Understanding structure-property relationships for multicomponent colloidal quantum dots: the case of quaternary Cu-Zn-In-Se system

Maksym Yarema,[a] Nuri Yazdani,[a] Nikola Dordevic,[a] Weyde M. M. Lin,[a] Olesya Yarema,[a] Deniz Bozyigit,[a] Petr Khomyakov,[b] Mathieu Luisier,[b] Vanessa Wood[a]

[a]*Laboratory for Nanoelectronics, Department of Information Technology and Electrical Engineering, ETH Zurich, CH-8092 Zurich, Switzerland*
[b]*Nano TCAD Group, Department of Information Technology and Electrical Engineering, ETH Zurich, CH-8092 Zurich, Switzerland*

For multicomponent quantum dots (QDs), composition-dependent tuning of properties is superimposed on quantum confinement effects stemming from QD size. The I-II-III-VI group semiconductor QDs represent excellent playground with broad miscibility ranges for binary chalcogenides and relatively large Bohr exciton radii, enabling both composition- and size-dependent properties for QDs < 5 nm. In addition, certain compositions allow particular orderings of cations and vacancies within the lattice (*i.e.*, ordered vacancy compounds, OVCs).

Here we present our investigation of the composition-dependent properties of quaternary Cu-Zn-In-Se (CZISe) colloidal QDs. [1] We employ an amide-promoted synthesis, which can provide independent composition and size control for multicomponent chalcogenides. [2] Applying the same reaction conditions, and varying the amount of introduced metal salts, we are able to vary the composition of CZISe QDs over a broad range while keeping constant QD size (D_{QD} = 3.3 nm, see Fig. 1). This allows us to map optical and structural properties as a function of CZISe QD composition, such as lattice constant, optical band gap, PL peak position, or PL quantum yield (see Fig. 1). We find that the PL quantum yield peaks at a composition close to $Cu_5Zn_2In_{11}Se_{21}$. Experimental and theoretical work suggests that the high PL efficiency of this composition originates from the fact that it belongs to a family of OVC structures with parent ternary composition of $Cu_2In_4Se_7$ and $^1/_7$ concentration of atomic vacancies on cation site. These results can provide better understanding of structure-property relationships for multicomponent QDs and ultimately guide the development of materials with optimized optical and electronic properties.

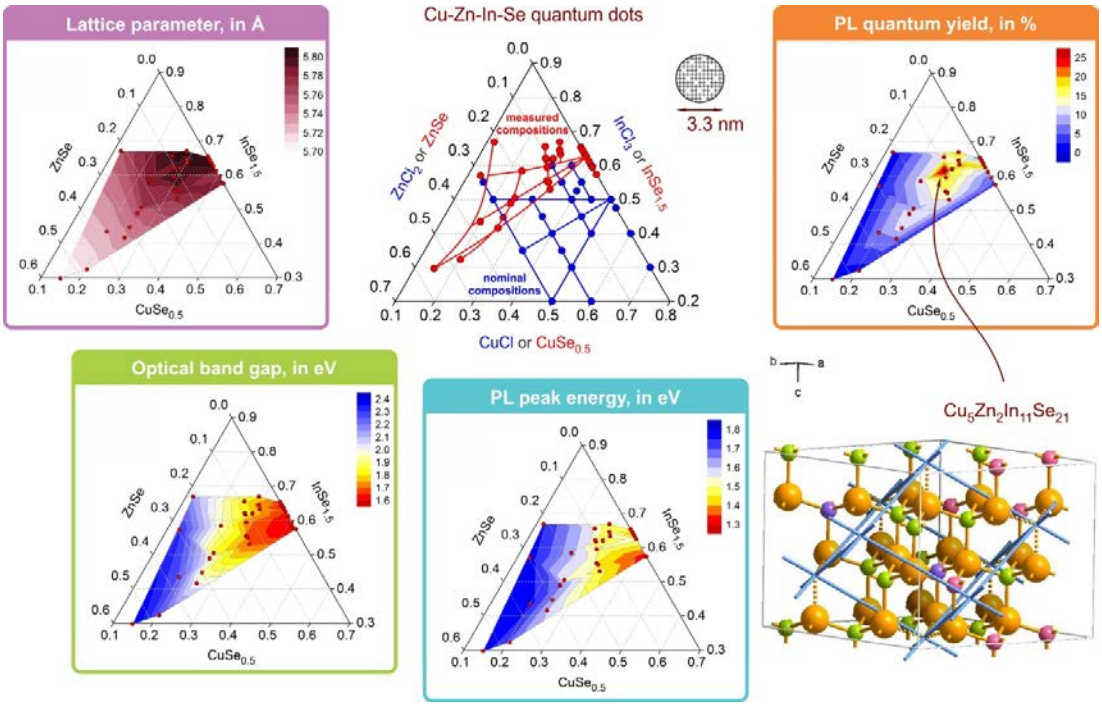

Fig. 1 Quasi-ternary $CuSe_{0.5}$-ZnSe-$InSe_{1.5}$ diagrams, showing nominal and obtained compositions for 3.3 nm in size Cu-Zn-In-Se quantum dots as well as property maps for cubic lattice parameter (in Å), optical band gap energy (in eV), photoluminescence peak energy (in eV), and photoluminescence quantum yield (in %). Calculated structure of $Cu_5Zn_2In_{11}Se_{21}$ quantum dots (*i.e.*, which exhibit the most efficient photoluminescence) is a rhombohedral sublattice of cationic vacancies (blue net) and particular ordering of cations (Cu in red, Zn in purple, In in pink).

[1] M. Yarema *et al*., *in preparation*.
[2] O. Yarema *et al*., *ACS Nano*, **2015**, *9*, 11134.