

Deoxygenation of IrO₂(1 1 0) Surface: Core-level Spectroscopy Study

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The core level spectra of Ir-4f during IrO₂(110) deoxygenation are measured after thermal reduction in UHV, and analyzed with DFT computation. The XPS spectra of increasing reduction level were taken at 130 eV, as shown in Fig. 1. The Ir-4f_{7/2} binding energy downshifts from 62.0 eV to 61.2 eV, as the reduction temperature increases. The signal of 1f-cus-Ir can be observed in the 383 K baked-out surface. Both of Ir⁰ and Ir⁴⁺ bulk features are present on the two partially reduced surfaces.

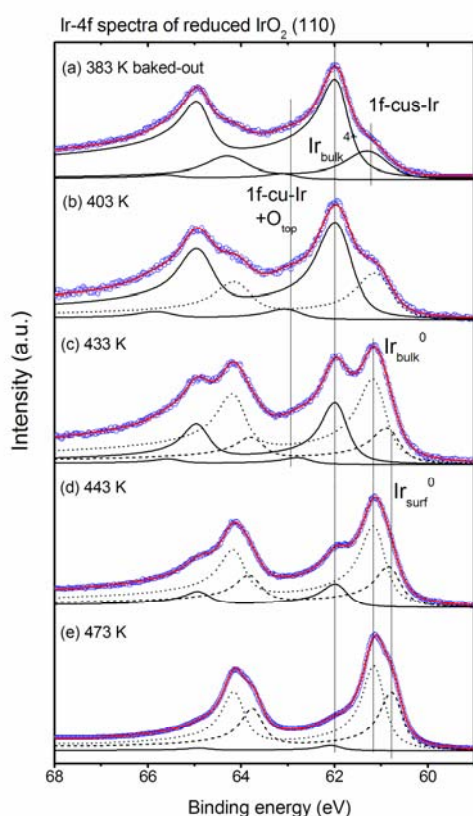


Fig. 1: indicates the Ir-4f of IrO₂ single crystal under different reduction temperature. The corresponding contributions are also labeled.

Further reduced at 433 and 443 K sequentially, the 4f_{7/2} bulk feature of Ir⁰ at 61.2 eV sharpens and its intensity increases significantly, meanwhile, the intensity of bulk Ir⁴⁺ component at 62.0 eV diminishes quickly, as illustrated in Figs. 1(c) and 1(d). In view of the evidently separable bulk and surface components in Fig. 1(e) and the narrow linewidth of the 61.2 eV bulk feature, the Ir⁰-4f_{7/2} profile is fitted with a Lorentzian linewidth of 300

meV for the bulk and the surface components. The 61.2 eV bulk feature is regarded as the binding energy of Ir metal phase on the IrO₂ crystal. Additional reduction of the IrO₂ (110) surface at 493 K lowers the binding energy down to 61.0 eV, which is the binding energy value of Ir-4f_{7/2} line reported in the XPS works on Ir metal single crystal. Figure 2 shows the details in separating the bulk and surface components of 473 K Ir-4f_{7/2} profile.

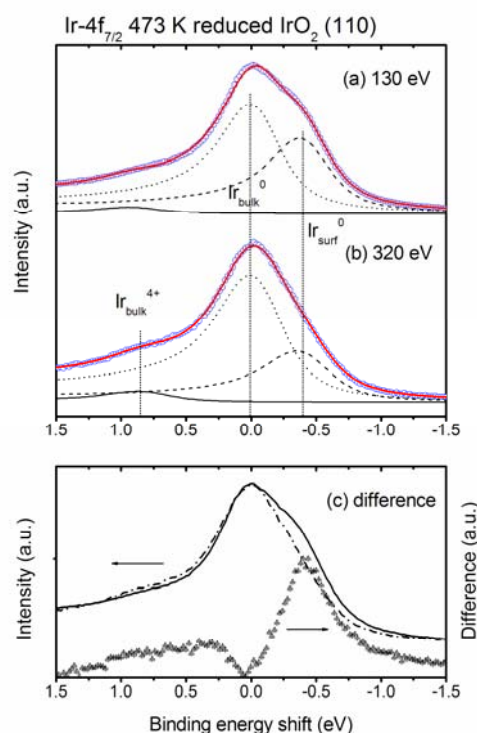


Fig. 2: Ir-4f_{7/2} core level spectra of the 473 K reduced surface, excited by (a) 130 eV and (b) 320 eV photon energies. The difference spectrum is plotted in Fig. (c), which is the intensity difference between Ir-4f_{7/2} peak of 130 eV (the solid line) and that of 320 eV (the dashed line).

Evidently, Iridium is a more noble metal than ruthenium. Under UHV conditions, the IrO₂ (110) surface is reduced at ~433 K, which is lower than the reduction temperature of RuO₂ (110) surface ~583K.

Reference

- [1] W.-H. Chung, C.-C. Wang, D.-S. Tsai, J.-C. Jiang, Y.-C. Cheng, L.-J. Fan, Y.-W. Yang, and Y.-S. Huang, *Surf. Sci.* **604**, 118 (2010).