Enhanced room temperature ferromagnetism in Co- and Mn-ion-implanted silicon

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(Received 14 April 2006; accepted 26 June 2006; published online 11 September 2006)

The authors report on ferromagnetism at room temperature in cluster-free, cobalt- and manganese-ion-implanted crystalline silicon. Through magnetic and structural analysis it is shown that the ion-implanted Si consists of two layers of Co- and Mn-containing silicon: (1) an amorphous Si layer on the surface and (2) single crystalline Si beneath. The amorphous layer shows very little magnetism by itself but seems to be responsible for partially canceling out or masking the ferromagnetism in the crystalline Si. The authors also observe that etching of the amorphous Si layer dramatically enhances the measured magnetism by as much as 400%. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2243802]

Further progress in spintronics[1,2] is critically dependent on the availability of room temperature magnetic semiconductors. The experimental proof of magnetism in (Ga, Mn)As and (In, Mn)As (Refs. 3 and 4) at Curie temperatures (T_C) < 160 K and theoretical understanding gained through a Zener model description of carrier-mediated ferromagnetism have been used to predict[5] magnetism in various other Mn- and transition-metal-doped semiconductors. While the III–V and oxide-based ferromagnetic semiconductors have been well explored,[2] the study of magnetism in the technologically important group IV semiconductors has lagged. An exception is Mn incorporated Ge,[6] where a Curie temperature (T_C) of up to 116 K was recorded. In earlier studies of Mn in Si (Refs. 7 and 8) it was not clear whether the magnetism was intrinsic or due to extraneous phase/cluster formation due to high temperature (>350 °C) processing. In this letter, we show, through extensive structural and magnetic characterizations, evidence of room temperature ferromagnetic behavior in Si ion implanted with Co and Mn.

It was shown through density functional theory calculations[9] that Mn in crystalline Si could give rise to ferromagnetic interactions, while preserving the electrical character of the host material. As the equilibrium solubility in Si of transition metals is extremely low,[10] we used a nonequilibrium technique, ion implantation below room temperature (∼−20 °C), to place the Co and Mn ions in the Si (p and n types, $\rho \sim 1\ \Omega$ cm) and circumvent the ambiguity and high probability of temperature induced magnetic cluster formation. While room temperature magnetism was observed in the n-Si samples also, we focus our discussion mainly on the p-Si samples here. The results from two samples (sample 1 at $10^{16}/\mathrm{cm}^2$ dose at 100 kV accelerating voltage and sample 2 with three sequential implantations of uniform doses of $10^{15}/\mathrm{cm}^2$ at 100, 50, and finally 25 kV performed to increase the overall implanted volume of Si) will be presented. All ion implantation was done at an angle of 7° to prevent channeling.

The magnetic measurements were performed in two separate superconducting quantum interference device (SQUID) magnetometers at UC San Diego and Quantum Design Inc. An alternating gradient magnetometer (AGM) was also employed to reconfirm the measurements for a third time. High resolution transmission electron microscopy (HRTEM, FEI Tecnai), equipped with energy dispersive spectroscopy (EDS), was used for structural analyses and phase determination.

It was seen through both HRTEM [Figs. 1(a) and 1(b)] and Rutherford backscattering spectroscopy (not shown) that the Co and Mn ions were implanted randomly into the Si lattice. A significant and relatively well defined amorphization of the top 150 nm of silicon, an effect of ion implantation, was observed. The material immediately below the amorphous layer is single crystalline silicon as seen through lattice imaging [Fig. 1(b)]. The atomic planes are continuous in all locations [Figs. 1(a) and 1(b)]. Careful EDS analyses indicated that both the amorphous Si layer and the crystalline silicon beneath contain cluster-free Mn and Co atoms.

Additionally, rapid thermal annealing (RTA) was used to note the effects of high temperature processing on Mn clustering behavior. Annealing (in the range of 600–950 °C and times ranging from 30 to 60 s) was found to reduce the thickness of the amorphized layer [Fig. 1(c)] substantially

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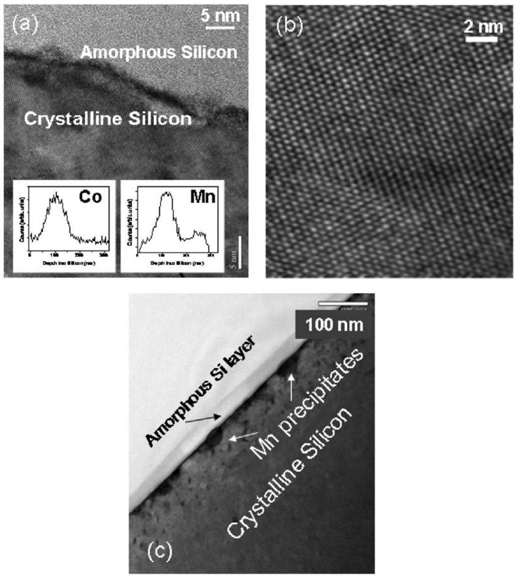

FIG. 1. (a) Amorphous layer on top of crystalline Si is observed for both Co- and Mn-ion as-implanted sample 1 through TEM. The Co and Mn distributions as probed through EDS are represented in the left and right insets. (b) A HRTEM image of the ferromagnetic silicon matrix, in the Mn-implanted Si, taken 30 nm away from the amorphous-crystalline interface, showing the absence of transition metal clustering. (c) TEM micrograph of sample 1 subject to RTA (950 °C, 60 s), showing Mn surface segregation.

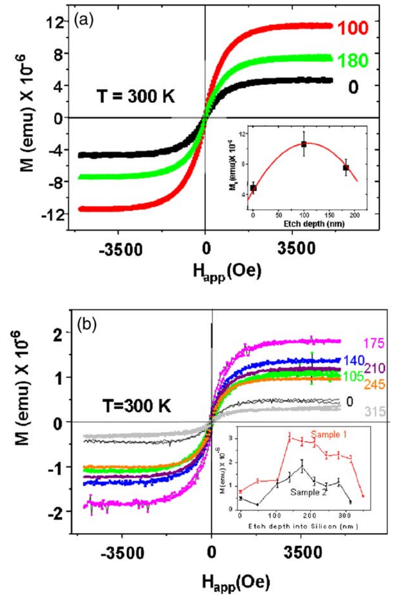

FIG. 2. (Color online) Room temperature M-H hysteresis curves for the (a) Co-implanted (sample 1) and (b) Mn-implanted magnetic silicon (sample 2), where the amorphous layer has been progressively removed through reactive ion etching (RIE). (The numbers next to the M-H loops refer to the thickness of the surface silicon removed.) The insets show the variation of the M_s with the etching depth for both ion-implantation doses.

and increase the saturation magnetization (M_s).[8] As is evident from Fig. 1(c), annealing introduces Mn and Co rich precipitates at the surface,[11] presumably drained from the underlying crystalline silicon. Such a clustering phenomenon, on annealing, has not been previously reported in Si and could have been a problem in previous high temperature ion-implantation studies.[8]

However, there is no transition metal aggregation seen in the as-implanted silicon [sample 1: Figs. 1(a) and 1(b)]. This provides a scientifically important and technologically relevant proof that room temperature magnetism from Co- and Mn-doped crystalline silicon could be possible.

For the as-implanted samples, room temperature measurement with up to 1.5 T of applied field showed clear signs of ferromagnetism with an M_s of $\sim 5\times 10^{-6}$ emu for the Co-implanted samples ($\sim 0.5\times 10^{-6}$ emu for the Mn-implanted samples) with a small coercive field (H_c), with near-saturation ($0.9M_s$) being reached at a relatively low field of ~ 1.5 kOe. To pinpoint the origin of magnetism in the Co- and Mn-implanted Si, we used reactive ion etching (RIE) to remove the surface amorphous layer material leaving only the transition metal incorporated crystalline Si. The RIE process involves relatively low power ~ 100 W and tetrafluoromethane (CF_4) etch gas with an etching rate of ~ 10 nm/s. The substrate temperature during RIE was maintained at ~ 5 °C. We can, therefore, rule out the possibility of magnetic Co–F and Mn–F phases on the surface [incidentally, both CoF_2 and MnF_2 are antiferromagnetic with a $T_N < 70$ K (Refs. 12 and 13)]. A cross-check was also performed through control samples fabricated through alternate wet-chemical etching procedures. Surprisingly, it was found that the M_s as well as the remnant magnetization (M_r) increased significantly (as much as a 400%!) as we etch deeper into the sample (Fig. 2) with a maximum magnetization occurring at ~ 100 nm etch for the Co-implanted sample [Fig. 2(a)], and at ~ 175 nm etch for the Mn sample [Fig. 2(b)]. This enhanced magnetic behavior, by removal of surface material, was independently confirmed through room temperature AGM (Fig. 2) and SQUID magnetometry (Fig. 3).

The M-H hysteresis loop of the RIE samples, e.g., in the 175 nm etched sample 2 (Fig. 2) exhibits an M_s of 1.8×10^{-6} emu ($4\pi M_s \sim 1.4$ emu/cm^3, ~ 17.6 G) and a low coercivity (H_c) of ~ 80 Oe with a near-saturation of $0.9M_s$ being reached at a low applied field of 1.4 kOe. As shown in

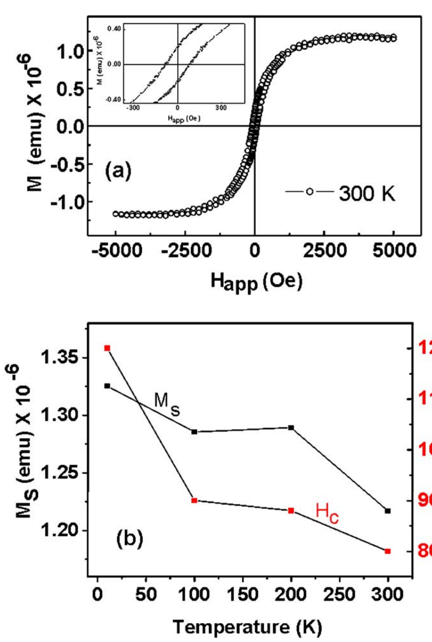

FIG. 3. (Color online) Ferromagnetic behavior of Mn-implanted Si (sample 1), where the top 250 nm has been removed through RIE. (a) A room temperature M-H hysteresis loop showing ferromagnetism with a saturation magnetization (M_s) of 1.3×10^{-6} emu and a coercivity (H_c) of ~ 80 Oe (see inset). (b) The temperature dependence of the M_s and H_c.

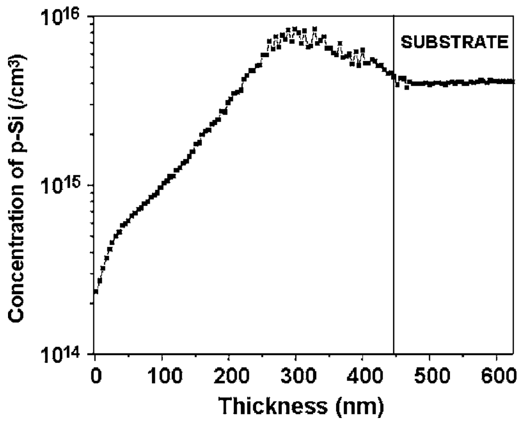

FIG. 4. Spreading resistance measurements for profiling carrier concentration through Mn-implanted silicon, with enhanced p doping found in the interior of the sample.

the insets to Fig. 2, the M_s of samples 1 and 2 go through a maximum as a function of sample surface removal. The initial ascending part is due to the gradual removal of the surface amorphous layer while the falloff after the peak is due to the cumulative loss of Mn from the crystalline silicon matrix with progressive etching.

Figure 3(a) shows the room temperature M-H loop of sample 1 where the top 250 nm, including the entire amorphized layer [including darker contrast boundary regions in Fig. 1(a)] was removed. The loop shape is indicative of a soft ferromagnetic material with a low H_c ($\sim$80 Oe—see inset) and relatively high magnetic permeability (μ_r) with near saturation ($0.9M_s$) reached at $\sim$1.5 kOe. Figure 3(b) shows the temperature dependence of M_s and H_c of the above etched sample.

An increase of magnetic moment as a portion of a magnetic material is removed, as seen in our samples, is very much counterintuitive. While the exact mechanisms are not clearly understood at the present, the following hypotheses are proposed.

(1) The Mn-doped amorphous Si layer may be contributing to increased diamagnetism or could be antiferromagnetic. If an antiferromagnetic pinning layer is indeed present, it presents intriguing possibilities for designing spin valves and magnetic tunnel junctions using crystalline/amorphous/crystalline silicon multilayers.

(2) It has been observed through electron paramagnetic resonance experiments[14] and theoretical studies[15] that interstitial sites are the equilibrium favored sites for Mn or Co in the Si lattice. In contrast to the magnetism in III-V magnetic semiconductors, where interstitials induce antiferromagnetic interactions,[16] it has been predicted[9] that, in Mn-implanted silicon, interstitial-interstitial and substitutional-interstitial interactions favor ferromagnetism. Isolated Mn, say, in the amorphous layer, could compensate the background p doping while dimers, e.g., Mn_i–Mn_{Si} and Mn_i–Mn_i pairs, in the crystalline matrix, which are neutral/acceptor-like, could enhance the magnetism.[9] We conducted spreading resistance measurements (Fig. 4) to profile the carrier concentration through the implanted layer thickness. While the surface of the wafer up to a depth of $\sim$220 nm seems to be compensated, below the background concentration of the p-Si substrate, there is an enhancement of carrier concentration from 220 to 400 nm. If it is assumed that the magnetism in Mn-doped p-Si is hole mediated through a Ruderman-Kittel-Kasuya-Yoshida (RKKY) type mechanism as in the case[6] of Mn_xGe_{1-x}, the hole compensation would reduce the net magnetic behavior. Additionally, the amorphized silicon on the surface of the semiconductor could also contribute defects, such as dangling bonds,[17,18] to compensate the p doping.

It is to be noted, however, that at low carrier densities employed here an impurity band model,[19,20] where the carrier wave functions are those due to the transition metals could be more appropriate for describing the magnetism. It is interesting that this model predicts an increased T_C with greater disorder[21] of Mn ions, due to difficulty in disordering widely separated magnetic regions.[22]

In summary, we have shown evidence for cluster-free, soft ferromagnetic behavior in silicon, at room temperature, through the subsurface implantation of Co and Mn ions. The removal of the surface amorphous layer formed during ion implantation resulted in a dramatic increase in the magnetic signal from the underlying crystalline silicon. We hope that our observations can contribute to an increased investigation of magnetism in silicon.

This work was supported through funding from the von Liebig foundation, the Iwama fund, and the UC Discovery Fund (ele02-10133/Jin). The authors also gratefully acknowledge support from the National Science Foundation (ECS-05-08514) and the Office of Naval Research (N00014-06-1-0234).

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