Copper doping of epitaxial Se-based quantum dots and quantum wells

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Motivation:

Observation of a strong spin-exchange interaction between paramagnetic Cu^{2+} dopants and the band carriers in copper-doped chalcogenide nanocrystals (Pandey, A. *et al.*, Nature Nanotechnology **2012**, 7, 792) has given raise to explore diluted magnetic systems based on Cu^{2+} magnetic ions.

In this work, CdSe:Cu/ZnSe quantum dots (QDs) and (Zn,Cd)Se:Cu/ZnSe quantum wells (QWs) are grown by molecular beam epitaxy. The aim of our investigations is to identify Cu-related optical transitions and determine whether Cu-ions are in the magnetic +2 or non-magnetic +1 charge state

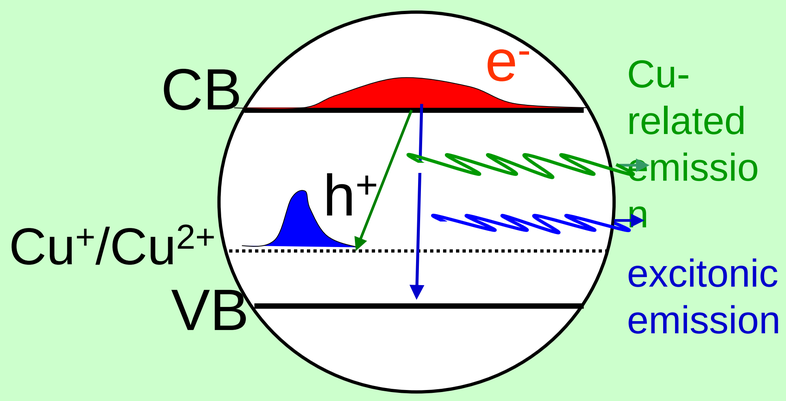

Figure 1 Schematics of the Cu related emission when Cu level lies within the energy gap. The conduction band (CB) electron recombines with the hole strongly localized on Cu^{+2} ion.
e.g. Knowles KE *at al*. Chemical Rev. 116, 10820 (2016)

Excitonic emission

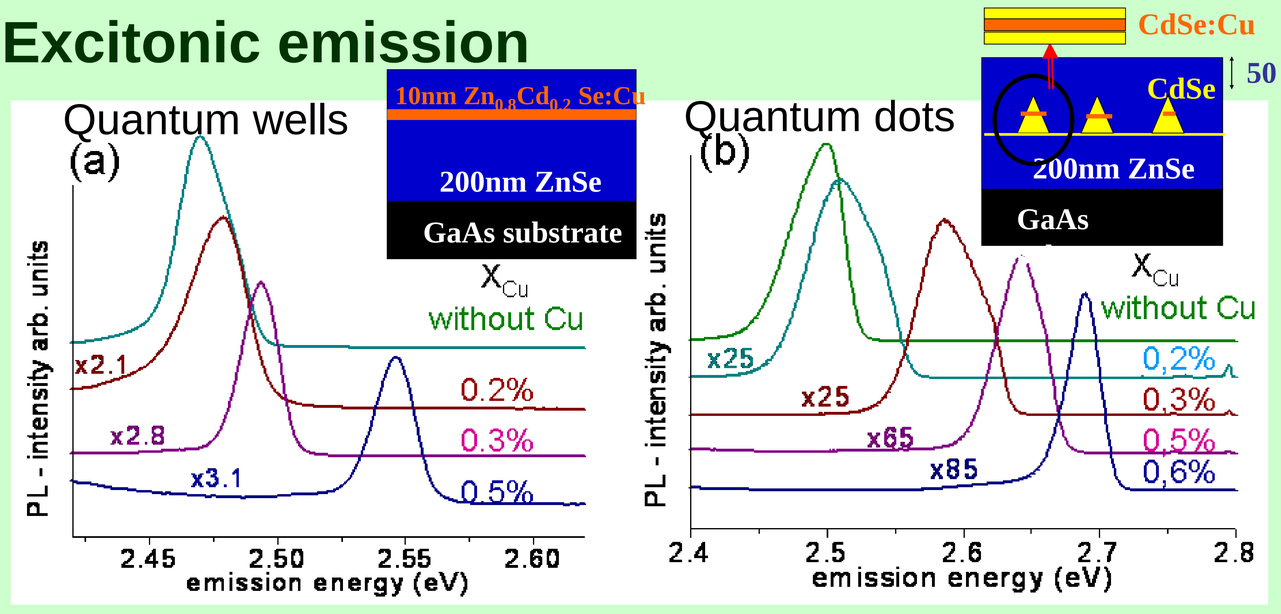

Figure 2. Normalized photoluminescence (PL) spectra from various samples containing (a) (Zn,Cd)Se:Cu QWs embedded in ZnSe and (b) CdSe:Cu/ZnSe QDs. Cu-concentration is controlled by Cu flux. The normalization factor is given for each spectrum, which indicates a significant quenching of the luminescence in the presence of copper. T = 5 K, excitation – 405nm

Identificaton of Cu-related emission

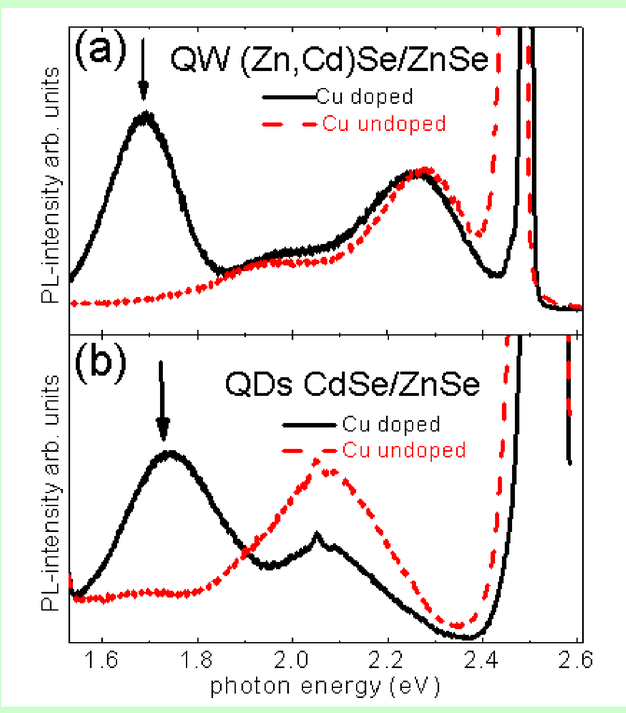

Figure 3. Comparison of the optical emission from Cu-doped and undoped structures, which leads to the identification of Cu-related optical emission from (a) ZnCdSe:Cu quantum wells with Cu content of 0.2% and (b) CdSe:Cu/ZnSe quantum dots with Cu content of 0.3%. The arrows indicate the emission showing up in the presence of Cu dopants. T=5K, excitation with 405 nm and 474 nm laser for (a) and (b), respectively.

Magneto-Photoluminescence

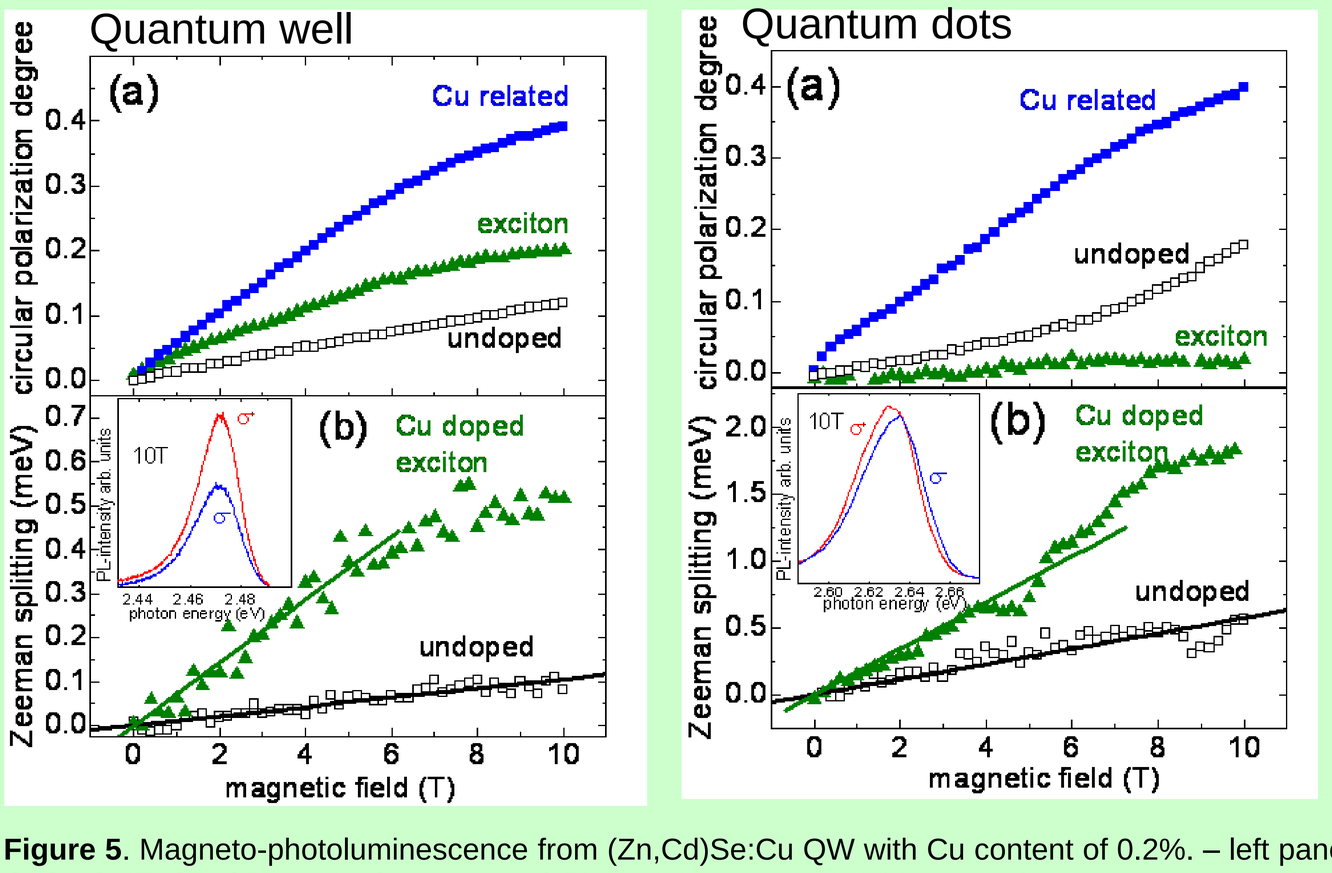

Figure 5. Magneto-photoluminescence from (Zn,Cd)Se:Cu QW with Cu content of 0.2%. – left panel and CdSe:Cu/ZnSe QDs with Cu content 0.5% - right panel (a) Magnetic field dependence of circular polarization degree for Cu-related (blue rectangles) and excitonic emission (green triangles) and for a udoped reference sample (empty black rectangles) (b) Zeeman splitting of the excitonic emission for Cu doped (green triangles) and undoped (empty black rectangles) QWs and QDs. Inset: PL-spectra for the Cu-doped structures at 10 T in both circular polarizations. T = 2 K, excitation 405 nm laser line, excitation power 100 μW , magnetic field applied in Faraday configuration, perpendicular to the sample surface.

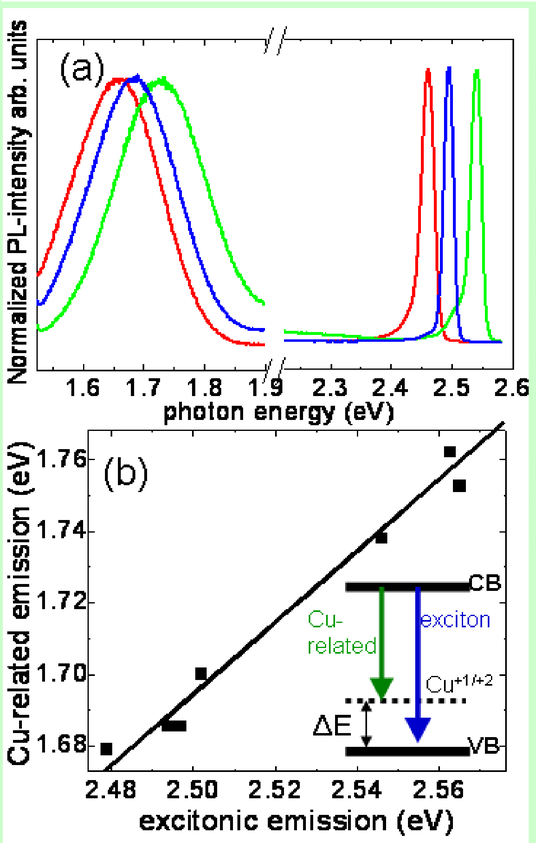

Figure 4. Correlation between the excitonic and Cu-related emission energy in (Cd,Zn)Se:Cu quantum wells. (a) normalized photoluminescence spectrum in Cu-related and excitonic emission from 3 quantum wells with different Cu concentrations (b) Cu-related emission energy plotted vs. excitonic emission energy for 7 different quantum wells with different Cu concentrations and quantum well widths. Cd content is always 0.2. Solid line represent a linear fit with the slope of 1 showing that the spectral distance between these two energies is **ΔE = 805 meV.** T=5K, excitation 474 nm laser diode

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Time resolved photolumiescence

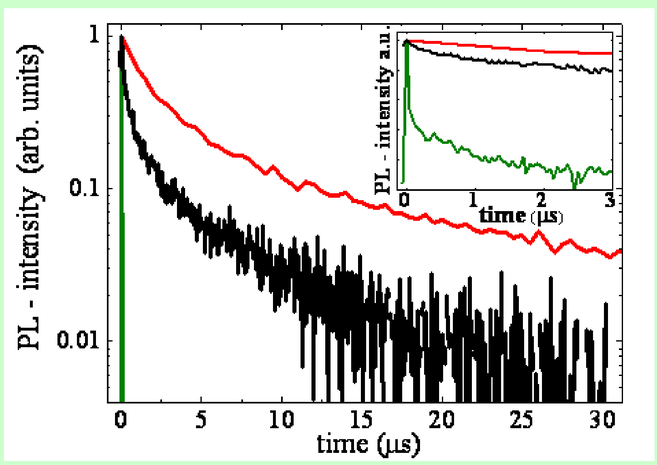

Figure 6. PL-decay times of the excitonic emission (green), Cu-related emission (red) in ZnCdSe:Cu QW with Cu content of 0.2% and Cu related emission from CdSe:Cu QDs with Cu content of 0.5% (black curve). Inset: close-up of PL at short delays. T = 5 K, excitation energy 405 nm.

Summary

✓ A significant blue shift of the emission energy from CdSe:Cu/ZnSe QDs and (Zn,Cd)Se:Cu/ZnSe QWs with an increasing Cu content is observed. The maximum value of this shift amounts to 220meV for CdSe quantum dots and 90 meV for (Zn,Cd)Se quantum wells

✓An additional emission line spectrally below the excitonic emission appears in the presence of copper within the structures. The energy of this Cu-related emission is strongly correlated to the energy of excitonic emission. The separation energy of these two emissions amounts in our case to 0.8 eV independently on their absolute values.

✓According to the well-established mechanism for Cu-related emission which involves recombination of the conduction band electron with a hole strongly localized on a copper ion (Figure 1), we may conclude that the majority copper ions are in +1 oxidation ground state, which after optical excitation changes to +2 paramagnetic state.

✓It is possible that some copper ions might be also in +2 oxidation state without optical excitation and give rise to an small increase of the Zeeman splitting of the excitonic emission due to sp-d exchange interaction (Figure 5b).

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