Electronic structure of the $Bi_4V_2O_{11}$ (001) surface by ARPES

Univ. of Tsukuba[1], IMSS, KEK[2], SOKENDAI[3] ○(D)Jiaqi Liu[1], Kenichi Ozawa[2,3], Kazuya Tajima[1], Namiki Uezono[1], Muhammad Monirul Islam[1], Kazuhiko Mase[2,3], and Takeaki Sakurai[1]

E-mail: s1936008@s.tsukuba.ac.jp

$BiVO_4$ is one of the most widely investigated photoanode catalysts for water splitting to produce O_2[1]. $Bi_4V_2O_{11}$ is composed of the same elements as $BiVO_4$ but exhibits different photocatalytic performance[2]. To elucidate the factors that play an essential role in the photocatalytic process, the electronic-structure understanding of the $Bi_4V_2O_{11}$ surface is adequate. Until now, the theoretical study based on the density functional theory[2] has predicted a direct bandgap nature of $Bi_4V_2O_{11}$. However, since experimental verification of the $Bi_4V_2O_{11}$ surface is insufficient, the current study provides a basis for understanding the relationship between the surface electronic structure and photocatalysis.

A single-domain $Bi_4V_2O_{11}$ film was deposited on the Nb-doped STO (001) substrate by RF-sputtering. We characterized the $Bi_4V_2O_{11}$ (001) surface by low-energy electron diffraction (LEED) and angle-resolved photoemission spectroscopy (ARPES) at BL-3B of the Photon Factory. The results show that the clean crystal surface exhibits a $\frac{\sqrt{2}}{2} \times \frac{\sqrt{2}}{2} R45°$ pattern (Figure 1b), consistent with the (001) orientation of the surface (Figure 1a). The valance band maximum (VBM) is composed of a hybrid state between the Bi 6s lone pair states and O 2p states[3]. This antibonding state is remarkable in $Bi_4V_2O_{11}$, which causes the shift of VBM to a lower binding energy position compared with $BiVO_4$. The ARPES results reveal that the Γ point is the local maximum of the VBM (figure 1c), which is consistent with the theoretical calculation[2]. By fitting the dispersion, the effective mass of the hole was obtained as 7.13 ± 0.60 m_e. This huge effective mass could be considered as one reason for unsatisfactory photocatalytic performance.

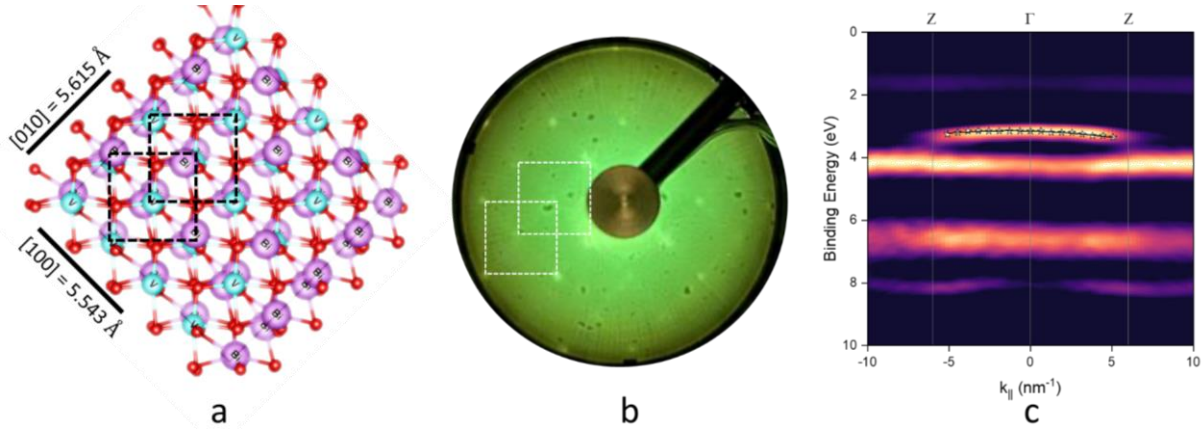

Figure 1. (a) Structure of $Bi_4V_2O_{11}$ (001) surface. (b) The LEED pattern (76 eV) displaying a $\frac{\sqrt{2}}{2} \times \frac{\sqrt{2}}{2} R45°$ pattern. (c) The representative ARPES image along the ΓZ direction measured with 59 eV photons.

References

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