Operando Spectroscopic View for Thin Film Gas Sensors

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Chemical reactions at surfaces have been widely used for chemical processes such as catalytic synthesis, energy conversion, environmental cleanup, and sensor. Surface science techniques enable us to understand physicochemical fundamental processes on surfaces. We have developed some in situ / operando experimental techniques for observing surface reactions on gas/solid interfaces. We have focused on the development and understanding of gas sensing materials to detect small molecules such as hydrogen, by ambient pressure X-ray photoelectron spectroscopy (AP-XPS). The experiments were carried out at a beamline BL-13 at the Photon-Factory of High Energy Accelerator Research Organization (KEK-PF). An important technical point of the AP-XPS system is that the high-pressure chamber, where quasi-atmospheric gases are introduced, and the electron analyzer are separated by a small aperture and pumped by a differential pumping system. Recently, a sensor material has been developed that can detect H_2 gas in air and breath with high sensitivity (1 ppm) using nanometer-thick platinum-based thin films for example Pt-Rh alloy. The Pt-Rh sensor detects the atmospheric concentration of H_2 gas by changing in electric resistivity ($\Delta R/R_0$). We have conducted operando AP-XPS measurement coupled with resistivity measurement for H_2 sensing Pt-Rh thin-film sensor. As a result, the resistivity decreases with exposing H_2 gas to the sensor surface, whereas it increases with exposing O_2 gas. It was found that corresponding Rh 3d and Pt 4f XPS change depending on background gas conditions. Before the gas dosing, the surface was dominated by Rh oxide. When the surface was exposed to the H_2 gas, the chemical state clearly changed. The Rh oxide was completely reduced to the metallic state. When, the surface was exposed to the O_2 gas, the oxygen-induced species grew up again. Those findings indicate the surface chemical state strongly relate to the material functions.

Keywords [optional]: Ambient-pressure XPS, gas sensing materials, thin films, electric resistance.

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