Supplemental Material for “Scaling law for the Rashba-type spin splitting in quantum-well films”

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A. ARPES setting and sample preparations

The laser-ARPES and SARPES measurements were performed at the Institute for Solid State Physics (ISSP), the University of Tokyo, using a hemispherical analyzer (Scienta-Omicron, DA30L) with a high-flux 6.994-eV laser. The $p$-polarized light was used in the experiment. The photoelectrons were detected along $\Gamma$-$M$ line of the surface Brillouin zone. The spectrometer resolved the spin component along $y$, which is perpendicular to the mirror plane of the surface [see main Fig. 1(a)]. The sample temperature was kept at $\sim 30$ K during the measurements. The instrumental energy (angular) resolutions of the setup was set to about 5 meV ($0.3^\circ$) and 15 meV ($0.7^\circ$) for ARPES and SARPES, respectively. The Au(111) substrate was prepared by cycles of Ar sputtering and annealing. Ag was evaporated by a resistively heated Knudsen cell onto a clean Au(111). During the evaporation, the sample temperature was kept at $\sim 100$ K and annealed at room temperature after evaporation to obtain crystalline Ag films. The quality of the Au substrate has been verified via measurements by low-energy electron diffraction, and the thicknesses of Ag films have been determined by the photoemission spectroscopy of quantum-well states referring to previous reports.

B. Spin splitting of the Shockley surface state

While the pristine Au(111) surface shows a large spin splitting of $\alpha_R \sim 330$ meVÅ, $\alpha_R$ of the surface state in Ag/Au(111) is expected to decrease upon increasing Ag coverage, since the state is localized at the surface. Indeed, the thickness-dependent spin splitting of the surface states was reported in previous ARPES studies, and a continuous decreasing has been observed as the thickness of Ag film increases. Hence, the spin splitting of the surface states of Ag/Au(111) films measured in this work is also expected to be much smaller than that of Au(111). To confirm this prediction, we performed SARPES measurements of the surface states of 12 ML Ag/Au(111). In spin-integrated ARPES results, the surface states show almost degenerate behavior similarly to the quantum well states (QWSs) [Fig. S1(a)]. However, SARPES band map indicates a small Rashba type spin splitting with the same spin texture as the surface states of Au(111) and Ag(111) [Fig. S1(b)]. The Rashba parameter has been determined to be $40 \pm 3$ meVÅ, which is much smaller than $\alpha_R$ of


Au(111) and slightly larger than that of Ag(111), which is reported to be 31 meVÅ\textsuperscript{8}. This value is about three times smaller than that of QWS in 12 ML Ag/Au(111), suggesting the importance of the Ag/Au interface to the observed spin splitting in QWSs.

![Image]

FIG. S1. (a) ARPES band map for the Shockley surface state of 12 ML Ag/Au(111) [a closeup of Fig. 1]. (b) Spin-polarization and intensity map obtained by laser-SARPES. Peak positions of spin-up and spin-down energy distribution curves are extracted and plotted in (a) by the red and blue triangles, respectively. (c) Momentum-dependent energy splitting for the Shockley surface state.

C. Numerical conditions

The slab models of Ag/Au(111) are constructed as follows: We use 60 ML of 1 × 1 Au units to describe the substrate. We also perform the calculation with 30 ML of Au units to confirm the convergence with respect to the thickness of the Au substrate. Above this Au substrate, we put 6 - 34 ML of 1 × 1 Ag units and relax interlayer distances. To perform first-principles calculations based on DFT, we use an open-source program package OpenMX\textsuperscript{9} which employs norm-conserving pseudopotentials\textsuperscript{10} and pseudo-atomic localized basis functions\textsuperscript{11, 12} to solve the Kohn-Sham equation. We choose the exchange-correlation energy proposed by Perdew-Burke-Ernzerhof\textsuperscript{13} through the generalized gradient approximation. The Brillouin-zone integrations are performed on 14 × 14 × 1 \textit{k}-point grid together with the Fermi-Dirac distribution function at 5,000 K to smear the rapidly varying electronic distribution. We treat the spin-orbit interaction by solving the Kohn-Sham equation in the spinor representation. The configuration of the basis set is as follows. Two, two, two, and one radial wavefunctions with a cutoff radius of 7.0 a.u. are used for the s-, p-, d-, and
where we define the orbital decomposed Rashba parameter $\alpha$ intrinsic magnetic-field terms as the Kohn-Sham system. This Hamiltonian is decomposed into the spin-independent and the Sham eigenstate at band $\nu$ where $\psi$ with the contribution of Ag orbitals marked by the red circles. The surface states and QWS analysis.

We note that such a decomposition is not unique and can be used for the quantitative and (tribution. Therefore the energy splitting is related by this splitting have the opposite spin moments and almost the same spacial distribution. Therefore the energy splitting is

$$\Delta E \approx 2 \sum_{ij} \begin{pmatrix} \psi_{\uparrow i}^{(k\nu)}* & \psi_{\downarrow i}^{(k\nu)*} \end{pmatrix} \begin{pmatrix} \frac{H_{\uparrow\uparrow ij}^{(k)}}{2} & -\frac{H_{\uparrow\downarrow ij}^{(k)}}{2} \\ \frac{H_{\uparrow\downarrow ij}^{(k)}}{2} & \frac{H_{\downarrow\downarrow ij}^{(k)}}{2} \end{pmatrix} \begin{pmatrix} \psi_{\uparrow i}^{(k\nu)} \\ \psi_{\downarrow i}^{(k\nu)} \end{pmatrix} \equiv 2k \sum_i \Delta \alpha_{Rvi},$$

where we define the orbital decomposed Rashba parameter $\alpha_{Rvi}$ as

$$\Delta \alpha_{Rvi} \equiv \frac{1}{k} \sum_j \begin{pmatrix} \psi_{\uparrow i}^{(k\nu)*} & \psi_{\downarrow i}^{(k\nu)*} \end{pmatrix} \begin{pmatrix} \frac{H_{\uparrow\uparrow ij}^{(k)}}{2} & -\frac{H_{\uparrow\downarrow ij}^{(k)}}{2} \\ \frac{H_{\uparrow\downarrow ij}^{(k)}}{2} & \frac{H_{\downarrow\downarrow ij}^{(k)}}{2} \end{pmatrix} \begin{pmatrix} \psi_{\uparrow i}^{(k\nu)} \\ \psi_{\downarrow i}^{(k\nu)} \end{pmatrix}.$$  

We note that such a decomposition is not unique and can be used for the quantitative analysis.

D. Band structures of Ag/Au(111) obtained by DFT calculations

In Fig. S2(a), a representative band structure calculated for 24 ML Ag/Au(111) is plotted with the contribution of Ag orbitals marked by the red circles. The surface states and QWSs
are obtained in the projected $sp$-band gap of Au(111) in consistent with ARPES results. The electronic localization of the surface states and QWSs have also been confirmed in the charge density distributions as shown in Fig. S2(b). The Rashba parameters are calculated using the equation $\alpha_R = \Delta E/2k$ at $k_x = 0.043$ Å$^{-1}$.

FIG. S2. (a) Band structure of 24 ML Ag/Au(111) obtained by DFT calculations. The contribution of Ag atoms to the wavefunctions are denoted by the sizes of the red circles. (b) Charge density distributions of the surface state (SS) and the quantum well states (QWSs). The orange (gray) circles indicate the positions of Au (Ag) atomic layers.

E. Plot of the Rashba parameters versus the charge densities at the Ag/Au interface

Here, we discuss the principal factor which governs the size of the Rashba parameter of QWS, namely the magnitude of the envelope function at the Au/Ag boundary, as follows: For 2D systems, the Rashba parameter $\alpha_R$ is estimated as

$$\alpha_R = \int d^3r \frac{1}{c^2} \frac{\partial V(r)}{\partial z} |\psi(r)|^2,$$

where $V(r)$ is the single-body potential, $\psi(r)$ is the wavefunction and we take the $z$-axis vertical to the surface. Since $V(r)$ has a large gradient near the nuclei and QWS mainly consists of the $p_z$ orbitals, the integrand of Eq. (1) can be depicted schematically as main Fig. 4 (b). In the vicinity of $i$-th nucleus, the wavefunction can be approximated as $\psi(r) \approx \psi_{p_z,i}(r - r_i)\psi_{env}(z)$, where $\psi_{p_z,i}$ is the $p_z$ like orbital at $i$-th atom and $\psi_{env}$ is the envelope
function. Then the Rashba parameter becomes

\[ \alpha_R \approx \sum_{i=-\infty}^{\infty} \int d^3r \frac{1}{c^2} \frac{\partial V_i(r - r_i)}{\partial z} |\psi_{p_z,i}(r - r_i)|^2 |\psi_{env}(z)|^2 \equiv \sum_{i=-\infty}^{\infty} \Delta \alpha_{R,i}, \quad (2) \]

where \( V_i \) and \( r_i \) are the potential and position of the \( i \)-th nucleus. The relatively smooth envelope function can be approximated around \( i \)-th nucleus as \(|\psi_{env}(z)|^2 \approx |\psi_{env}(z_i)|^2 + d|\psi_{env}|^2/dz|_{z=z_i}(z - z_i)\).

\[ \Delta \alpha_{R,i} \approx |\psi_{env}(z_i)|^2 \int d^3r \frac{1}{c^2} \frac{\partial V_i(r)}{\partial z} |\psi_{p_z,i}(r)|^2 + \frac{d|\psi_{env}|^2}{dz} \int d^3r \frac{1}{c^2} \frac{\partial V_i(r)}{\partial z} |\psi_{p_z,i}(r)|^2 z \]

\[ = \frac{1}{c^2} \frac{d|\psi_{env}|^2}{dz} \bigg|_{z=z_i} \left\langle \left\{ \frac{\partial V}{\partial z} \right\}_i \right\rangle \quad (3) \]

where

\[ \left\langle \left\{ \frac{\partial V}{\partial z} \right\}_i \right\rangle \equiv \int d^3r \frac{\partial V_i(r)}{\partial z} |\psi_{p_z,i}(r)|^2 z. \quad (4) \]

The first term of the first line of Eq. (3) vanishes because of the symmetries of \( V_i \) and \( \psi_{p_z,i} \). \( \Delta \alpha_{R,i} = 0 \) when the gradient of the envelope function is 0 [middle of main Fig. 4(b)], while \( \Delta \alpha_{R,i} \) is positive (negative) when the envelope function increases (decreases) as shown in the left (right) of main Fig. 4(b). By inserting Eq. (3) into Eq. (2), we get the total Rashba parameter as

\[ \alpha_R \approx \sum_{i=-\infty}^{\infty} \frac{1}{c^2} \frac{d|\psi_{env}|^2}{dz} \bigg|_{z=z_i} \left\langle \left\{ \frac{\partial V}{\partial z} \right\}_i \right\rangle \quad (5) \]

In the structure shown in main Fig. 4(c), since the averaged gradient \( \left\langle \delta V \right\rangle_i \) in this summation takes only two values, the average for Au (\( \left\langle \delta V \right\rangle_{Au} \)) and Ag (\( \left\langle \delta V \right\rangle_{Ag} \)), we can move that average outside of \( \sum \) as

\[ \alpha_R \approx \left\langle \left\{ \frac{\partial V}{\partial z} \right\}_i \right\rangle \sum_{i=-\infty}^{0} \frac{1}{c^2} \frac{d|\psi_{env}(z)|^2}{dz} \bigg|_{z=z_i} + \left\langle \left\{ \frac{\partial V}{\partial z} \right\}_i \right\rangle \sum_{i=1}^{\infty} \frac{1}{c^2} \frac{d|\psi_{env}(z)|^2}{dz} \bigg|_{z=z_i}. \quad (6) \]

If the envelope function \(|\psi_{env}(z)|^2 \) varies slowly, these summations can be approximated with integrals as

\[ \alpha_R \propto \left\langle \left\{ \frac{\partial V}{\partial z} \right\}_i \right\rangle \int_{-\infty}^{0} dz \frac{d|\psi_{env}(z)|^2}{dz} + \left\langle \left\{ \frac{\partial V}{\partial z} \right\}_i \right\rangle \int_{1}^{\infty} dz \frac{d|\psi_{env}(z)|^2}{dz} \]

\[ = \left\langle \left\{ \frac{\partial V}{\partial z} \right\}_i \right\rangle |\psi_{env}(0)|^2 - \left\langle \left\{ \frac{\partial V}{\partial z} \right\}_i \right\rangle |\psi_{env}(1)|^2 = |\psi_{env}(0)|^2 - c_r|\psi_{env}(1)|^2, \quad (7) \]
FIG. S3. (a–c) Rashba parameters of QWSs in Ag/Au(111) as a function of local charge densities at the interface layers. In (a), only the charge density at the interface Au layer is considered. (b) is the duplicate of the main Fig. 4(e). In (c), the coefficient for the Ag term is set to be 0.50, leading to the overestimation of the contribution of the Ag layers.

where we use that the envelope function vanishes at $z \pm \infty$, and $c_r$ is a constant. This illustrates that $\alpha_R$ is determined by the charge density at the interface regardless of the detailed structure inside the well, given that the atomic species used for the film are specified. In addition, the difference of the potential gradients $\partial V / \partial z$ of the two atoms plays a significant role in enhancing the Rashba effect, considering that the gentle slope of the envelope function usually leads to similar values for $\psi(0)$ and $\psi(1)$.

Figs. S3 (a–c) present the plot of the Rashba parameters versus the charge densities at the interface layers with the different coefficient for the Ag contribution. In Fig. S3 (a), only the Au layer is considered, while the coefficients of 0.30 and 0.50 are used to evaluate the contribution of Ag layers in Figs. S3 (b) and (c). Interestingly, when we set the coefficient to 0.30, the Rashba parameters are placed almost on the same line regardless of the quantum number. This value (0.30) is close to the ratio of $\zeta$ of Ag 5p orbital (1.90 eV) to that of Au 6p orbital (6.34 eV) computed in the earlier work [14] as

$$\zeta_i \equiv \int_0^\infty dr \frac{dV_r}{dr} r R_i^2(r),$$

where $R_i(r)$ is the normalized atomic radial wavefunction. This parameter is proportional to the $\langle \left| \frac{\partial V}{\partial z} \right| \rangle_i$ in Eq. (4) of the main text as follows: Assuming $\psi_{pz,i}(r) \equiv r^{-1} R_i(r) \sqrt{3/(4\pi)} \cos \theta$,

7
we get

\[
\left\langle \left| \frac{\partial V}{\partial z} \right| \right\rangle_i \approx 2\pi \int_0^\infty dr r^2 \int_0^\pi d\theta \sin \theta \cos \theta \frac{dV_i(r)}{dr} r \cos \theta R_i^2(r) \frac{3}{4\pi} \cos^2 \theta
\]

\[
= \frac{3}{5} \int_0^\infty dr \frac{dV_i}{dr} r R_i^2(r) = \frac{3}{5} \zeta_i.
\]

This fact validates our discussion in the main text that the charge densities at the interface and the potential gradients \( \partial V/\partial z \) well describe the spin splittings of QWSs. The results indicate that the variation of the SOC coefficients between two atoms is a key to enhance the spin splittings of QWSs.

**F. Linearity of the Rashba effect in Ag/Au(111) films**

In the main text, we have estimated the Rashba parameter from the slope of \( k \)-linear fitting to the data of spin-split energies. To check the validity of this analysis, we have investigated the linearity of the spin splittings by DFT calculations, as shown in Fig. S4(a), which plots the momentum dependence of spin-splitting energies for different film thicknesses.

![Figure S4](image_url)

**FIG. S4.** (a) Momentum-dependent energy splitting of \( \nu = 1 \) QWSs around \( \bar{\Gamma} \) obtained by DFT calculations with lines to check the linearity. (b) Band structure of 8 ML Ag/Au(111), where QWS is energetically close to other states at larger \( k > 0.043 \ \text{Å}^{-1} \). The red dashed lines indicate the momentum where the Rashba parameters are calculated (\( k = 0.043 \ \text{Å}^{-1} \)).
at \( \nu = 1 \) (\( \nu \): quantum number). We have drawn lines between two points, \( k = 0 \) and \( k = (\bar{\Gamma} - \bar{M})29 \) (\( k = 0.043 \, \text{Å}^{-1} \)), and confirmed that the splittings show almost linear behavior in the region of our interest; we note that the theoretical values of the Rashba parameter in our manuscript were determined from these slopes. A slight deviation from the linear behavior is seen in 8 ML because the QWS is so close to bulk states in the momentum space that it is hybridized with those [Fig. S4(b)]. However, this deviation is rather small, thus our conclusion of the scaling law is not affected by that.

The above discussion would become clearer by expressing the energy shift by SOC using the Hamiltonian:

\[
H_{SOC} = \frac{2}{c} \nabla V \cdot (p \times s). \tag{10}
\]

We obtain the energy shift by SOC (\( \epsilon_k^{SOC} = \epsilon_k^{Rashba}/2 \)) as

\[
\epsilon_k^{SOC} = \int d^3 r \psi_k^*(r) \left\{ \frac{2}{c^2} \nabla V \cdot (p \times s) \right\} \psi_k(r) = \epsilon_k^{SOC \, 1} + \epsilon_k^{SOC \, 2} \tag{11}
\]

\[
\epsilon_k^{SOC \, 1} \equiv \int d^3 r u_k^*(r) \left\{ \frac{2}{c^2} \nabla V \cdot (k \times s) \right\} u_k(r) = \alpha_R k/2 \tag{12}
\]

\[
\epsilon_k^{SOC \, 2} \equiv -i \int d^3 r u_k^* \left\{ \frac{2}{c^2} \nabla V \cdot (\nabla u_k \times s) \right\}. \tag{13}
\]

Here \( \psi_k(r) = e^{ik \cdot r} u_k(r) \) is the Bloch function. The first term \( \epsilon_k^{SOC \, 1} \) in Eq. (11) represents the \( k \)-linear energy shift, and the Rashba parameter (\( \alpha_R \)) is defined [Eq. (12)]. On the other hand, the second term \( \epsilon_k^{SOC \, 2} \) [Eq. (13)] cannot be described as \( k \)-linear and its \( k \)-dependence is affected by the hybridization between QWSs and bulk states. Therefore, while the linearity of spin splitting is lost if the bands for QWSs are very close to the bulk bands in the momentum space, it would be preserved as long as the QWSs bands are located sufficiently far from bulk bands, even if QWSs are not ideal 2DEG systems.

### G. Modulations of the potential gradient in Ag/Au(111) films

In the main text, we discussed the asymmetry of wavefunction and the potential gradient separately, although they are related with each other by the Schrödinger equation. To examine the effect of the wavefunctions on the potential, we have calculated the Mulliken charge population at each atomic layer in our study setting of Ag films on Au(111) substrate, and plotted its difference from that of each isolated atom Ag and Au in Fig. S5. Finite
values are obtained at the interface and the surface. However, these are negligibly small (0.05 electrons) compared with the number of electrons that form the potential gradient around the nuclei. Therefore, we can ignore the effect of the wavefunctions on the potential and discuss them separately.

![Graph](image)

**FIG. S5.** Difference of the number of electrons for each atomic layer from those of isolated atoms obtained by DFT calculations. Slight modulations have been only at the interface and the surface, which have negligible effects on the potential gradient.

**H. Evaluation of experimental errors**

The peak positions of the spin-resolved energy distribution curves (EDCs) were determined by fitting a Lorentzian function with a constant background to the data, as shown in Fig. S6. The typical value of the errors in this fitting was estimated to be $\sim 1$ meV; hence, we can identify the energy separation in the spin-ARPES spectra down to $\sim 2$ meV with enough accuracy. The errors of the Rashba parameters were determined by weighted least squares of errors for the peak separations and for the linear fitting to those plots: obtained values were $\sim 2$ meV Å, while it depends on the statistical quality of each data set. Our experiments, therefore, can reliably determine the Rashba parameter as small as $\sim 5$ meV Å, which is smaller than the sizes of most markers plotted in the main Fig. 3.

The energy resolution is, of course, very important for obtaining intrinsic ARPES spectra. However, the stability of the light source is also crucial for the accurate determination of the Rashba parameters, especially because the spin-ARPES is far less efficient ($\sim 100$ times
less) than normal ARPES, thus it takes much time for accumulation of the spin-resolved spectra. In our experimental setup, we used a high-flux 6.994-eV laser extremely stable in photon energy, which ensures the reliability of spectral peak positions even after long spectral accumulation. This contrasts to ARPES with synchrotron light sources, which cannot avoid the energy drift with time usually reaching $\sim$5 meV in half a day. This shift is directly translated to the uncertainty of the spectral peak positions. Thus, we stress that the stable laser was a requisite in our study, which required the determination of very small Rashba parameters.

![Graph](image)

**FIG. S6.** Determination of the peak positions of spin-resolved energy distribution curves (EDCs). Red and blue solid curves denote the Lorentzian curves fitted to spin-up and spin-down EDCs, respectively. The peak positions and errors $(x \pm \Delta x)$ are displayed on the right of each EDC.


