水中光合成による ZnO/CuO ナノフォレストの作製と光機能発現の解明

The origin of opto-functional enhancement in ZnO/CuO nanoforest structure fabricated by submerged photosynthesis

北大電子研[1]，北大工(院生)[2]，北大工[3]　○ジェーム メルバート[1]，高橋 優樹[2](D3)，張 麗華[3]，渡辺 精一[3]

Hokkaido Univ. ○Melbert Jeem[1], Yuki Takahashi(D3)[2], Lihua Zhang[3], Seiichi Watanabe[3]

E-mail: m_jeem@es.hokudai.ac.jp

When two semiconductors' surface are joint, each of their Fermi energy (E_F) levels must equilibrate, leading to interface-induced gap states (IFIGS) or band bending, where the charge neutrality reside ~10meV above the E_F level. In the case of ZnO/CuO, the charge neutrality theory determines the Schottky barrier height, in which however has been consistently aggravated by interface dipole feature[1]. This is caused by the ionic and/or chemical potentials difference between the lattices, inherited from defects, lattice mismatch, and impurity during its atomic configuration. This research addresses those aspects in order to elucidate the origin of opto-functional properties in ZnO/CuO hetero-nanostructure.

Herein, a hetero-epitaxial ZnO/CuO nanoforest (NFRs) growth was demonstrated by a galvanic submerged photo-synthesis (G-SPSC) method[2,3], which utilizes light illumination in pure water. The method incorporates both galvanic reactions and photo-induced water splitting for ZnO nanorods growth on a CuO surface. We observed an interesting physical characteristic at the interface: ZnO(001)/CuO(001) planes linkage were established, even though with 13.62 – 28.15 % local lattice discrepancies along the *c* axis. Further, ternary oxide $ZnCuO_2$, zinc interstitial (I_{Zn}) and oxygen vacancies (V_O) were found. Meanwhile, the NFRs exhibited emission at 650 – 700 nm and absorbance at 450 – 500 nm.

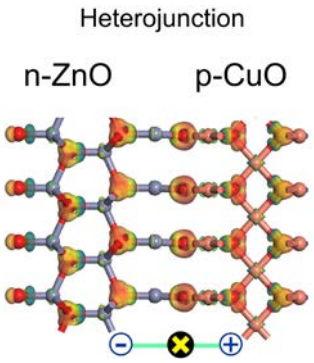

Fig. 1. Electrons distribution at ZnO/CuO interface.

To relate those physical characteristics to its optical properties, we conducted a first ZnO/CuO interface *ab initio* calculation. We perceived a prevailing Jahn-Teller distortion from CuO→ZnO electrons transfer under equilibrium E_F. Complemented by STEM-VEELS measurements, electrons occupancy at Cu 3*p* was responsible for 2.0 eV peak of the interface absorption coefficient. In particular, an interface dipole under interface-induced gap states (IFIGS) was clarified, caused by quasi defects zinc antisite (Zn_O). This led to an incommensurate charge density (ICCD) for a coherent ZnO(001)/CuO(001) interface (Fig. 1). This is the origin for the opto-functional enhancement of the ZnO/CuO NFRs, where a maximum 12 % IPCE at 550 nm, a 20 % increase from similar NFRs morphology was demonstrated.

1) J. Tersoff, *Phys. Rev. B*, **30**, 4874-4877 (1984). 2) Y. Takahashi *et al.*, *Appl. Surf. Sci.*, **489**, 313-320 (2019). 3) Y. Takahashi *et al.*, *Appl. Mater. Today* accepted (2022).