Thermal annealing effect on spin coherence in ZnO single crystals

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(Received 21 November 2010; accepted 24 May 2011; published online 6 July 2011)

The spin coherence time ($T_s^*$) in ZnO single crystals at 8.5 K decreases significantly from $\sim$11.2 ns to $\sim$2.3 ns after annealing at 500 °C, as indicated by time-resolved Kerr-rotation pump-probe magneto-optical spectroscopy. The annealing-induced spin coherence degradation in ZnO arises neither from crystallinity degradation during the annealing process, as confirmed by x-ray rocking curves; nor from reflection variations of the probe laser beam induced by surface roughness changes during the annealing process, as confirmed by atomic force microscopy. Temperature-dependent Hall-effect studies indicate that decreased mobility and increased shallow-donor concentration in the annealing-induced surface conducting layer on top of the bulk ZnO are most likely to be the reasons for the spin coherence degradation in ZnO during the annealing process. © 2011 American Institute of Physics. [doi:10.1063/1.3601869]

ZnO-based materials have great potential1 in the areas of optoelectronics2–5 and spintronics6 because of a direct bandgap, large exciton binding energy,1 and both theoretically predicted7 and experimentally observed8–10 above-room-temperature Curie temperature. For spintronic applications, spin coherence is a critically important parameter. Experimental studies of spin coherence in ZnO were first reported by Ghosh et al.11 using time-resolved Faraday rotation (TRFR) pump-probe magneto-optical spectroscopy, with an observation of a spin coherence time as long as 20 ns at $T = 30$ K in bulk ZnO samples. More recent experimental studies have shown an improvement in the spin coherence time in ZnO with an applied in-plane electric field confirmed by TRFR12 and spin dynamics in ZnO quantum dots using TRFR13; theoretical works have studied mechanisms of spin dynamics in ZnO.14,15 Many ZnO device applications, e.g., those requiring Ohmic contacts, involve an annealing step,2–5,16 and it is not clear yet how spin coherence properties change during annealing. In this letter, spin coherence changes during annealing are reported and discussed.

Three identical high-quality ZnO single crystal samples kept un-annealed and annealed at 500 °C and 800 °C (for 2 min under N$_2$ ambient in a rapid-thermal-annealing oven) were employed in this study. The three samples are labeled as A–C, as shown in Table I. Time-resolved Kerr rotation (TRKR) pump-probe magneto-optical spectroscopy was employed to investigate the electron spin dynamics,17 with $\sim$360 nm wavelength used for both pump and probe laser sources, which matches ZnO bandgap ($\sim$3.437 eV at $T < 10$ K). Figure 1 shows the TRKR angle $\theta_K$ as a function of time delay $\Delta t$ of samples A (top), B (middle), and C (bottom) measured at a temperature of 8.5 K and a magnetic field of $B = 90$ mT. The spin coherence times $T_s^*$ of each sample shown in Fig. 1 are obtained by fitting $\theta_K \sim \Delta t$ relation using the equation

$$\theta_K(\Delta t) = A \cos(\omega_L \Delta t) \exp(-\Delta t/T_s^*).$$

The solid lines in Fig. 1 show the fitting curves. The other two fitting parameters, amplitude $A$ and spin precession Larmor frequency $\omega_L$, are summarized in Table I together with $T_s^*$ for all three samples. The effective electron $g$-factor $g^*$ of each sample is calculated using the equation

$$\omega_L = g^* \mu_B B / \hbar$$

and shown in Table I, where $\mu_B$ and $\hbar$ are Bohr magneton and Planck constant, respectively. The spin coherence time decreased from $\sim$11.2 ns in sample A, to $\sim$2.3 ns in sample B, and finally to $\sim$2.0 ns in sample C, while $g^*$ does not change much. The significantly decreased spin coherence time between unannealed ZnO ($\sim$11 ns) and annealed ZnO ($\sim$2 ns) samples indicates that additional spin scattering centers are formed during the annealing process. At elevated measurement temperatures, no analyzable spin coherence oscillation was obtained within the detection limit of the TRKR setup.

X-ray rocking curves (XRCs) were performed on the ZnO (0002) peaks (at $2\theta \sim 34.7^\circ$, which dominates in the $\theta-2\theta$ x-ray diffraction patterns5) to investigate the crystallinity5,18 of samples A, B, and C, respectively, as shown with top, middle, and bottom curves in Fig. 2. The full-width-at-half-maximum (FWHM) of the XRC curves, obtained from

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standard Gaussian fitting, decreases slightly from $\sim 68$ arc sec (sample A), to $\sim 54$ arc sec (sample B) and $\sim 65$ arc sec (sample C) after annealing. This indicates that the ZnO crystallinity does not degrade but actually improves slightly after annealing. Surface roughness may affect the reflection of the probe laser beam in TRKR measurements; however, atomic force microscopy (AFM) studies do not show any significant surface roughness changes in the annealed ZnO samples, with a root-mean-square roughness of $\sim 1$ nm for all three samples. The inset in Fig. 2 shows a $2\mu m \times 2\mu m$ AFM image of sample A. So, neither crystallinity degradations nor surface roughness changes during annealing should be responsible for the spin coherence degradation in ZnO. In order to clarify the origin of the annealing-induced spin coherence degradation in ZnO, temperature-dependent Hall-effect measurements and two-layer fittings were performed on the unannealed and annealed ZnO samples.

Figures 3(a) and 3(b) show the temperature dependence of the electron carrier concentration and mobility of samples A (squares), B (circles), and C (triangles) from 20 to 320 K. The symbols and the solid lines are the experimental data and theoretical fits, respectively. The fitting parameters are summarized in Table II. The most significant changes from sample A to B are those involving the surface conducting layer on top of the bulk layer: a thickness ($d_{surf}$) decrease (120 down to 19 nm), carrier concentration ($n_{surf}$) increase ($2 \times 10^{17}$ up to $1 \times 10^{19}$ cm$^{-3}$), and mobility ($\mu_{surf}$) decrease (1000 down to 230 cm$^2$V$^{-1}$s$^{-1}$). Much smaller changes occur in the bulk donor and acceptor concentrations. The laser penetration depth in ZnO is around 60–100 nm. For sample A, the laser absorption is mostly in the surface layer (120 nm), but the surface layer of sample A is of better “quality” than the surface layers of the annealed samples,
with a mobility of ~1000 cm²/Vs, and a relatively low total
surface concentration $n_{\text{surf}} = n_{\text{surf}} \times d_{\text{surf}} = 2.4 \times 10^{12}$ cm⁻².
In sample B, the surface scattering is much stronger, since
the mobility is much smaller, and the sheet carrier density,
$n_{\text{surf}} = 1.9 \times 10^{13}$ cm⁻², is much larger, even though the
surface layer is thinner. From the above analyses, we con-
clude that these changes in the surface layer may be respon-
sible for the significantly decreased spin coherence time in
ZnO after 500 °C-annealing. The spin coherence difference
between samples B and C (~2.3 versus ~2.0 ns) is small
comparing to that between samples A and B (~11.2 versus
~2.3 ns). In sample C, $n_{\text{surf}} = 8.7 \times 10^{12}$ cm⁻², which is
also larger than in sample A, and based on a simple compari-
sion of $n_{\text{surf}}$ values alone, sample C should have a longer $T_2^*$
than that of sample B. However, it also may be important
that $d_{\text{surf}}$ is larger in sample C than in sample B, and, thus,
the spins spend more time in the relatively poor surface
region. The slightly poorer crystallinity of sample C than B
may also contribute to the small difference in $T_2^*$. Based
on the PL analyses, the donor state $N_{D1}$ in Table II is associ-
ated with hydrogen (H) and group-III elements (Al/Ga/
In), while the acceptor state $N_A$ is possibly due to Zn
vacancies. Loss of H after annealing is observed for the
dominating PL peak red shifts, which is commonly observed in
ZnO samples annealed at temperatures above 500 °C. The
reason of formation of surface conducting layer on top of the
bulk ZnO with decreased mobility and increased shallow-donor concentration after annealing is most likely to be the surface accumulation of group-III ele-
ments (Al/Ga/In) during annealing, indicated by PL spectra,
which is consistent with previous secondary-ion mass spec-
troscopy studies. The possible dominating spin de-coherence
mechanisms were discussed in the supporting materials (ref. 17).

In summary, time-resolved-Kerr-rotation pump-probe
magneto-optical spectroscopy was employed to investigate the
spin dynamics in ZnO single crystal samples before and after
annealing. It is observed that the spin coherence time ($T_2^*$)
in unannealed ZnO sample is as long as ~11.2 ns at 8.5
K, but significantly decreases to ~2.3 ns after 500 °C anneal-
ing. X-ray rocking curves and atomic force microscopy con-
firm that the crystallinity and surface roughness do not change appreciably during annealing and, thus, are not re-
sponsible for the spin-coherence degradation. Temperature-
dependent Hall effect measurements indicate that the anneal-
ing-induced spin coherence degradation is likely due to
decreased mobility and increased carrier concentration in the
thin conducting layer on the surface of the bulk ZnO.

This work was supported by ONR/DMEA (HQ0003-08-2-
0803) through the Center for Nanomaterials and Nanodevi-
ces (CNN). The work of DCL was supported by AFOSR
Grant FA9550-10-1-0079 (K. Reinhardt) and NSF Grant
DMR0803276 (L. Hess).