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Structural and chemical characterization of Co-doped ZnO layers grown on Si and sapphire

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Motivation

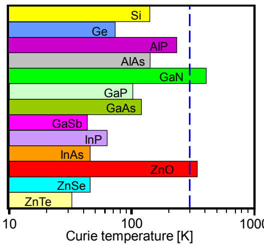


Fig. 1. Computed values of the Curie temperature for various p-type semiconductors containing 5% Mn and 3.5 x 10^{20} holes per cm^3 [1]

- Calculated Curie temperature for p-type compositions doped with 5% Mn (see Fig. 1) → ZnO is a candidate for ferromagnetism above room temperature (doping with e.g. Co or Mn)
- Origin of ferromagnetism is still unclear, experimental results are spreading widely → growth of Co:ZnO layers on Si and Al_2O_3 and correlation of magnetic properties with microstructure/microchemistry

Sample preparation and characterization

- Radio-frequency sputtering from a composite ZnCo target (90:10 wt.%) at 500 °C

Substrate	Si(001)	Si(001)	Sapphire(0001)	Sapphire(0001)
Atmosphere	Ar oxygen-poor	Ar/O_2 oxygen-rich	Ar oxygen-poor	Ar/O_2 oxygen-rich
Post-annealing	no	no	750 °C, 3 h, vacuum	550 °C, 2 h, 1 bar O_2

- Conventional and high-resolution TEM (CTEM/HRTEM), selected-area electron diffraction (SAED) at a Philips CM 200 FEG/ST
- Electron energy loss spectroscopy (EELS) and energy-filtered TEM (EFTEM) using a LEO 922 Omega and a Philips CM 20 FEG / GIF 200
- Magnetic-field measurements by SQUID magnetometry

Characterization of $Zn_{0.94}Co_{0.06}O$/Si(001)

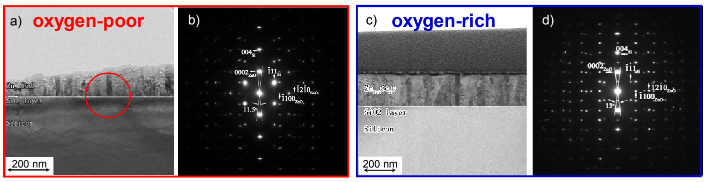


Fig. 2. a) Cross-section TEM-BF image of the O-poor $Zn_{0.94}Co_{0.06}O$ layer, b) SAED pattern of the region marked with a circle in Fig. 2a, c) TEM-BF image of the O-rich sample, and d) SAED pattern

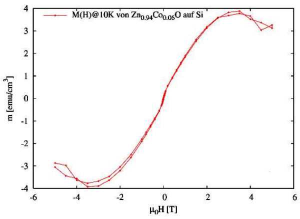


Fig. 3. SQUID measurements of the O-poor $Zn_{0.94}Co_{0.06}O$/Si sample

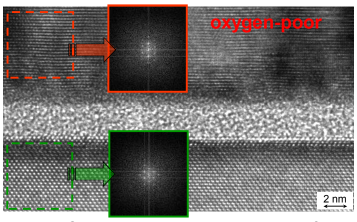


Fig. 4. Cross-section HRTEM image of the Co:ZnO/Si interface region (oxygen-poor sample)

- Similar morphology of O-poor and O-rich $Zn_{0.94}Co_{0.06}O$ layers on Si: columnar growth of ZnO (0001) // Si(001) in the direction normal to the surface with a deviation angle less than ~ 5° ; existence of some 30° rotation domains between ZnO [11-20] and ZnO [10-10]
- Presence of Co-rich regions within the Co:ZnO layer of the O-rich sample → identification of CoO supported by O-K ELNES (cf. Fig. 5)
- Paramagnetic behavior by SQUID experiments [2]

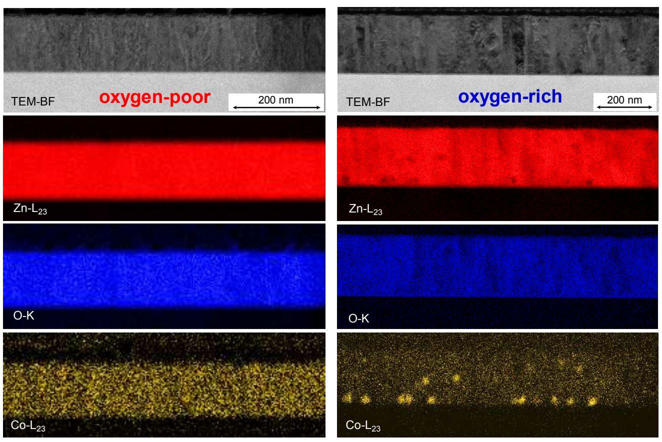
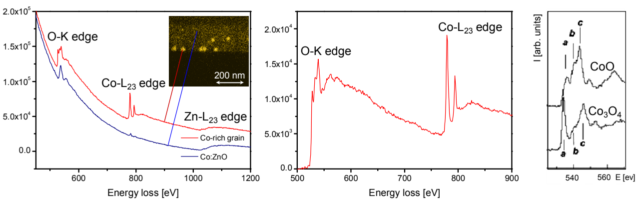


Fig. 5. Element distributions as revealed by EFTEM in the O-poor (left column) and O-rich (right column) samples, EELS analyses (lower row) of the Co-rich regions and O-K ELNES of CoO and Co_3O_4 (lower right) [3]



Characterization of $Zn_{0.94}Co_{0.06}O$/sapphire(0001)

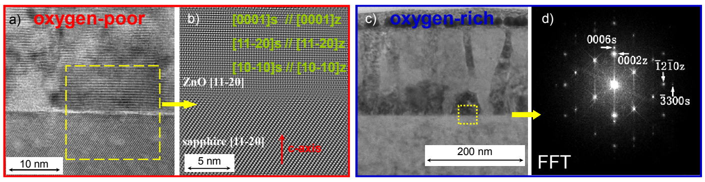


Fig. 6. a) HRTEM image of the Co:ZnO/Al_2O_3 interface region (O-poor) and b) FFT-filtered detail, c) TEM-BF image of the O-rich $Zn_{0.94}Co_{0.06}O$ layer, d) FFT pattern from the selected area of c)

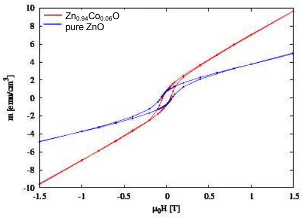


Fig. 7. Comparison of SQUID results from an O-poor $Zn_{0.94}Co_{0.06}O/Al_2O_3$ sample and a 150 nm thick ZnO layer

O-poor $Zn_{0.94}Co_{0.06}O$ layers on sapphire:

- Main orientation relationship is [11-20]ZnO//[11-20]Al_2O_3 (~ 90%)
- Homogeneous Co distribution

O-rich $Zn_{0.94}Co_{0.06}O$ layers on sapphire:

- Orientation relationships are [10-10]ZnO//[11-20]Al_2O_3 (~ 80%) and [11-20]ZnO//[11-20]Al_2O_3 (~ 20%)
- 95% of the dark regions belong to ZnO domains with [10-10] orientation
- Extended Co-rich regions

Evidence of ferromagnetic behavior for annealed O-rich sample by SQUID (*but also for pure ZnO on Al_2O_3*), paramagnetism for as-prepared O-poor sample

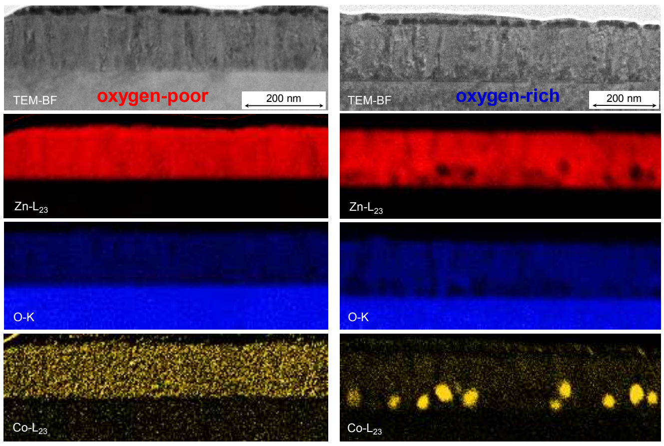


Fig. 8. Energy-filtered TEM images of the O-poor and O-rich $Zn_{0.94}Co_{0.06}O/Al_2O_3$ samples

Conclusions

- Detection of CoO regions for Co:ZnO layers grown under O-rich conditions – presumably no influence on ferromagnetism
- Ferromagnetism for $Zn_{0.94}Co_{0.06}O$/sapphire (but also for ZnO/sapphire), paramagnetism for $Zn_{0.94}Co_{0.06}O$/Si
  → strong dependence of magnetic properties on substrate
  → necessity of further investigations

References

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