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

P. Wojnar^{*}, Ł. Kłopotowski, M. Wiater, K. Fronc, J. Mikulski, J. Kossut

Institute of Physics, Polish Academy of Sciences, Al Lotników 32/46, 02-668 Warsaw, Poland

II-VI semiconductor nanostructures doped with copper attract a great interest because they combine the unique optical properties of copper-doped semiconductors with the spectral tunability of nanostructures [2]. Moreover, recent observation of a strong spin-exchange interaction between paramagnetic Cu^{2+} dopants and the band carriers in copper-doped chalcogenide nanocrystals has given raise to explore diluted magnetic systems based on Cu^{2+} magnetic ions [1]. All these effects have been intensively studied in colloidal nanocrystals. On the other hand, the properties of Cu-doped epitaxial nanostructures, such as quantum dots and quantum wells are less explored.

In this work, we report on the optical properties of copper doped (Zn,Cd)Se/ZnSe quantum wells (QWs) and self assembled CdSe/ZnSe quantum dots (QDs) grown by molecular beam epitaxy. All these structures are characterized by low temperature photoluminescence and micro-photoluminescence. First of all, we observe that the copper doping has a significant impact on the excitonic emission energy from QDs and QWs despite of a relatively low Cu concentrations inside of them (a few percent). The energy shift can be as large as 200 meV for CdSe QDs and 80 meV for (Zn,Cd)Se quantum wells. The origin of this unusual effect is still not clear until now. Most likely, the presence of copper changes slightly the lattice constant of the host semiconductor and induces an additional strain, which affects the emission energy from the nanostructures.

Beside excitonic luminescence an additional emission related directly to the presence of cooper appears. From the study of several (Zn,Cd)Se:Cu/ZnSe quantum wells with various thicknesses, copper and cadmium concentrations, it is found that the Cu related emission appears always about 805meV below the excitonic emission. The explanation of this effect relies on the fact, well established for colloidal nanocrystals, that Cu-related emission originates from a recombination of a hole trapped on a cooper level with a conduction band electron. In the first approximation, in which the copper level is pinned relative to vacuum, this energy corresponds to the spectral distance between the copper level and the top of the valence band.

In an external magnetic field applied in Faraday configuration, excitonic- and Cu-related emission from cooper-doped quantum wells exhibit both an increase of the circular polarization. The degree of circular polarization increases almost linearly with an increasing magnetic and depends strongly on the temperature of the measurement. The lower the temperature the faster the increase of the circular polarization degree. These features can be explained in terms of exchange interaction induced singlet-triplet splitting of the electron- and Cu^{+2} -spin similar to the case of colloidal Cu-doped nanocrystals [1].

Moreover, we observe that the spectral width of the copper related emission is usually significantly larger then the spectral width of the excitonic emission and amounts typically to about 150meV. It is, most likely due to electron phonon coupling of the strongly localized the hole, which includs an anticipated Jahn-Teller effect. The decay of Cu-related emission is highly non-exponential with typical life-time values of several of micro-seconds. It is, therefore, one order of magnitude larger than for colloidal nanocrystals which reflects most likely a relatively weak overlap of electron wave-function with localized copper-ions in quantum wells (in comparison to nanocrystals).

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[2] Pandey, A.; Brovelli, S.; Viswanatha, R.; Li, L.; Pietryga, J.; Klimov, V., I; Crooker, S. *Nature Nanotechnology* **2012**, 7, 792