



Ion implantation of Gd⁺, Er⁺ and Au⁺ into various crystallographic cuts of ZnO – structural and photoluminescence properties

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Zinc oxide (ZnO) is a wide-bandgap semiconductor ($E_g \approx 3.3$ eV) hexagonal crystal with low phonon energy and very good physical and chemical stability [1]. Nowadays, ZnO crystal material is broadly studied in photonics for many applications. Doping of ZnO with various ions follows mainly two different motivations: enabling either new optical properties or new magnetic properties of the modified ZnO crystal. In this contribution, we report on the results of ion implantation of Gd⁺, Er⁺ and Au⁺ ions accelerated to 400 keV into the single-crystal ZnO wafers with <0001> crystallographic orientation (the implanted samples were subsequently annealed in oxygen). Ions used in this study were chosen for their different chemical nature as well as specific use in science and industry – erbium belong to the rare earth elements used for photonics and optical telecommunications, gadolinium is used because of its magnetic properties and gold is used in bio-applications. We focused particularly on the relationship between the two main intrinsic luminescence bands of ZnO – NBE peak and DLE band at around 375 and 530 nm, respectively. We studied in detail the possibility of controlling the luminescence properties of ZnO by varying the position of the short-wavelength bands.

EXPERIMENTS

Substrates

- Single crystalline **zinc oxide (ZnO)** wafers with <0001> crystallographic orientation

Ion implantation

- Implanted ions **Gd⁺, Er⁺, Au⁺**
- Beam energy **400 keV**
- Fluences **5.0×10^{14} - 5.0×10^{15} ions/cm²**

MEASUREMENTS

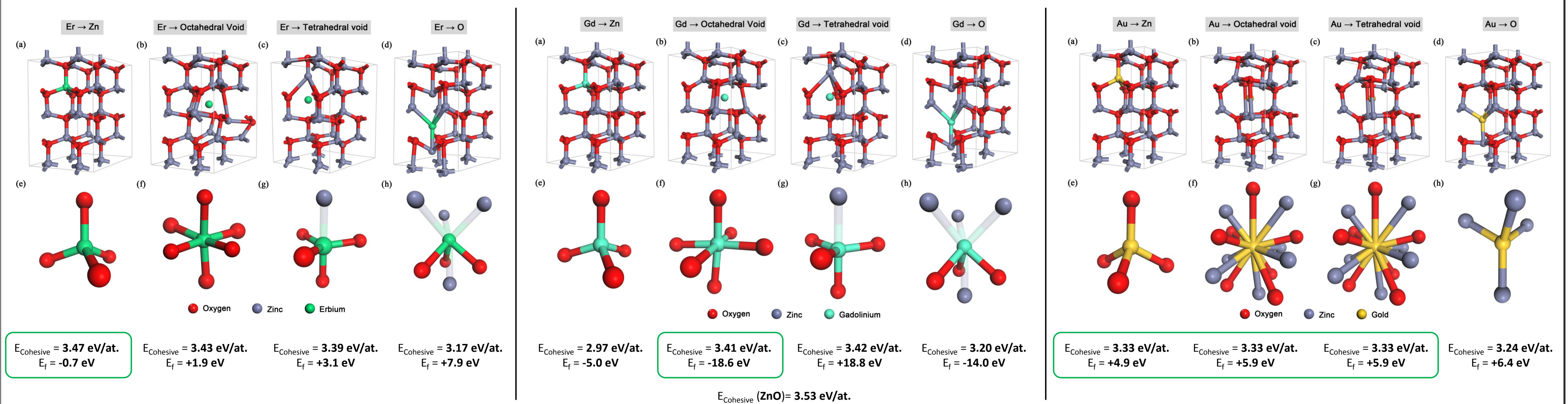
- Rutherford Backscattering Spectrometry (RBS)** – Er concentration depth profiles, Er positions, degree of damage
- Photoluminescence (PL) spectroscopy VIS/NIR** – intensity of luminescence in the visible and near-infrared spectral regions
- Theoretical DFT calculations**
- Used programs: CASTEP [2] and Accelrys Materials Studio

Er:ZnO

Gd:ZnO

Au:ZnO

Theoretical results – DFT calculations (geometry optimization of local structure around Er, Au, Gd)

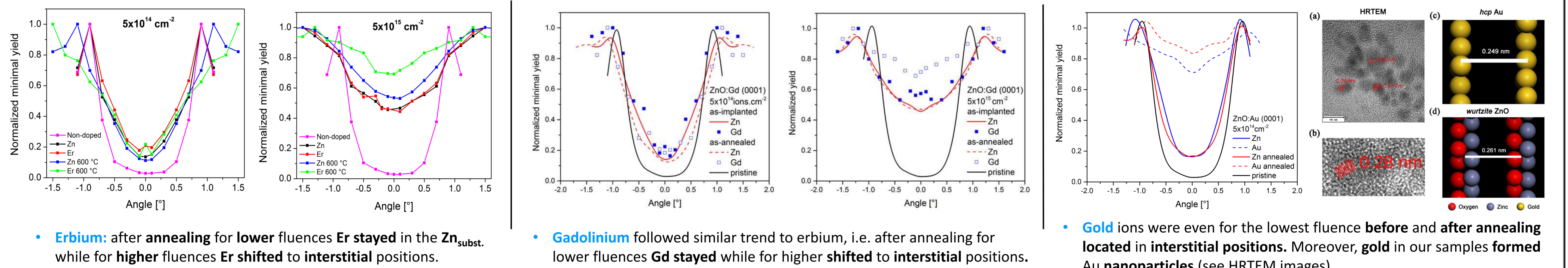


- Erbium:** geometry optimizations showed that Er will be most probably located in **substitutional position of Zn** (or alternatively V_{Oct}).

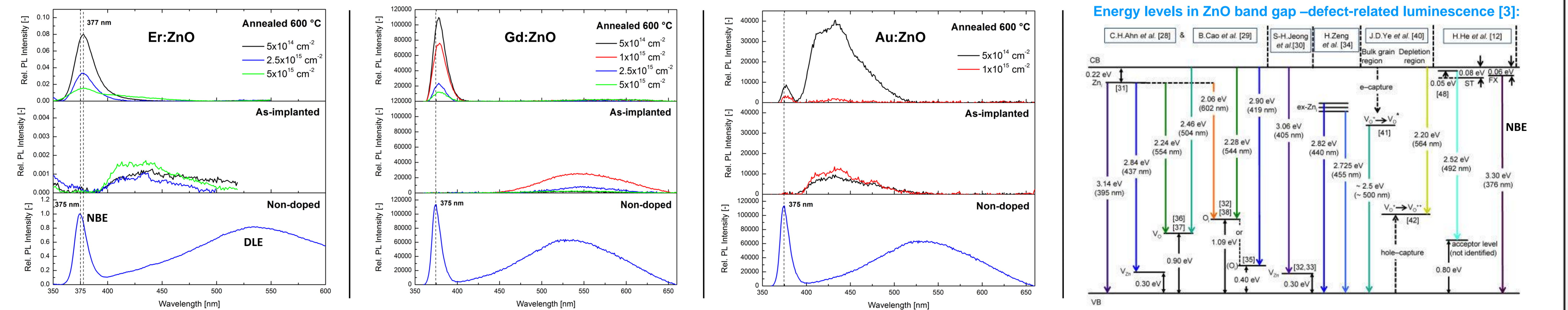
- Gadolinium:** theoretical calculations showed that Gd will be most probably located in **octahedral void** (or alternatively Zn_{subst}).

- Gold:** theoretical calculations showed that Au will be located in all four positions with the same (**low**) probability, i.e. Au is practically inert.

Experimental results – Fine scans of RBS Channeling (positions of Er, Au and Gd ions in the ZnO structure)



Experimental results – Photoluminescence spectra (luminescence of Er-, Au- and Gd-doped ZnO samples)



CONCLUSIONS

- According to the theoretical simulations and experimental angular scans, **erbium and gadolinium** ions in the single-crystal ZnO will most probably be located in the **Zn substitutional positions and large octahedral voids**. **Gold** ions showed their inert behaviour – **no preferential position** from simulations and measurements.
- Annealing** caused movement of all three ions from substitutional to interstitial positions which was more prominent for higher implantation fluences.
- The structural damage of ZnO was increasing with increasing implantation fluence in the range of approx. **10–30%**.
- Due to inert noble-metal behaviour of Au (i.e. no willingness to form bonds with oxygen atom in ZnO), the **Au nanoparticles** were detected by HRTEM measurements.
- Ion implantation** caused vanishing of luminescence of ZnO (mainly excitonic NBE peak), while after annealing at 600 °C in oxygen the excitonic peak of ZnO recovered. Samples with Au ions differed from Er and Gd samples in that **Au samples** had emission band at around 430 nm which can possibly be assigned to formation of vacancies and interstitials (Zn and Au).

References:

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