Research Group for Nanoscale Structure and Function of Advanced Materials

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Macroscopic matter is assembly of microscopic matter and functional materials, whose characteristics are exposed by investigation of both local and whole state. An experimental technique that can be used to selectively investigate a local state can extend the field of materials research. Existing technical developments enable us to efficiently produce high-intensity beams of muons, positrons, neutrons, and ions, which are useful for studying various atomic structures and dynamics of functional materials at the length scale of advanced beams. In addition, experiments that can obey local states at surface, interface, or around impurity have been developed as well, and they can be used to obtain new scientific insights. Our objectives are to study the nanoscale structures and functions of materials, and develop advanced measurement technologies.

Hydrogenation and hydrogen diffusion at the anatase TiO_2(101) surface [1]

Titanium dioxide (TiO_2) has fascinating properties that enable hydrogen sensors and photocatalytic water splitting. Since both phenomena are accompanied by proton motion and electron transfer, it is important to understand the behaviour of hydrogen and its associated effects on the electronic structure of TiO_2 surfaces in order to elucidate the mechanism behind the hydrogen-induced phenomena.

We have studied the hydrogenation of anatase TiO_2 surfaces by irradiation with low-energy hydrogen ions. After 500-eV hydrogen ion irradiation, an in-gap state was formed at about 1 eV below the Fermi level with a downward band bending as shown in the inset of Fig. 1, suggesting formation of a small polaron state. This is in contrast to the H adsorption on the anatase surface, where no small polaronic state was observed, probably because of oxygen vacancy formation under H ion irradiation.

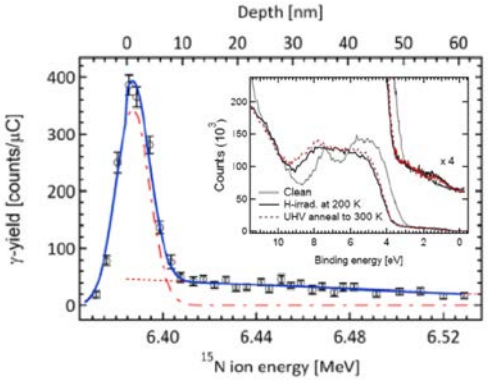

Fig. 1 Depth profile of H measured for anatase TiO_2(101) after H ion irradiation at 200 K. Inset: Ultraviolet photoemission spectra of clean TiO_2(101), after H ion irradiation at 200 K and subsequent annealing at 200 K.

Nuclear reaction analysis with $^1H(^{15}N,\alpha\gamma)^{12}C$ shows that the H depth profile reveals a maximum at a depth of about 1 nm with an enhanced intensity corresponding to 11.8 ML. In addition to the surface peak, the H depth profile exhibits a broad distribution extending to 50 nm with an average concentration of 0.8 at. % indicating substantial diffusion of H at 200 K. The diffusion coefficient is analysed to be 2.7×10^{-13} m^2s^{-1} from the H depth profile. This value indicates that H diffusion is much faster in anatase TiO_2 than in rutile TiO_2.

Magnetic structure and phase transition at the surface region of Fe_3O_4(100) [2]

Magnetite (Fe_3O_4) is a ferrimagnet, where spin 5/2 at the tetrahedral (A) site is antiferromagnetically coupled with spin 5/2 and 3/2 at the octahedral (B) site with a curie temperature of 858 K. Lowering of symmetry at surfaces exerts significant effects on the magnetic properties at surfaces such as spin orientation and phase transition, because the exchange interaction and magnetic anisotropy at surfaces are modified as compared to the bulk.

We have investigated the magnetic structure and phase transition of the near-surface region of Fe_3O_4 with Conversion Electron Mössbauer spectroscopy (CEMS) (inset of Fig. 2) and theoretical calculations. It is revealed that at 300K the magnetization is in-plane in the surface region and cants from the in-plane to the ⟨111⟩ direction in a deeper region suggesting the presence of a noncollinear magnetic structure in the near-surface region. From the temperature dependence of the internal magnetic field obtained from the CEMS (Fig. 2), the critical exponents for the tetrahedral and octahedral sites are estimated to be 0.24±0.01 and 0.28±0.01, respectively, suggesting two-dimensional features for the magnetic phase transition at the surface.

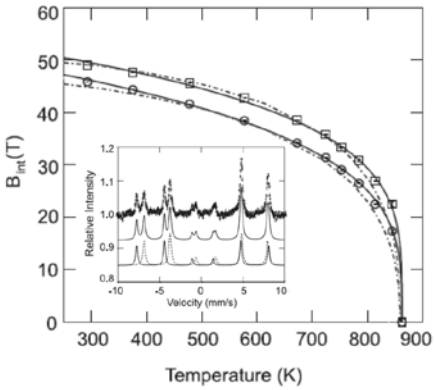

Fig. 2 Temperature dependence of the internal magnetic fields at the A (□) and B (○) sites. Solid curves are fits, and the dash-dotted curves are the data taken from the bulk data. Inset: CEMS spectrum taken for the Fe_3O_4 surface with fits shown by solid and dashed curves below.

References

[1] N. Nagatsuka et al., J. Chem. Phys. 152, 074708 (2020).
[2] T. Kawauchi et al., J. Phys. Commun. 4, 115001 (2020).