Effect of strain and surface proximity on the acceptor grouping in ZnO:N

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The experimentally observed two types of photoelectron spectra of different crystallites in ZnO:N indicate the grouping of acceptor and donor complexes in separate domains [1]. Density Functional Theory (DFT) studies suggest that the acceptor domains can involve zinc vacancy (V_{Zn}) and -$(NHx)_O$ groups and provide complexes-related acceptor states near the valence band maximum. However, the formation energies of these complexes are relatively high, and the acceptor-related sample properties in general depend on a number of factors such as growth or annealing conditions [2]. As the formation of defects involves distortion of the crystal lattice, it may be assumed that micro-strain plays an important role here.

DFT study of the effect of strain and surface proximity on the formation of (V_{Zn}) -$(NHx)_O$ complexes was performed using QUANTUM-ESPRESSO package [3] within the generalized gradient approximation (GGA) with the Hubbard-like +U term describing the on-site Coulomb interactions. The formation of complexes require the migration of the constituent defects and was computed using the Nudged Elastic Band (NBE) approach under (a) tensile and compressive biaxial strains in planar plane and along z-axis, (b) hydrostatic pressure, (c) local lattice distortion provoked by uncontrolled impurities as CH_x groups, and finally (d) surface proximity. In the last case, defects were introduced into the 0D nanocrystal object, as quantum dot (QD). DFT results indicates a strong strain effect on the electronic structure and activation of migration energy (E_A). In particular, 4% compressive biaxial strain reduced migration barrier of zinc vacancy moving around $(NH)_O$ from 0.65 eV to 0.24 eV. Moreover, the presence of a CH_x group near the complex lowers this value to zero. The effect of strain explains lowering of acceptor formation energy and might be also responsible for grouping of acceptors which can be formed only in crystallites showing compressive strain. In support to the DFT results, low-temperature cathodoluminescent CL maps reveal more intensive acceptor CL for the higher average micro-strain values.

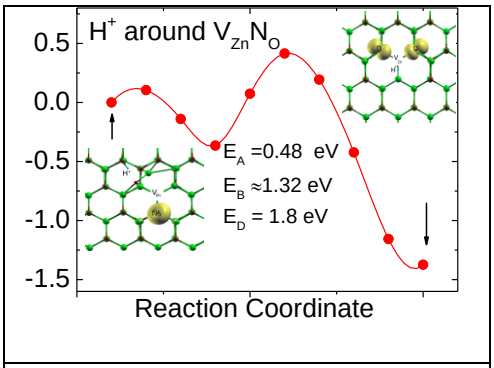

Fig. 1 The calculated energy profiles of the migrating H^+ along VN. The energy zero is set to the initial configurations. E_A, E_B, and E_D are activation, binding, and dissociation energies, respectively.

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