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Interface Electronic Structures in Two-dimensional Perovskites: Focusing on Doping and Energy Level Alignment

Kitae Kim[1,2], Yeonjin Yi[1], Soohyung Park[2,3]

[1] Department of Physics, Yonsei University, Seoul 03722, Republic of Korea

[2] Advanced Analysis & Data Center, Korea Institute of Science and Technology (KIST), Seoul 02792, Republic of Korea

[3] Division of Nano & Information Technology, KIST School, University of Science and Technology (UST), Seoul 02792, Republic of Korea

In the last several years, two-dimensional halide perovskites (2DHPs) have been established as one of the central materials in perovskite research. 2DHPs possess a characteristic layered structure in which perovskite layers, composed of metal-halide octahedra, are intercalated by spacer layers consisting of large organic molecules. This structure results in fascinating optical and electronic properties where the small electronic dispersion in the vertical direction contributes to a relatively larger band gap and higher exciton binding energy in comparison to 3DHPs. Moreover, this structure also effectively prevents the infiltration of moisture and oxygen, providing 2DHPs with enhanced environmental stability. Due to the many advantages mentioned above, interface engineering using 2DHPs has become the prevailing trend in the latest perovskite devices. For example, the 2D/3D structure, where a 2DHP layer caps a 3DHP layer, has been established as one of the mainstream approaches for fabricating perovskite solar cells.

Although the importance of 2DHP interfaces keeps growing, understanding of interfaces in 2DHPs remains lacking. The presence of the organic spacer layer makes the valence and conduction bands of 2DHPs exist discretely within a hybrid multiple quantum well structure, preventing direct contact with adjacent layers. This suggests that interfaces involving 2DHPs exhibit significantly different characteristics compared to conventional semiconductor interfaces. Hence, the following two aspects should be understood for further development: (i) How can the energy levels of 2DHPs be modified to achieve favorable alignment? (ii) How does the energy level alignment of 2DHPs occur and what factors influence it?

Here, we show a series of studies relevant to this topic that were recently carried out by us using photoelectron spectroscopy. First, to address the abovementioned aspect (i), we

attempted surface transfer doping on a 2DHP, by depositing organic dopants. Couple of kinds of p-type and n-type dopant were stepwise deposited onto the 2DHP film for energy level control by extracting and injecting electrons, respectively. The resulting changes in the electronic structure were meticulously observed. We found that electron extraction not only shifts the energy levels but also enhances surface stability. The deposition of a p-type dopant leads to a surface passivation effect which rapidly suppresses surface metallic lead defects caused by photo-induced degradation, and also prevents future degradation. Whereas, electron injections have the opposite effect, deteriorating the surface crystal structure. The n-type dopant also shifts the energy levels as the p-type dopant does. However, it seems to cause metallic lead defects and create new chemical states on the 2DHP surface. This result suggests that doping in 2DHPs is effective, while it should be approached in a judicious manner as it may induce additional effects. Second, to address the aspect (ii), we investigated the energy level alignment of 2DHPs. We selected a series of 2DHP films with different kinds of organic spacers. Here, the organic spacers belonging to the same functional group but differing in size were selected to induce a gradual variation in structural properties. By fabricating these on various substrates at various thicknesses, we analyzed band bending at the interface. As a result, we observed the relationship between trends in energy level alignment and the organic spacer.

We believe these findings can expand the fundamental understanding of interfaces in 2DHPs, highlighting the impact of doping on electronic structure and energy level alignment, which are considered crucial for advancing optoelectronic devices in related fields.