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Ferromagnetism in self-assembled Ge quantum dots material followed by Mn-implantation and annealing

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Abstract

Ten and twenty layers of self-assembled Ge QDs with 44 and 59-nm-thick Si barrier were grown on high resistivity (100) p-type Si substrates by rapid thermal chemical vapor deposition followed by Mn ion implantation and post-annealing. A presence of ferromagnetic structure was confirmed in the insulating GeMn diluted magnetic quantum dots (DMQD) and semiconducting GeMn DMQD. The DMQD materials were found to be homogeneous, and to exhibit p-type conductivity and ferromagnetic ordering with a Curie temperature, $T_C = 350$ and 230 K. The X-ray diffraction (XRD) data show that there is a phase separation of Mn_5Ge_3 from MnGe nanostructure. Temperature dependent electrical resistivity in semiconducting DMQD material indicates that manganese introduces two acceptor levels in germanium at 0.14 eV from the valence band and 0.41 eV from the conduction band implying Mn substituting Ge. Therefore, it is likely that the ferromagnetic exchange coupling of DMQD material with $T_C = 230$ K is hole-mediated due to formation of polarons and the ferromagnetism in sample with $T_C > 300$ K is due to Mn_5Ge_3 phase.

Keywords: Ferromagnetism; Diluted magnetic semiconductor; Quantum dot

1. Introduction

Diluted magnetic semiconductors (DMSs), often referred to as semimagnetic semiconductors, that are based on III–V semiconductors have attracted a great deal of attention recently because of their potential application in spintronic devices that exploit the charge and spin of electrons [1]. The lattices of these materials consist of magnetic ions partially substituting for some of the cations, thereby inducing a local magnetic moment in the lattice and donating carriers into the system. The ferromagnetic nature of these materials is caused by the exchange interaction between localized magnetic moments introduced by the magnetic ions and the carrier spins. Therefore, for device applications, it is desirable to find materials that exhibit ferromagnetism at as high a temperature as possible. Since Dietl et al. [2] predicted that wide band-gap DMS materials, such as GaMnN and ZnMnO, can have Curie temperatures (T_C) above room temperature, based on the mean-field Zener model of ferromagnetism, several materials with Curie temperatures greatly above room temperature have been found in many studies [3–8]. In particular, group-IV-based DMS materials [9–13] with high Curie temperatures have attracted much attention because of their compatibility with conventional semiconductor integrated circuit manufacturing techniques since Park et al. reported an epitaxially grown single crystal of Mn_xGe_{1-x} ($x = 3.5\%$)

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with a magnetically ordered phase with a Curie temperature up to 116 K because of a long-range ferromagnetic interaction [9]. The structural, electronic, and magnetic properties for Si_xGe_{1-x} alloys doped with Mn have been investigated theoretically and experimentally [14–17].

In this paper, we report on the magnetic and transport properties of GeMn diluted magnetic quantum dots (DMQD), formed through ion implantation and post-annealing. Energy dispersive X-ray fluorescence (EDX), X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), superconducting quantum interference device (SQUID), Hall effects and Raman spectroscopy measurements were performed to characterize the samples.

2. Experimental

Ten and twenty stacked Ge QDs with 44 and 59-nm-thick Si barrier (hereafter referred as sample A and B) were grown on p-type (1 0 0) Si substrates by rapid thermal chemical vapor deposition (RTCVD) using SiH_4 and GeH_4 as source gases. The samples underwent the following growth procedures: after baking at 1000 °C in hydrogen, a Si buffer layer of 210 nm was deposited on Si substrate at 850 °C and self-assembled Ge QDs were grown on top of the Si buffer layer at 700 °C with a pressure of 100 mTorr. The Ge quantum dots (QDs) were deposited in the Stranski–Krastanow growth mode and the growth rate of Si layer was 1 ML/s in active layers. Atomic force microscopy (AFM) revealed that the Ge self-assembled QDs have an average height of 15 nm and an average base length of 100 nm. The density of the dots was approximately 2×10^8 cm^{-2}. The Ge QDs sample A and B grown by RTCVD were uniformly implanted with Mn^+ ions at energy of 200 keV and dose of 2.5×10^{16} and 5×10^{16} cm^{-2}, respectively. After implantation, thermal annealing was performed at 650 °C under Ar gas ambient 10 min in a rapid thermal annealing (RTA) furnace to recover the damage.

Hysteresis loops were measured at temperatures in the range 4–300 K using a SQUID, and a high-sensitivity (10^{-8} emu) alternating gradient magnetometer (AGM). In all the measurements, the magnetic field was applied parallel to the sample surface. The concentration of Mn in the sample A and B using an EDX was determined at around 3.0% and 5.0%, respectively. The grown sample doped with manganese exhibited p-type conductivity through Hall effect measurements. The hole concentration and resistivity of the sample A are determined to be 1×10^{14} cm^{-3} and 1.7×10^4 Ω cm, respectively. The hole concentration and resistivity of the sample B are determined to be 1×10^{15} cm^{-3} and 1.2×10^3 Ω cm, respectively. In addition, Raman spectroscopy was performed at room temperature using the 514.5 nm line of Ar^+ ion laser with a power of 20 mW as the excitation source. The scattered signal was detected by a CCD camera through a 1.0 m triple monochromator.

3. Results and discussion

Fig. 1 shows Raman spectra of the Mn-implanted Ge QDs taken in micro-Raman setup at a temperature of 300 K. We observe a typical spectrum of Ge/Si QDs [18]. Strong substrate peak is observed in the Raman spectra at 520 cm^{-1}, denoted as Si_{LO-TO} which corresponds to the longitudinal optical–transverse optical (LO–TO) phonon. The peak near 399 cm^{-1}, denoted as Si–Ge is the longitudinal Si–Ge vibrational mode. The Ge–Ge optical phonon mode observed usually around 300 cm^{-1} was not resolved in our sample. The peak near 438 cm^{-1}, denoted as Local Si–Si is local Si–Si vibrational mode. Strain and intermixing in the structures are very likely to be responsible for the shift of the Si–Ge and local Si–Si vibrational mode [18,19]. The shoulder in the Raman spectra at about 193 cm^{-1} is interpreted as second-order scattering by 2TA(Ge) originating from the X or (and) Σ points of the Brillouin zone in Ge QDs. On the other hand, the shoulder in the Raman spectra around 967 cm^{-1} denoted by 2Si(LO–TO) is interpreted as the second-order Si phonon mode around originating from the bulk Si [20].

Fig. 2 shows the XRD patterns of the as-grown and the annealed samples A and B. Si(0 0 2) and Si(0 0 4) substrate peaks can be observed from the as-grown sample. The XRD spectra for the annealed samples A and B are similar, containing a dominant Mn_5Ge_3 phase. This phase has been known to have a theoretical Curie temperature over room temperature [21]. Fig. 3 shows cross-sectional HRTEM images of twenty stacked Ge QDs with Si spacers of 59 nm in thickness. The density of the dots was approximately 2×10^8 cm^{-2}. They demonstrate that the Ge QDs are vertically ordered and fully contrasted with the Si spacer. Any presence of misfit dislocations was not observed from the TEM images.

Fig. 4 shows the magnetic field-dependent magnetization, M, at 5 K for DMQD samples A and B after RTA for 10 min, with the magnetic field applied parallel to the plane of the film using an AGM. Clearly elongated hyster-

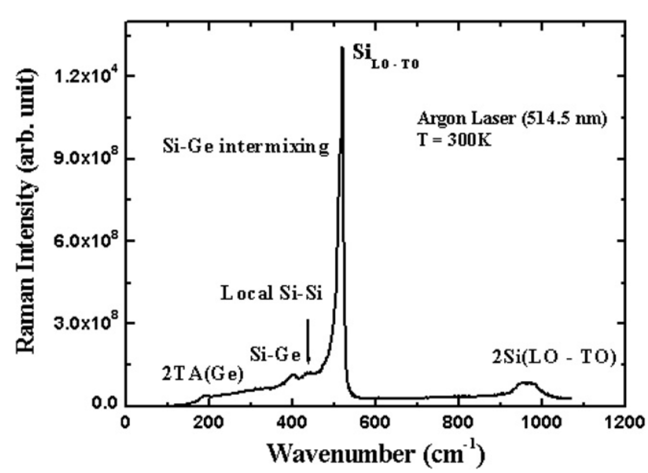

Fig. 1. Raman scattering spectrum of a 10-period self-assembled Ge quantum dot superstructure. The thickness of Si spacer layer is 44 nm.