical spin devices that function at ambient temperature. To date, however, the T_c values obtained from Mn- and Fe-doped Ge DMS bulk films have been limited to low temperatures.[5,7] Most recently, we observed a salient quantum confinement effect on the increase of the Curie temperature in a $Mn_{0.05}Ge_{0.95}$ quantum dot (QD) system.[8] The cluster formation was found to be considerably suppressed in comparison with their bulk counterparts grown under the same conditions. To further explore the possibilities of high-Curie-temperature nanostructures, the transition metal Fe was selected as a promising dopant because of its smaller tendency to cluster relative to that of Mn.[8,9] In this communication, we report the successful synthesis of DMS $Fe_{0.02}Ge_{0.98}$ QDs with a Curie temperature above 400 K. In contrast to $Fe_{0.02}Ge_{0.98}$ bulk films, no clusters were observed in this system. The $Fe_{0.02}Ge_{0.98}$ QDs were found to be epitaxially coherent with Si. We also provide a qualitative explanation for the observation of the high Curie temperature based upon the effect of quantum confinement on the density of states (DOS).

Figure 1 shows the evolution of $Fe_{0.02}Ge_{0.98}$ QDs as a function of growth time. During the growth, the Fe doping concentration was fixed at 2 atom % while the growth time was adjusted to 120, 160, and 180 s, corresponding to Figure 1a−c, respectively. It was found that the dot density increased as a function of growth time, following the scheme of the Stranski−Krastanov growth mode, in which the island growth occurs when a critical layer thickness (wetting layer) is reached and continues to develop as a function of time. When the growth reached 180 s, the multilayer QDs were developed and started to coalesce with each other. Figure 1d−f shows color displays for Figure 1a−c, respectively.

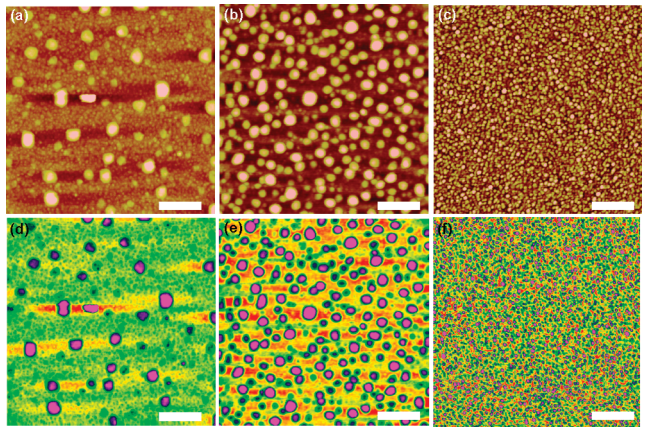

Figure 1. Evolution of the formation of $Fe_{0.02}Ge_{0.98}$ QDs as a function of growth time: (a) 120, (b) 160, and (c) 180 s. (d−f) Color displays for (a−c), respectively. Scale bars represent 200 nm.

Cross-sectional transmission electron microscopy (TEM) was performed to investigate the structural and chemical characteristics of the grown QDs, and an example is shown in Figure 2. The high-resolution TEM (HRTEM) image reveals a dome-shaped QD with a base diameter of 30 nm and a height of ∼6 nm (Figure 2a). Importantly, the QD shows a nearly perfect epitaxial growth on the underlying Si substrate, as evidenced in Figure 2b. Few dislocations or stacking faults were observed. This is similar to the $Mn_{0.05}Ge_{0.95}$ QDs except for the absence of Fe diffusion into the underlying Si. Energy-dispersive X-ray (EDX) spectroscopy was performed to determine the Fe composition, and the result is shown in Figure 2c. On the basis of the 20 $Fe_{0.02}Ge_{0.98}$ QDs examined, the Fe composition is estimated to be 2 atom %. In addition, with extensive HRTEM on a large scale (see Figure S1 in the Supporting Information), no secondary clusters were detected. This implies a single-crystalline DMS system.

Magnetic properties were studied using a superconducting quantum interference device (SQUID) magnetometer. The magnetization moments were recorded as a function of magnetic field and temperature. Figure 3a shows the hysteresis loops at 10, 350, and 400 K, respectively. From these, the saturation magnetic moment per Fe atom was calculated to be $\sim 0.6\mu_B$ at 10 K. In view of the magnetic moment per Fe atom of $2.22\mu_B$,[10] a fraction of 27% was magnetically activated. The appearance of the hysteresis loop at 350 K confirmed the ferromagnetic properties above room

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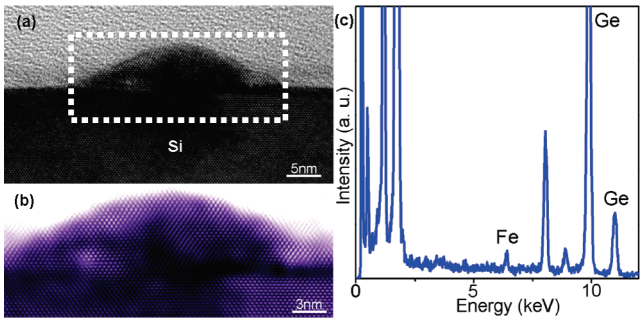

Figure 2. (a, b) HRTEM results for the $Fe_{0.02}Ge_{0.98}$ QDs: (a) typical HRTEM image showing one QD on Si; (b) magnified Fourier-filtered image of the marked area in (a), showing nearly perfect lattice coherence between Si and $Fe_{0.02}Ge_{0.98}$ QDs. (c) EDX results for Fe concentration (2 atom %).

temperature. At 400 K, however, the QDs became superparamagnetic. It is believed that the magnetization of the QDs became random at this temperature, resulting in a zero coercive force (Figure 3b inset). Zero-field-cooled (ZFC) and field-cooled (FC) magnetizations were measured with a magnetic field of 100 Oe (Figure 3b). The magnetic moments did not drop to zero, suggesting a high Curie temperature beyond 400 K. From these two curves, one can also infer the formation of single-phase magnetic nanostructures in this system, i.e., DMS QDs, similar to the high Curie temperature DMS $Mn_{0.05}Ge_{0.95}$ nanowires and QDs.[8,11] Our experiments suggest a high Curie temperature over 400 K, i.e., the QD/*p*-Si system is ferromagnetic at room temperature.

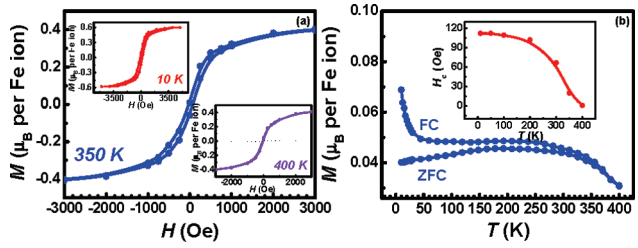

Figure 3. Magnetic properties of the $Fe_{0.02}Ge_{0.98}$ QDs. (a) Hysteresis loops at 10, 350, and 400 K. (b) ZFC and FC magnetization curves under a small magnetic field of 100 Oe. The coercivity as a function of temperature is displayed in the inset.

Atomic force microscopy (AFM) and magnetic force microscopy (MFM) measurements were also carried out to investigate the morphology and ferromagnetism, respectively, of the $Fe_{0.02}Ge_{0.98}$ QDs at 350 K. Consistent with the TEM observations, the average dot size was 20−40 nm in base diameter and 6 nm in height. The corresponding MFM image was taken by lifting the MFM probe 20 nm above the topographic height of the sample in phase-detection mode (Figure 4b). The appearance of bright-and-dark areas in the MFM image clearly showed the formation of magnetic domains in the $Fe_{0.02}Ge_{0.98}$ QDs, similar to previous observations for (In, Mn)As DMS QDs.[1] Overall, the above MFM results agree well with the TEM observations and the ferromagnetic order at high temperature obtained in the SQUID measurements.

Apart from the advantage of suppression of clustering in nanostructures, quantum confinement typically also aids in increasing the Curie temperature of nanostructures relative to their bulk counterparts (see Figure S2 for the magnetic properties of a $Fe_{0.02}Ge_{0.98}$ thin film).[1,4,12] This effect of quantum confinement was demonstrated for GaMnAs and MnGe using first-principles calculations.[13] On the basis of the DOS of an Fe-doped Ge bulk film (Figure S3), we believe the same effect of quantum confinement may be responsible for the observation of the high Curie temperature in our $Fe_{0.02}Ge_{0.98}$ QDs, which can be understood qualitatively as follows: When ferromagnetism in a DMS is mediated by free carriers, T_c is determined by (1) the effective coupling between the p-like carriers and the d-like localized dopants (hybridization) and (2) the ability of the p-like carriers to travel freely between the dopants.[14] The hybridization between the p and d levels grows with decreasing system size. This happens because the d-like states introduced by dopants (Fe in our case), which are more localized, are less affected by quantum confinement than the p-like host states (Ge in our case), and as a result, the DOS of the p-like carriers and the localized d-like magnetic states should move toward each other on the energy scale (Figure S3).[13] On the other hand, the increase in hybridization should reduce the moving ability of the carriers, thus in turn leading to a reduction of effective exchange coupling between the neighboring magnetic dopants (in the limit of very small QDs, there are no free carriers to mediate exchange, and ferromagnetism is then believed to be mediated by *double exchange*).[15] The above picture implies that there must be a region of sizes (and possibly shapes) between the bulk and very small quantum dots where the T_c should peak.

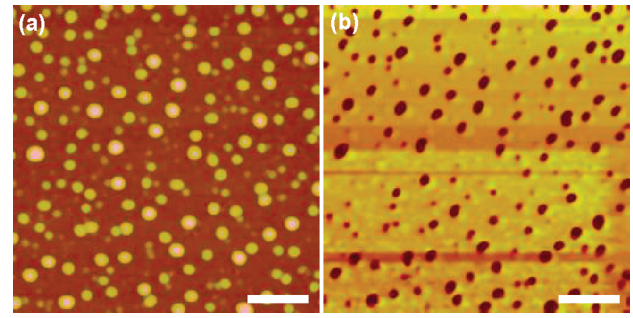

Figure 4. AFM and MFM images of the $Fe_{0.02}Ge_{0.98}$ QDs measured at 350 K: (a) typical AFM image; (b) corresponding MFM image with the tip magnetization pointing toward the sample surface. Scale bars represent 200 nm.

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Supporting Information Available: Additional HRTEM images of $Fe_{0.02}Ge_{0.98}$ QDs; magnetic properties of $Fe_{0.02}Ge_{0.98}$ thin films; theoretical calculation of the DOS for an Fe-doped Ge bulk film. This material is available free of charge via the Internet at http://pubs.acs.org.

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