Ferromagnetism and anomalous Hall effect in $\text{Co}_x\text{Ge}_{1-x}$

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We report the growth of Co-doped Ge ($\text{Co}_x\text{Ge}_{1-x}$) thin films by low-temperature molecular-beam epitaxy and the ferromagnetic properties without any additional carrier doping. The as-grown $\text{Co}_{0.02}\text{Ge}_{0.98}$ has a Curie temperature, $T_C \sim 15$ K, while those $\text{Co}_x\text{Ge}_{1-x}$ with $x \geq 4.0$ at. % are ferromagnetic above room temperature. On the other hand, $\text{Co}_{0.02}\text{Ge}_{0.98}$ exhibit ferromagnetic ordering up to $T_C \sim 150 \pm 10$ K after a low-temperature annealing. A redshift in the Raman Ge–Ge mode was observed, indicating the substitution of Ge with Co atoms. The measured $\text{Co}_{0.02}\text{Ge}_{0.98}$ are of $p$ type and exhibit pronounced anomalous Hall effects. © 2006 American Institute of Physics.

Semiconductor spintronics is an emerging field that makes use of both charge and spins of electrons in semiconductors. 1–3 Diluted magnetic semiconductor (DMSs) is a promising candidate as a source of spin-polarized carriers in semiconductor devices. 1–3 but DMS are alloys in which some atoms in nonmagnetic semiconductor are randomly replaced by magnetic atoms, such as Mn. Not only can it be easily integrated into current semiconductor technology, DMS also allows tunability of the magnetic properties by various means such as electric field, which is not possible by using magnetic metals. One of the major challenges is to obtain a DMS with ferromagnetic (FM) property above room temperature without interfacial reaction. Most experimental efforts have been concentrated on group III-V- and III-VI-based DMSs. 4–6 Ge-based DMS have recently received attention owing to its compatibility with current Si-based semiconductor technology. Pure Mn$_x$Ge$_{1-x}$ DMS has been reported to be FM up to 116 K. 7 Ferromagnetisms were also observed in Cr- and Fe-doped Ge with Curie temperatures, $T_C$, of 126 (Ref. 8) and 233 K, 9 respectively. Besides single doping, Ge with co doping with Mn and Co, as well as Mn and Fe show ferromagnetisms with $T_C$ up to 270 (Ref. 10) and 350 K, 11 respectively. Co$_x$Ge$_{1-x}$ were shown to have a solubility limit of $x \sim 4.0$ at. %, 10,12 It was theoretically 13,14 shown that Co doping into Ge may result in a slightly FM state. However, ferromagnetism has not been observed in Co$_x$Ge$_{1-x}$ yet. In this letter, we report the FM ordering and anomalous Hall effects (AHEs) in the Co$_x$Ge$_{1-x}$ films.

Unlike the combinatorial method that employed “multilayer” approach to produce Co$_x$Mn$_y$Ge$_{1-x-y}$, 10 we grow Co$_x$Ge$_{1-x}$ with $0.02 < x < 0.20$ by codeposition of Ge and Co simultaneously at a low substrate temperature, $T_s$, 150 °C, in order to avoid phase separation. The undoped Ge (001) substrates were annealed for oxide desorption at $T_s \sim 450$ °C and then a thin Ge buffer was grown at 250 °C before the codeposition. The total thickness of the film is $\sim 180 \pm 25$ nm. Low-temperature postgrowth annealing was carried out at 200 °C for 60 min in the ultrahigh vacuum chamber for some cleaved samples. Growth was monitored in situ by 20 keV reflection high-energy electron diffraction (RHEED). Raman spectroscopy and Cu Ka high-resolution x-ray diffraction (HRXRD) were carried out at room temperature to study the crystal qualities. The Co concentrations were determined by x-ray photoelectron spectroscopy (XPS) with an error of $\pm 0.5$ at. % below 5.0 at. %. Magnetic properties were investigated by a superconducting quantum interference device (SQUID) magnetometer and vibrating sample magnetometer (VSM) with an in-plane applied magnetic field. Hall measurements were carried out in a van der Pauw configuration.

Figure 1 shows the $(2 \times 1)$ streaky RHEED pattern observed after the growth of Co$_{0.02}$Ge$_{0.98}$, indicating two-dimensional (2D) epitaxial layers is obtained. A spotty pattern was observed for $x \sim 0.04$ due to the roughening of the surface, indicating a three-dimensional (3D) island growth mode. As $x$ increases up to $x \sim 0.08$, the pattern becomes diffuse, indicating the film has degraded in crystal quality.

FIG. 1. RHEED patterns at the end of the growth for the Co$_x$Ge$_{1-x}$ films with (a) $x \sim 0.02$ and (b) $x \sim 0.04$.  

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Figure 2 shows the as-grown film in the field-dependent magnetization ($M$-$H$) measurement at room temperature. No hysteresis was observed for $Co_{0.02}Ge_{0.98}$, indicating the film is predominantly paramagnetic and the net magnetization at 300 K is zero. On the other hand, a clear hysteresis curve with coercive field, $H_c \sim 200$ Oe, was obtained for $Co_{0.04}Ge_{0.96}$ films. It is noteworthy that FM behaviors above room temperature were observed for all the films with $x \geq 0.04$. The inset of Fig. 2 shows the redshift of Ge–Ge Raman peak for $Co_{x}Ge_{1-x}$ with respect to that of bulk Ge. A shift of $\sim 2.30$ cm$^{-1}$ was clearly observed for $x \sim 0.02$, while a smaller shift of $\sim 1.50$ cm$^{-1}$ was observed for $x \sim 0.04$. These indicate that more Co atoms substituted Ge host lattices for $x \sim 0.02$.

In the temperature-dependent magnetization ($M$-$T$) measurement, a steep increase of magnetization below 15 K was observed for the as-grown $Co_{0.02}Ge_{0.98}$ film (Fig. 3), which may be related to the short range exchange interaction of neighboring cobalt atoms in $Co_{x}Ge_{1-x}$. Neither the $M$-$T$ nor $M$-$H$ curves indicate a trace of FM cobalt precipitates with $T_C \sim 1382$ K. We thus attribute this behavior to weakly FM $Co_{x}Ge_{1-x}$ DMS phase. The critical temperature was determined to be $\sim 15$ K. As for $Co_{0.04}Ge_{0.96}$, the magnetization still exceeds zero at 300 K in the $M$-$T$ curve, in consistent with our $M$-$H$ result. The origin of this FM behavior is likely due to phase separation. Since the $x$ is above the solubility limit reported$^{10,12}$ and cobalt is the only possible phase that is FM above 300 K in Co–Ge and Co–O phase diagrams, it is thus most likely to be due to cobalt precipitation out of the $Co_{x}Ge_{1-x}$ matrix. Figure 3 also shows the $M$-$T$ curve for $Co_{0.02}Ge_{0.98}$ films after a low-temperature annealing.

The shape of the $M$-$T$ curve is rather convex between 15 and 100 K, but it differs from Brillouin function due to the sharp upturn below 15 K, and a tail above 125 K, which may be due to inhomogeneous dopant distribution. A $T_c \sim 150 \pm 10$ K was obtained in this sample. As shown in the inset of Fig. 3, we did not observe any feature that can be associated with spin glass or superparamagnetic behavior from the zero-field-cooled (ZFC) and field-cooled (FC) $M$-$T$ curves for the annealed $Co_{0.02}Ge_{0.98}$ film.

Room temperature Hall measurements reveal that the as-grown and annealed $Co_{0.02}Ge_{0.98}$ are of $p$ type. The measured effective carrier densities of the films ranged from 3 to $9 \times 10^{15}$ cm$^{-3}$. It is noteworthy that the measured hole densities can be complicated by the anomalous Hall effect and the shallow Co donor level (90 meV) near Ge valence band.$^{15}$ The temperature dependent resistances of $Co_{x}Ge_{1-x}$ films have been measured. Our results reveal that all of the $Co_{x}Ge_{1-x}$ films exhibit metallic behaviors. This is in agreement with Mott criterion.$^{16}$ since the carrier concentration of our film is larger than $10^{17}$ cm$^{-3}$, $Co_{x}Ge_{1-x}$ is expected to be on the metallic side of metal-insulator transition due to high impurity doping. Figures 4(a) and 4(b) show the hysteresis curves obtained by $M$-$H$ and Hall resistance measurements ($R_{HF}$-$B$) of the annealed $Co_{0.02}Ge_{0.98}$, respectively. The results show that the film exhibits AHE, a common feature that reveals the charge carrier polarization in a FM DMS. The AHE curves follow $R_{HF}=(R_o/d)B+(R_i/d)M$, where $R_{HF}$, $R_o$ ($R_i$), $B$, $M$, and $d$ correspond to the Hall resistance, Hall coefficients, applied field, magnetization, and film thickness, respectively. The first and second terms are the ordinary and the AHE, respectively. The field dependencies of the AHE curves are in good agreement to the $MH$ curves obtained by SQUID, particularly at 10 K, where both saturate at $\sim 5$ kOe. Similar AHE curves were also observed for the as-grown $Co_{0.02}Ge_{0.98}$ sample, indicating the existence of...
FM Co$_{0.02}$Ge$_{0.98}$ DMS phase though undetectable by SQUID. No AHE was observed in Co$_{0.04}$Ge$_{0.96}$ sample.

It is likely that the as-grown Co$_{0.02}$Ge$_{0.98}$ was metastable and thus possibly results in random distribution of Co atoms in the host lattice with a high density of point defects such as Co interstitials. Therefore, there are many magnetically inactivated Co atoms in the as-grown film which results in the suppression of FM interactions. It is known that low-temperature postgrowth annealing could strongly modify several key parameters such as defect densities, carrier concentrations, and $T_C$, just as it had been demonstrated in Ga$_{1-x}$Mn$_x$As DMS. Similarly, the effect of low-temperature annealing on Co$_{0.02}$Ge$_{0.98}$ film can be attributed to magnetically activation of Co atoms. Another possible explanation is the formation of a secondary phase due to annealing. However, no secondary phases were detected by our HRXRD scan within the detection limit. From all of the phases obtained from Co–Ge and Co–O phase diagrams, none of them can explain the FM property observed. All of the Co–Ge intermetallic compounds are non-FM, except for the low-temperature and high-temperature Co$_2$Ge phases synthesized by mechanical milling, which are FM with $T_C$ $\sim$ 46.4 K and 6 K, respectively.

From the percolation approach, the $T_C$ is proportional to the difference between the FM and antiferromagnetic ordering energies ($\Delta_{AF}$) (Ref. 13) and the $T_C$ of Co$_x$Ge$_{1-x}$ is expected to be lower than that of Mn$_x$Ge$_{1-x}$. Taking the reported $T_C$ of Mn$_x$Ge$_{1-x}$ to be 116 K and assuming a similar magnetically active fraction, we estimated the $T_C$ of Co$_x$Ge$_{1-x}$ from the $\Delta_{AF}$ (Ref. 13) to be 17.5 $\pm$ 1.5 K. This value is quite close to the $T_C$ of our as-grown Co$_{0.02}$Ge$_{0.98}$, but much lower than that of our annealed film. On the other hand, the $T_C$ of the annealed Co$_{0.02}$Ge$_{0.98}$ is remarkably comparable to that reported for Mn$_x$Ge$_{1-x}$, even though Co is known to have a deeper acceptor level (250 meV) than Mn in Ge (160 meV) and an additional donor-like level near the valence band which can lead to compensation. However, according to Fig. 2(c) in Ref. 10, the $T_C$ of Co$_{0.7}$Mn$_{0.3}$Ge$_{1-x}$ can be extrapolated to be $\sim$ 125 K when $x$ $\rightarrow$ 0 (i.e., almost no Mn), and $T_C$ $\sim$ 150 K when $x$ $\sim$ 0.02. Our $x$ and $T_C$ values of the annealed Co$_{0.02}$Ge$_{0.98}$ film are in good agreement with their results. Nevertheless, further works are required to elucidate the origin of ferromagnetism in this system.

In conclusion, we have grown $p$-type Co$_x$Ge$_{1-x}$ epitaxial films and observed FM ordering in Co$_x$Ge$_{1-x}$, without any additional carrier doping. The as-grown film is FM with $T_C$ $\sim$ 15 K when $x$ $\sim$ 0.02, and FM above room temperature when $x$ reaches the solubility limit, i.e., $x$ $\sim$ 0.04. Ferromagnetism with $T_C$ $\sim$ 150 $\pm$ 10 K was observed in Co$_{0.02}$Ge$_{0.98}$ after a low-temperature annealing. The observation of AHE provides further evidence on the FM ordering in Co$_{0.02}$Ge$_{0.98}$. These results have considerable implications for the fundamental understanding of FM in DMS materials and for Si-based device applications.

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