Prominent 5d-orbital contribution to the conduction electrons in gold probed by polarization-dependent hard X-ray photoemission

Single-element materials in the same column in the periodic table often show mutually similar features, as seen in alkaline(-earth) metals and halogens. On the other hand, it is known that among noble metals, gold has considerably different chemical stability from that of silver even though their electronic structure near the Fermi level, as well as Fermi surface topology, is thought to be almost equivalent. For instance, it is well known that solid gold is very stable under many circumstances, whereas solid silver is gradually oxidized in air. The valence-band electronic configurations of these solids per atom have so far been recognized to be composed of fully occupied nd states (nd^{10}) plus one conduction electron occupying an $(n+1)sp$ state ($n = 4$ for silver and $n = 5$ for gold), but it has not been experimentally verified whether these configurations are correct or not.

Hard X-ray photoemission spectroscopy (HAXPES) shows, in addition to high bulk sensitivity, such characteristic features as (1) comparable s and ip ($i > 3$) photoionization cross sections to those for the d and f orbitals and (2) orbital-dependent photoelectron angular distribution with respect to the polarization of excitation photons [1]. Figure 1 shows the photoelectron angular distribution for the Ag 4d, 5s, and In 5p (nearly equivalent to the Ag 5p) orbitals in the HAXPES region as a function of take-off angle δ, which is defined as the angle between the direction of the electric field (polarization) of photons and the horizontal plane in which the momentum direction of the photoelectrons to be detected is involved. Here, $\delta = 0°$ (90°) corresponds to the p-polarization (s-polarization) configuration. One can recognize from the figure, that the Ag 4d photoelectron intensity is not very suppressed in the s-polarization configuration compared with that in the p-polarization configuration, whereas the Ag 5s and 5p photoelectron intensities are strongly suppressed in the s-polarization configuration. As an overall tendency, the theoretical calculation [1] predicts that the photoelectron intensity at the s-polarization configuration relative to that at the p-polarization configuration is as low as $< 0.1 - 0.2$ for the s and jp ($j > 4$) states compared with that for the d and f states at the photoelectron kinetic energy of ~ 10 keV, which has been experimentally verified for several inner-core orbitals [2]. Therefore, the orbital contribution in the valence bands in solids could be revealed by linear polarization-dependent HAXPES.

In order to realize the linear polarization-dependent HAXPES, we have switched the linear polarization of the excitation light using a single-crystalline (100) diamond phase retarder with the 220 reflection [2,3] with a thickness of 0.7 mm, placed downstream of the post-monochromator (channel-cut Si crystal). The transmittance of the X-ray at ~8 keV for the diamond was confirmed to be ~35%. The polarization-dependent HAXPES was performed at **BL19LXU** using an MBS A1-HE photoelectron spectrometer. Polycrystalline gold and silver prepared by *in situ* evaporation were measured at 12−15 K. The energy resolution was set as ~280 (~400) meV for the measurement of silver (gold). The spectral weights were normalized by the photon flux. It should be noted that this technique is useful even for polycrystalline samples, as we demonstrate here.

Figure 2 shows the polarization dependence of the valence-band spectra for polycrystalline silver and gold. For silver, the relative spectral weight from the Fermi level (E_F) to the binding energy of
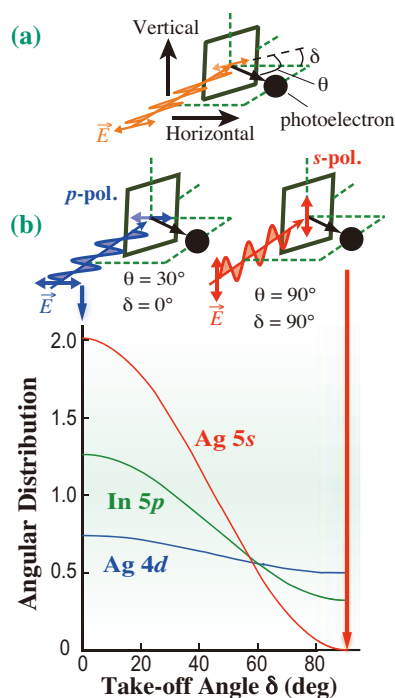

Fig. 1. **(a)** Geometrical configuration representing the directional relationships among the photoelectron propagation to be detected, the excitation-light propagation, and the electric field (linear polarization) of the excitation light for the s-polarization, p-polarization, and the geometry with the take-off angle of θ. **(b)** Photoelectron angular distribution calculated using parameters in Ref. [1] with respect to the direction of the linear polarization of excitation photons at the kinetic energy of 10 keV for the Ag 4d, 5s, and In 5p orbitals, where the angle between the propagation directions of the excitation photons and the photoelectrons to be detected is fixed at 120°. The angular distribution for the In 5p orbital is a substitute for the "Ag 5p" orbital (keeping in remind that no occupation is assumed for the 5p orbital of a neutral Ag atom, and hence no parameter for the calculation is given to this orbital).
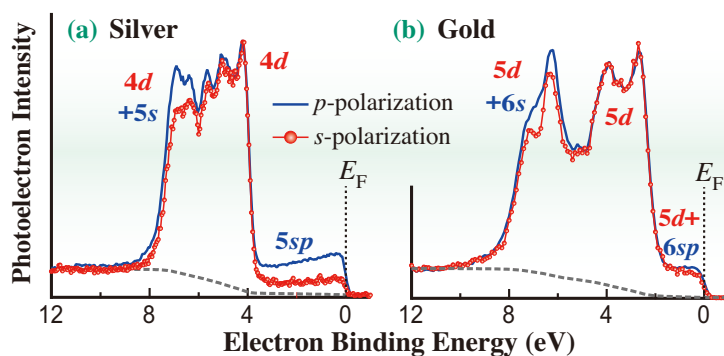
Fig. 2. Polarization-dependent valence-band HAXPES spectra of silver **(a)** and gold **(b)** at hν ~8 keV. The spectra have been roughly normalized by the intensity at the binding energy of 4−5 (2−5) eV for silver (gold).

3 eV is markedly suppressed in the s-polarization configuration compared with that in the p-polarization configuration, where both spectra are roughly normalized at the intensity at the binding energy of 4−5 eV. This polarization dependence as a function of the binding energy reveals that the $4d$ bands are located far below E_F and are well separated from the conduction $5sp$ band in the energy region from E_F to ~3 eV. It is thus experimentally confirmed that the $4d$ orbitals are nearly fully occupied whereas the conduction electrons are, to some extent, free-electron-like with a negligible $4d$ contribution in the solid silver, as has long been expected. On the other hand, the polarization dependence of the valence-band spectra near E_F for bulk gold is not only quantitatively but also qualitatively different from that for silver. When the spectra are normalized by the intensity in the binding energy region of 2−5 eV, where the Au $5d$ bands are located, the spectral weight near E_F is negligibly suppressed even in the s-polarization configuration. Our detailed analysis has shown the prominent (about 50%) $5d$-orbital contribution to the conduction electrons in gold.

The revealed qualitative difference in the mixing of d-orbitals in the conduction bands crossing E_F between silver and gold, which is schematically shown in Fig. 3, originates from the different strengths of the electron correlation. In the case of silver, the Ag $4d$ electron correlation effects cannot be neglected when to discussing its electronic structure, whereas the Au $5d$ correlation effects are much weaker. Considering our finding and the fact that platinum with a band structure almost equivalent to that of gold is also very stable in air, where the $5d$ contribution to the conduction electrons is undoubtedly predominant, we can conclude that the prominent $5d$ contribution to the conduction electrons has a role in protecting gold from oxidation in air.

Our result has also revealed the presence of intrinsic $5d$ holes in gold. It is expected that there are $5d$ holes even in the previously investigated gold nanoparticles that show magnetism at beamline **BL39XU** [4]. The number of $5d$ holes will increase if the conduction electrons are transferred from the nanoparticles to neighboring molecules as discussed in Ref. [4]. In this context, it is natural to consider a role of $5d$ holes in the magnetism of gold nanoparticles, although our result does not give direct evidence of such a situation.
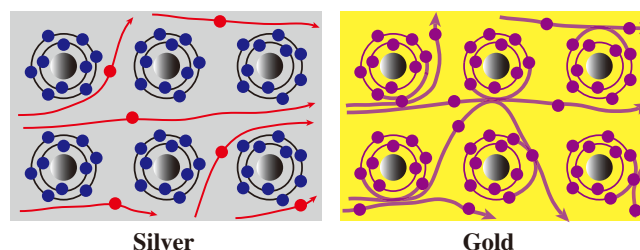

Silver   **Gold**

Fig. 3. Schematic picture summarizing our finding, where the $5sp$-orbital conduction electrons nearly freely moving inside silver (red circles with bold lines) are well separated from the $4d$-orbital electrons (blue circles), but the $5d$-orbital electrons are strongly mixed with the $6sp$-orbital electrons and therefore contribute prominently to the conduction electrons in gold. The large gray circles denote nuclei.

Akira Sekiyama[a,b,*], Atsushi Higashiya[b,c] and Shin Imada[d]

[a] Division of Materials Physics, Osaka University
[b] SPring-8/RIKEN
[c] Faculty of Science and Engineering, Setsunan University
[d] Department of Physical Science, Ritsumeikan University

*Email: sekiyama@mp.es.osaka-u.ac.jp

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