Ferromagnetism in Mn- and Co-implanted ZnO nanorods


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ZnO nanorods with diameters of 15–30 nm were grown on Ag-coated Si substrates by catalyst-driven molecular beam epitaxy and then implanted with Mn$^+$ or Co$^+$ ions to doses of $1–5 \times 10^{16} \text{ cm}^{-2}$. After subsequent annealing at 700 °C for 5 min, the structural properties of the nanorods were unaffacted, but they exhibited ferromagnetism that persisted to temperatures of 225–300 K. The coercive fields were $\approx 100 \text{ Oe}$ even at 10 K. The results are similar to those obtained for implantation of Mn$^+$ or Co$^+$ ions in bulk single-crystal ZnO and indicate promise for nanorods for nanoscale spintronic applications. © 2003 American Vacuum Society.

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I. INTRODUCTION

ZnO is a direct band gap ($E_g = 3.35 \text{ eV}$) semiconductor which is piezoelectric and has been used for gas sensing, surface acoustic wave devices, varistors, and transparent thin film transistors.1–25 Recently, several groups have demonstrated site-specific growth of ZnO nanorods using catalyst-driven molecular beam epitaxy (MBE) or vapor transport.26,27 The large surface area of the nanorods makes them attractive for gas and chemical sensing, and the ability to control their nucleation sites makes them candidates for microlasers or memory arrays. It has also been predicted that $p$-type, Mn-doped ZnO might be a room-temperature ferromagnet, while other groups have suggested that $n$-type ZnO with high concentrations of Fe, Co, or Ni might also have high Curie temperatures.28–30 Experimental results show Curie temperatures of $\approx 250 \text{ K}$ in Mn-implanted bulk $n$-type ZnO (Ref. 31) and $\approx 45 \text{ K}$ in Mn-doped ZnO epitaxial films.32 In the case of Co doping there is evidence that the observed ferromagnetism may be due to Co precipitates rather than to carrier-mediated exchange in the ZnO matrix.33,34

In this article we report on the magnetic properties of Mn$^+$ and Co$^+$ ion-implanted ZnO nanorods prepared by MBE on Si substrates. For both types of implanted dopants, the resultant magnetization after annealing persisted to temperatures in the range of 225–300 K. The results are similar to those obtained previously in $n$-type, bulk ZnO substrates implanted and annealed under the same conditions,31,34 and this indicates that transition metal-doped ZnO nanorods may have application in nanoscale ultraviolet (UV) light emitters, sensors, or data storage elements.

II. EXPERIMENT

The preparation of the nanorods was described in detail previously.27 Briefly, discontinuous thin films ($\approx 100 \text{ Å}$) of e-beam evaporated Ag were deposited on $p$-Si (100) wafers terminated with native oxide. A scanning electron micrograph (SEM) of such a surface is shown in Fig. 1 (top). ZnO nanorods were deposited by MBE using a Zn metal and an $\text{O}_3/\text{O}_2$ plasma discharge as the source chemicals. The growth time was $\approx 2 \text{ h}$ at 400 °C. The typical length of the resultant nanorods was $\approx 2 \mu \text{m}$, with typical diameters in the range of 15–30 nm. The samples were subsequently implanted with Mn$^+$ and Co$^+$ ions at fixed energy of 250 keV and doses of $1–5 \times 10^{16} \text{ cm}^{-2}$, while the samples were held at $\approx 350 \text{ °C}$ to avoid amorphization. The projected range for both types of ion is $\approx 1500 \text{ Å}$, with peak transition metal concentrations corresponding to roughly 1–5 at. %. The samples were then annealed at 700 °C for 5 min under flowing $\text{N}_2$ to promote migration of the transition metal ions to substitutional positions. The thermal exposure of the Ag/$\text{SiO}_2/\text{Si}$ substrates to the nanorod growth temperature and the subsequent implant activation annealing cause further islanding of Ag. An example is shown at the center and at the bottom of Fig. 1 for a Ag/$\text{SiO}_2/\text{Si}$ sample that was annealed at 700 °C for 5 min without any growth of nanorods in order to see the effect on the sample morphology.

III. RESULTS AND DISCUSSION

The implantation and annealing process did not alter the appearance or dimensions of the nanorods. Figure 2 shows SEM micrographs of the Mn-implanted (dose $= 5 \times 10^{16} \text{ cm}^{-2}$) nanorods after annealing, in both plan view (top) and cross section (bottom). Even at this highest dose condition, the nanorods are stable to the implant/anneal...
cycle. A comparison of micrographs before and after this cycle did not show any observable change in the nanorods.

Energy dispersive spectrometry (EDS) data from the Mn (top) and Co (bottom) implanted samples are shown in Fig. 3. Both of the peak intensities of these dopants are consistent with concentrations of a few atomic percent and there were no other impurities introduced during annealing, at least within the sensitivity of EDS. There is no evidence of the formation of nitrides after the anneal in N\textsubscript{2}.

In addition, photoluminescence (PL) measurements using a He–Cd excitation source are shown in Fig. 4 that reveal a significant decrease in band-edge intensity as a result of the Mn implantation and annealing (bottom), whereas the deep level emission at around 2.32 eV (top) is largely unchanged. The increase in the signal beyond the band edge is due to laser lines from the He–Cd source. We could not identify particular emission bands specifically related to either Mn or Co.

The magnetic properties of the as-grown and annealed nanorods and their implanted counterparts were all examined using a Quantum Design superconducting quantum interference device (SQUID) magnetometer. Figure 5 shows the magnetization versus field behavior at 100 K for a Mn-implanted (5×10\textsuperscript{16} cm\textsuperscript{-2}/dose) nanorod sample after the 700 °C, 5 min anneal. Hysteretic behavior is clearly present, with a coercive field at 100 K of ≤100 Oe. The possible
explanations for these data include ferromagnetism, superparamagnetism or spin-glass effects. The magnetization of unimplanted, annealed nanorods was as much as three orders of magnitude lower than in the implanted, annealed samples, demonstrating that transition metals are responsible for the magnetic properties observed. The calculated moment from the saturation magnetization was \( \sim 2.2 \) Bohr magnetons per Mn ion, showing that a significant fraction of the implanted Mn contributes to the magnetization.

Field-cooled and zero-field-cooled magnetization measurements were performed over the temperature range of 4–300 K. The raw scans are shown in Fig. 6 for an applied field of 500 Oe on an Mn-implanted nanorod sample annealed at 700 °C. The shape of the scans is consistent with the presence of ferromagnetism. Taking the difference between the field-cooled and zero-field-cooled magnetism conveniently subtracts the paramagnetic contribution, leaving only the contribution from the hysteretic ferromagnetic regime. Figure 7 shows the difference in field-cooled and zero-field-cooled magnetization for nanorods implanted with two different doses of Mn (1 and \( 5 \times 10^{16} \) cm\(^{-2} \)) and annealed at 700 °C. The ferromagnetic contributions to the magnetization are present to temperatures of 225–300 K.

Figure 8 shows the difference in field-cooled and zero-field-cooled magnetization (top) and the magnetization versus the field at 100 K (bottom) for a Co-implanted (5 \( \times 10^{16} \) cm\(^{-2} \)/dose) nanorod sample annealed at 700 °C. Hysteresis is clearly present at 100 K and this ferromagnetic contribution persists to \( \sim 225 \) K.

In assigning the origin of the ferromagnetism observed in the transition metal doped nanorods, the possibility of secondary phase formation must be considered. Table I shows potential second phases that could form in ZnO nanorods, nucleated on Ag/SiO\(_2\)/Si templates and subsequently implanted with Mn or Co. Some of the Ag-related phases have ferromagnetic behavior. In the case of Mn, metallic Mn precipitates would be antiferromagnetic (Néel temperature of \( \sim 100 \) K) and the only Mn oxide that is ferromagnetic is Mn\(_3\)O\(_4\) with a Curie temperature of only 42 K. Another possible mechanism for the observed magnetic property is that Mn is not randomly distributed on Zn sites but is present as atomic scale clusters. Some mean field theories suggest that Mn clustering can significantly influence \( T_c \) as a result of the localization of spin-polarized holes near regions of higher Mn concentration. There is also some support for this assertion from local spin density approximation calculations which predict it is energetically favorable for the formation of magnetic ion dimers and trimers at second nearest-

\[ \text{Fig. 3. EDS spectra of Mn- (top) and Co- (bottom) implanted nanorods. The dose was } 5 \times 10^{16} \text{ cm}^{-2} \text{ in each case.} \]
neighbor sites which are ferromagnetic. None of the potential second phases identified in Table I can account for the observed magnetic behavior. Thus for Mn-implanted nanorods, it does not appear that secondary phases plays a significant role in the magnetic properties. The magnetization results for the Mn-implanted nanorods are very similar to those reported previously for Mn-implanted, bulk n-type ZnO single crystals, in which using high resolution x-ray diffraction no secondary phases were observed. We note also that the solubility limits for Mn in ZnO are between 13% for equilibrium conditions and 35% for incorporation by pulsed laser deposition. These values are well beyond the concentrations employed here.

By sharp contrast, in the case of Co-implanted ZnO, macroscopic Co precipitates are ferromagnetic with Curie temperatures up to 1382 K when large enough to exhibit bulk properties. Bulk, single crystals of ZnO implanted with Co under the same conditions employed here showed the presence of (110)-oriented hexagonal Co nanocrystals with average diameters of ~35 Å, well below the superparamagnetic critical diameter of Co near room temperature of ~50 Å. This is consistent with the magnetization data for the Co-implanted nanorods, which do not show ferromagnetism at

FIG. 4. Room temperature PL spectra of nanorods before and after Mn implantation at $1 \times 10^{16}$ cm$^{-2}$ and annealing at 700 °C for 5 min. Both band-edge and deep level emission regions are shown.

FIG. 5. Magnetization loop at 100 K for field applied parallel to the plane of a ZnO nanorod sample implanted with $5 \times 10^{16}$ cm$^{-2}$ Mn$^+$ and annealed at 700 °C for 5 min.

FIG. 6. Temperature dependence of field-cooled and zero-field-cooled magnetization for a ZnO nanorod sample implanted with $1 \times 10^{16}$ cm$^{-2}$ Mn$^+$ and annealed at 700 °C for 5 min.

FIG. 7. Temperature dependence of difference in field-cooled and zero-field-cooled magnetization at field of 100 Oe for ZnO nanorods implanted with either 1 or $5 \times 10^{16}$ cm$^{-2}$ Mn$^+$ and annealed at 700 °C for 5 min.
TABLE I. Potential second phases that can form in Mn- and Co-doped ZnO

<table>
<thead>
<tr>
<th>Phase</th>
<th>Nature of magnetism</th>
<th>Applicable magnetic temperature (K)</th>
<th>Reference(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>Antiferromagnetic</td>
<td>100</td>
<td>31</td>
</tr>
<tr>
<td>Co</td>
<td>Ferromagnetic</td>
<td>1373</td>
<td>39</td>
</tr>
<tr>
<td>MnO</td>
<td>Antiferromagnetic</td>
<td>122</td>
<td>39, 40</td>
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<tr>
<td>MnO₂</td>
<td>Antiferromagnetic</td>
<td>84</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>Antiferromagnetic</td>
<td>17</td>
<td>41</td>
</tr>
<tr>
<td>Mn₃O₄</td>
<td>Ferromagnetic</td>
<td>1443</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>Ferromagnetic</td>
<td>42</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>Ferrimagnetic</td>
<td>46</td>
<td>41</td>
</tr>
<tr>
<td>MnSi</td>
<td>Ferromagnetic</td>
<td>1298</td>
<td>42</td>
</tr>
<tr>
<td>ZnMnO₄</td>
<td>Ferromagnetic</td>
<td>30</td>
<td>32</td>
</tr>
<tr>
<td>Zn₀.₅Mn₀.₅O</td>
<td>Ferromagnetic</td>
<td>45</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>Antiferromagnetic</td>
<td>29.5</td>
<td>43</td>
</tr>
<tr>
<td>MnZn (15% Mn)</td>
<td>Ferromagnetic</td>
<td>150</td>
<td>40</td>
</tr>
<tr>
<td>MnAu</td>
<td>Ferromagnetic</td>
<td>360</td>
<td>44</td>
</tr>
<tr>
<td>MnAu₂</td>
<td>Ferromagnetic</td>
<td>365</td>
<td>44</td>
</tr>
<tr>
<td>CoO</td>
<td>Antiferromagnetic</td>
<td>291</td>
<td>40, 45</td>
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<tr>
<td>Zn₀.₅Co₀.₅O</td>
<td>Ferromagnetic</td>
<td>280</td>
<td>45</td>
</tr>
<tr>
<td>Zn₀.₇Co₀.₃O₅</td>
<td>Ferromagnetic</td>
<td>300</td>
<td>45</td>
</tr>
<tr>
<td>Zn₀.₅Co₀.₅O</td>
<td>Ferromagnetic</td>
<td>280</td>
<td>45</td>
</tr>
<tr>
<td>CoZn</td>
<td>Ferromagnetic</td>
<td>468</td>
<td>44</td>
</tr>
</tbody>
</table>

Fig. 8. Temperature dependence of the difference in field-cooled and zero-field-cooled magnetization at field of 100 Oe for ZnO nanorods implanted with $5 \times 10^{16}$ cm$^{-2}$ Co$^+$ and annealed at 700 °C for 5 min (top) and magnetization loop at 100 K for the same sample (bottom).

IV. SUMMARY AND CONCLUSIONS

ZnO nanorods implanted with Mn or Co at high doses (corresponding to percent volume concentrations) exhibit significant ferromagnetism at temperatures $\leq 300$ K. The results are similar to those obtained by implantation of these same species into bulk, single-crystal ZnO. One can envision implanting Mn into $p-n$ junction nanorods to investigate the possibilities of spin-polarized UV light emission or using Mn-doped nanorods as magnetic storage elements.

ACKNOWLEDGMENTS

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