Effects of Mn Doping on ZnS and CdS Quantum Dot Inks

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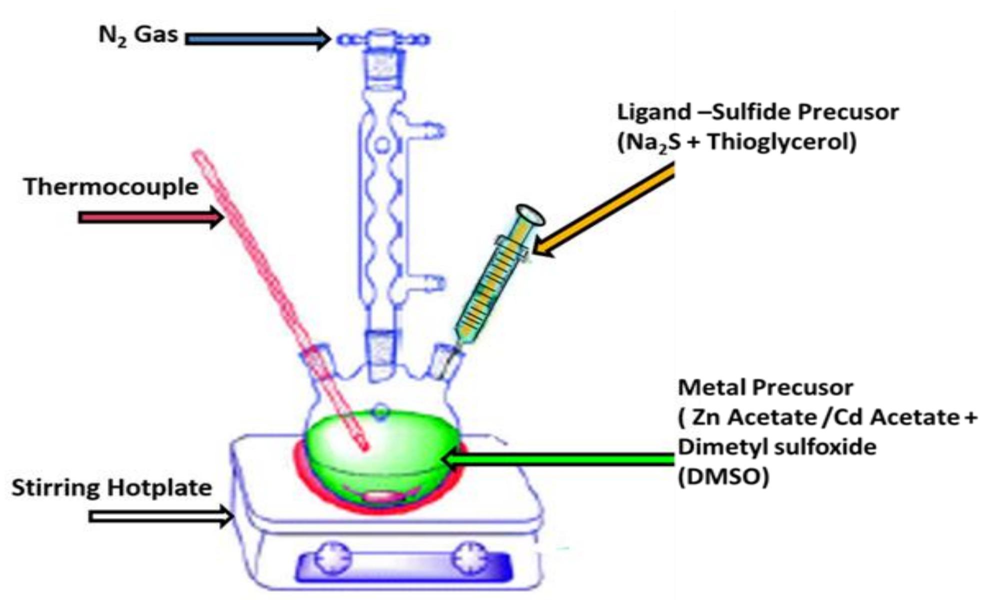
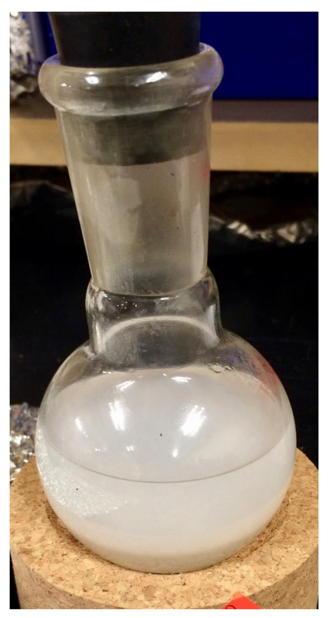
Motivation

Device performances of semiconducting quantum dots solar cells can be improved by doping the quantum dots with transition metals [1,2]. It is a useful method for further tailoring the band gap of quantum dots beyond just changing the size [3]. Understanding the mechanism of how these transition metals influence the electronic band structure is vital for obtaining precise doping control. Moreover introducing transition metals, which are magnetic materials, into semiconductor quantum dots may exhibit non conventional magnetic properties compared to their bulk counterparts. Here we explore the effect of Mn doping on the band structure and the magnetic properties of ZnS and CdS quantum dot inks for applications in inkjet printing of solar cells.

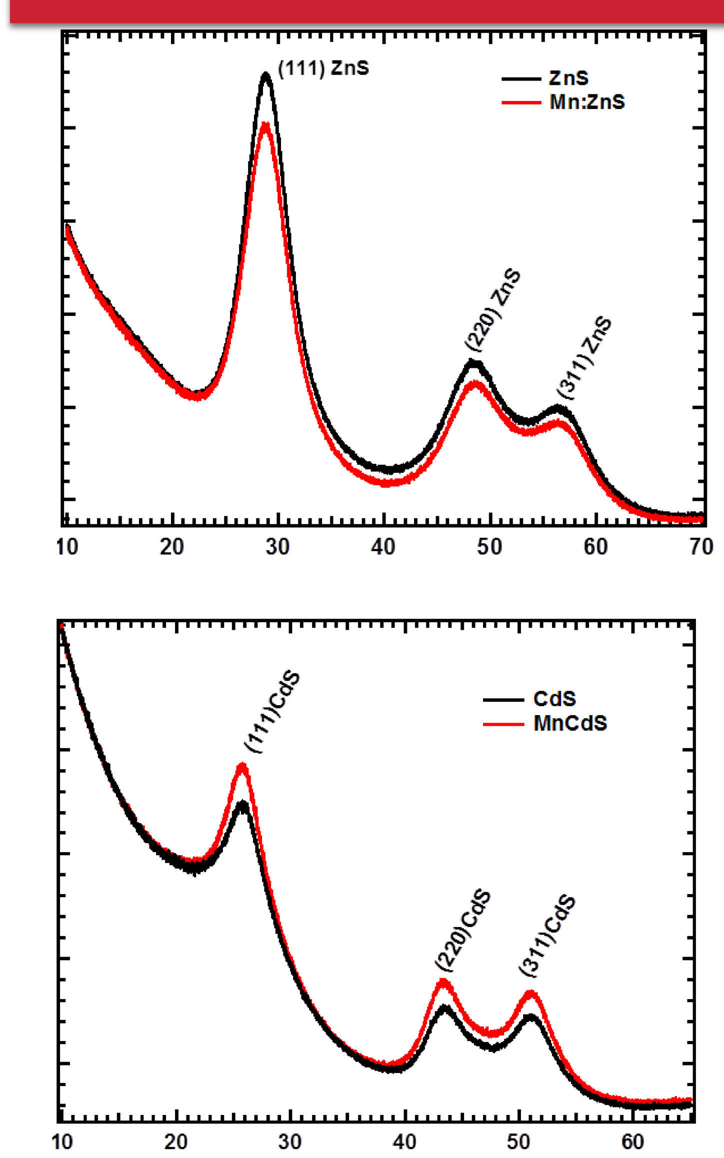
Quantum Dot Ink Synthesis



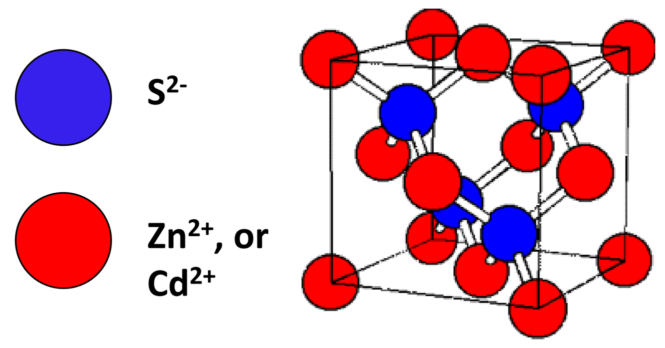


- Zn/Cd Acetate was dissolved in DMSO and then 1-thioglycerol was added dropwise.
- Mixture heated to 60-70^0 C, constant stirring, aqueous Na_2S solution is injected
- Heated for 9 hours with constant stirring.
- Acetone is added to precipitate out ZnS/CdS quantum dots.
- Precipitate is rinsed and centrifuged with methanol and isopropanol three times each.
- A quantum dot ink is created and drop cast onto a Si (001)
- Mn doped ZnS/CdS were synthesized by adding Mn Acetate to the solution of ZnS/CdS acetate solution.

X-ray Diffraction



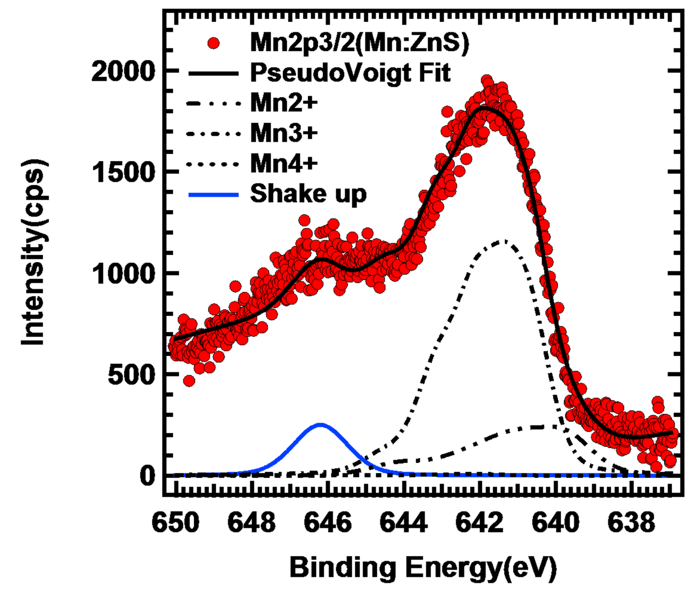
Zinc Blend Structure

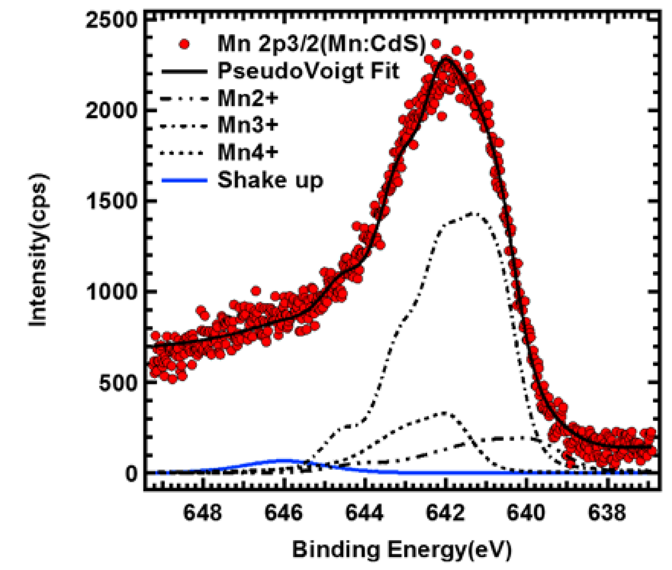


For both undoped and doped systems in ZnS and CdS XRD shows a zinc-blend structure (space group F43m) with broad peaks

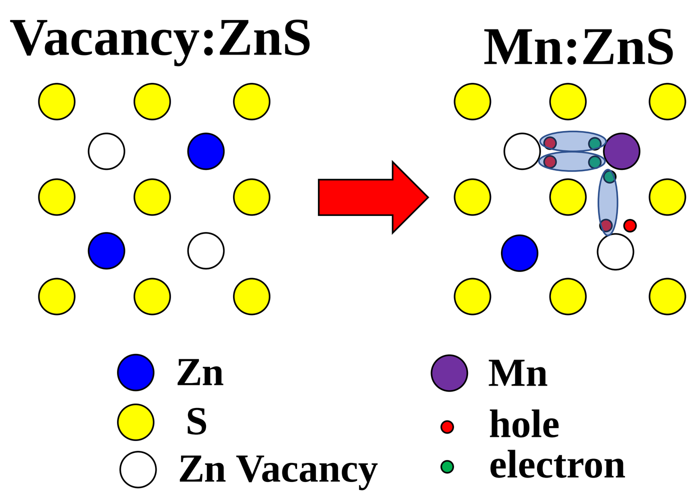
It is important to notice that upon Mn doping the crystal structure, size, and lattice constants remain mostly unchanged for both the ZnS and CdS systems. Therefore any changes in electronic properties will not be related to changes in structure, size, or lattice constants

XPS Measurements



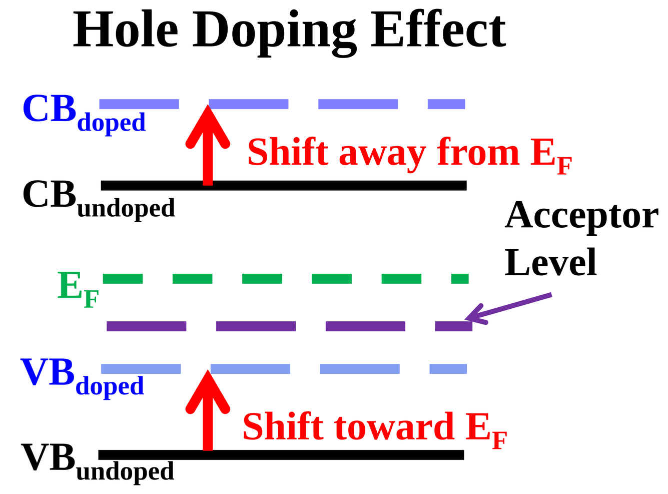


X-ray photoemission spectroscopy measured for both Mn:ZnS (left) and Mn:CdS (right), Mn is present in multiple oxidation states, namely Mn 2+, Mn 3+, and Mn 4+, where the majority of Mn is in the 3+ state.

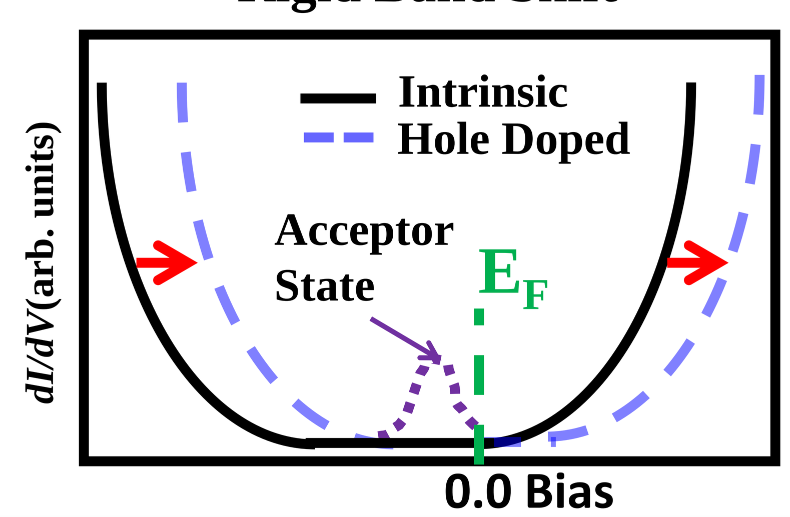


- Mn^{3+} states substitute the Zn^{2+} states giving excess electrons. But there are Zn vacancies in ZnS lattice which has holes and the excess electron will cancel out with some of these holes giving excess holes.
- The conduction band should shift away from the Fermi level. Hence if we do STS measurements then it should show us rigid band shift and hole doping effect

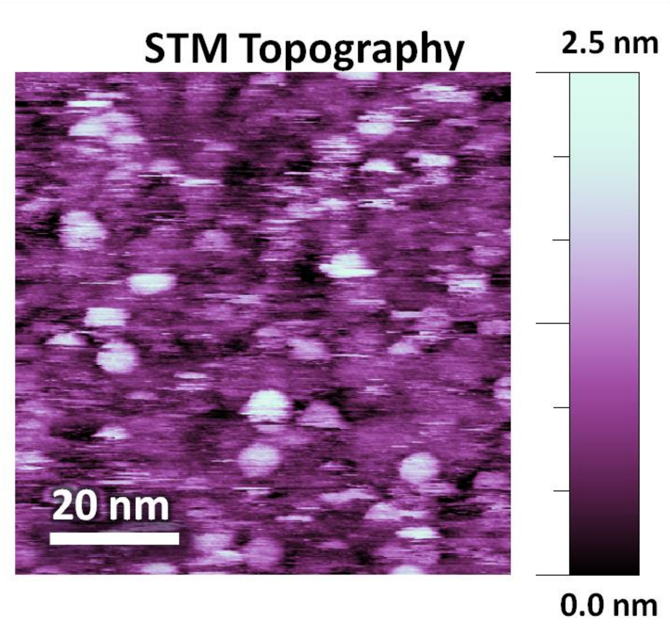
Hole Doping Effect

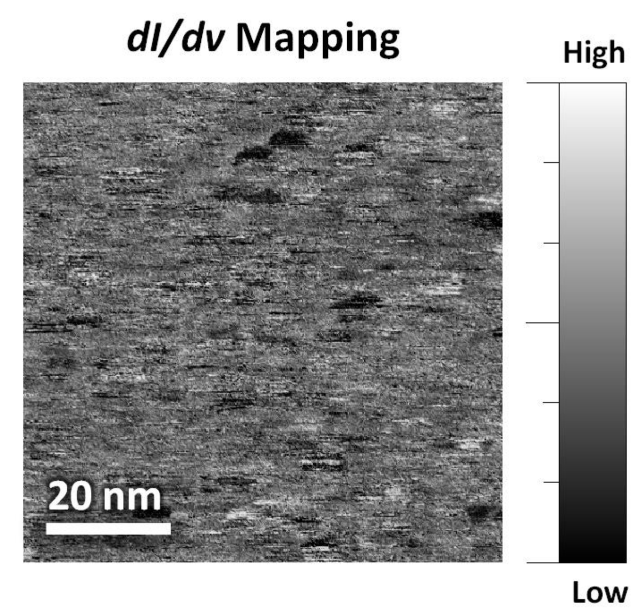


Rigid Band Shift

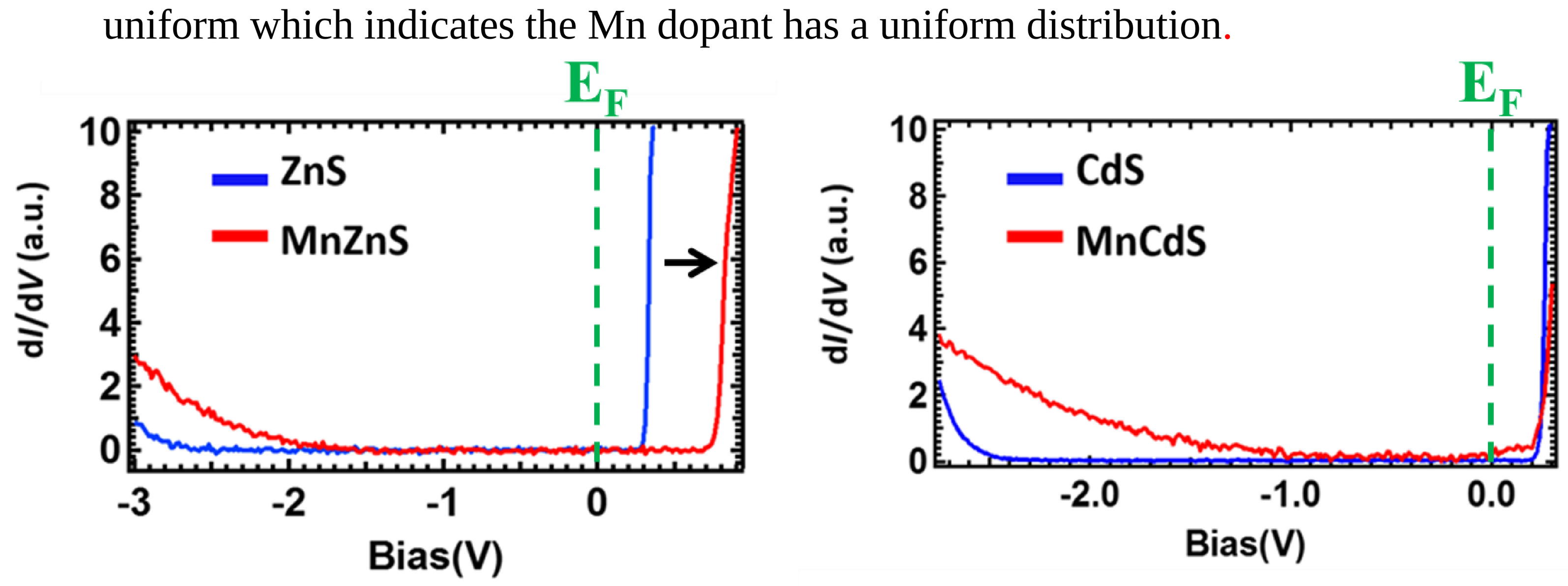


STM/S Measurements



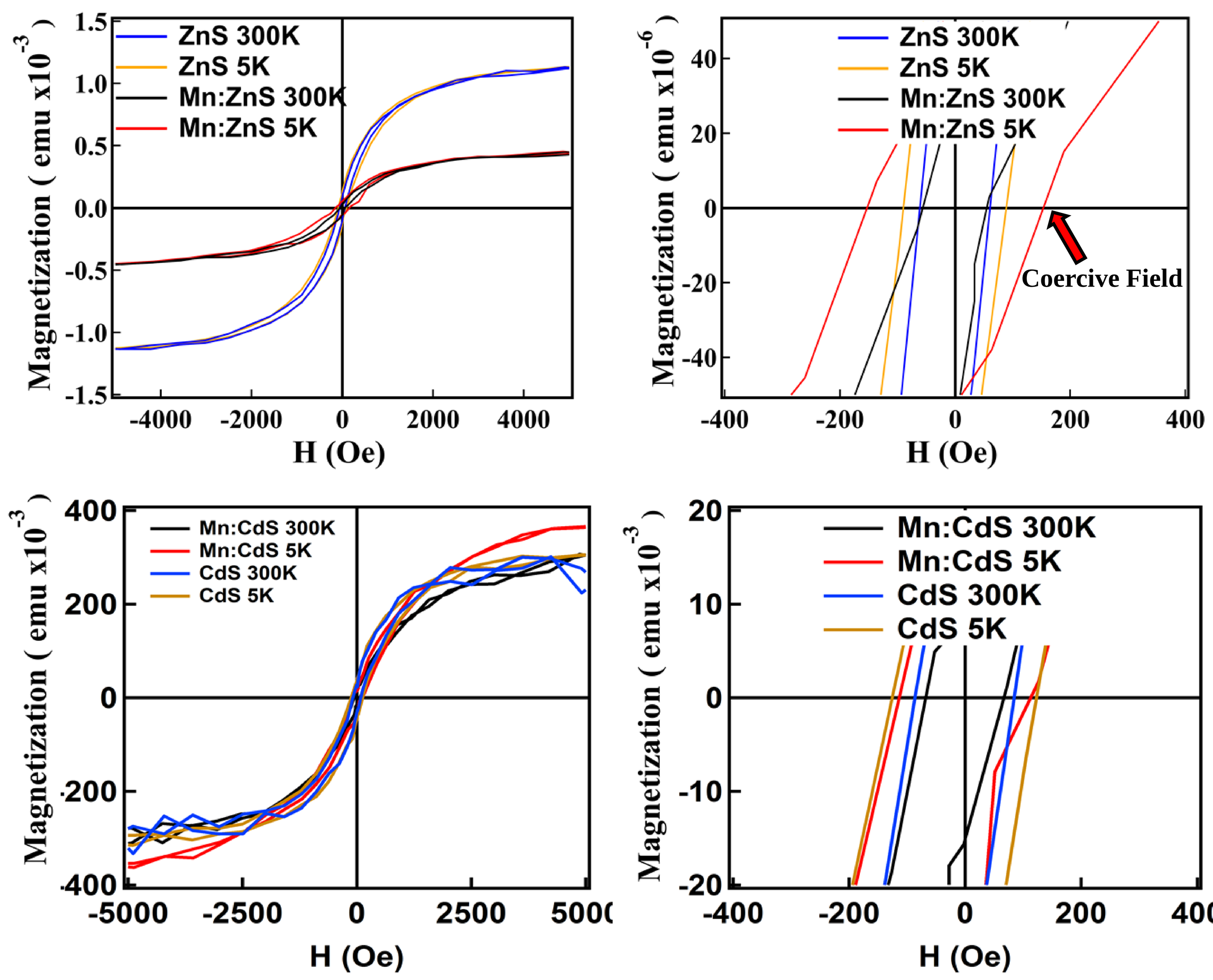


The STM topography for both ZnS and CdS indicates that the quantum dots are similar in size between both systems and the density of states mapping appears uniform which indicates the Mn dopant has a uniform distribution.

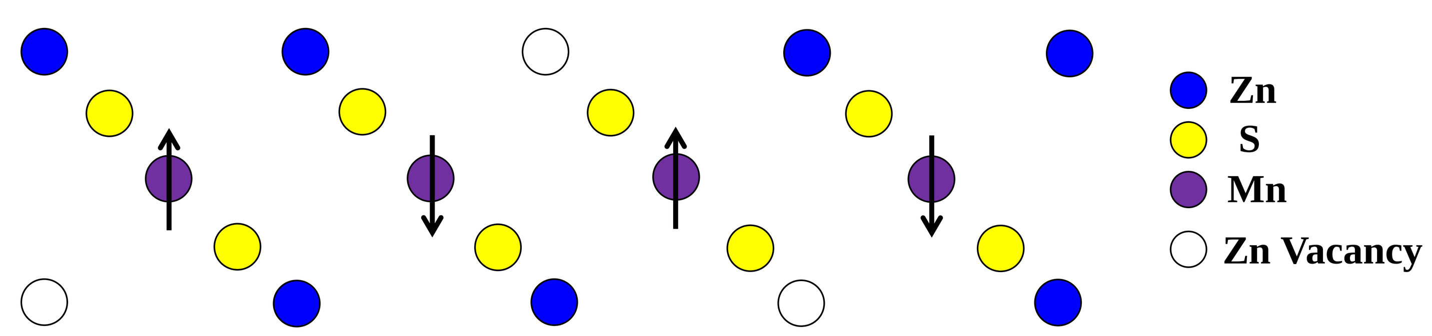


A rigid band shift was observed in Mn:ZnS where as no band shift was observed in Mn:CdS. Rigid band shift in Mn:ZnS is due to the hole doping mechanism. No band shift was observed in Mn:CdS and this is due to the strong sp-d hybridization in CdS which is the dominant effect on the band structure rather than the hole doping effect.

Magnetic Properties



ZnS and CdS are known to exhibit d^0 ferromagnetism due to vacancy formation. When we doped these QDs with Mn , the ferromagnetism of the ZnS QDs reduces but the doping in CdS has no effect. Looking closer at the coercive field shows that the doped ZnS has a much larger coercive field suggesting a large anisotropy barrier in Mn:ZnS. The large anisotropy barrier and the reduce magnetization suggest that the Mn-Mn interaction is anti-ferromagnetic.



Conclusion

•This study has shown that upon Mn doping the electronic band structure of ZnS experiences a rigid band shift due to a hole doping mechanism and Zn vacancy formation where as in CdS no rigid band shift is observed.

•The magnetization of Mn:ZnS reduces upon doping where as there is no much change in the magnetization of Mn:CdS. Suggesting antiferromagnetic alignment of Mn-Mn nearest neighbors.

•The oxidation states of a transition metal dopant play a major role in tailoring band gap properties and magnetic properties in dilute magnetic semiconductors

Acknowledgements

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Nebraska MRSEC

Nebraska Public Power District

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