Spin-selective pathways in linear and nonlinear photoemission from ferromagnets

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(Received 26 October 2011; published 23 April 2012)

We observe an enhanced spin polarization and reduction of surface sensitivity due to the intermediate unoccupied electronic states in spin-resolved two-photon photoemission (2PPE) from ultrathin ferromagnetic cobalt films. By comparison to one-photon photoemission (1PPE) measurements, we disentangle the 2PPE signals coming from the initial and intermediate electronic states and determine the influence of the unoccupied quantum-well states in the nonlinear two-photon transitions. Our results point out the importance of spin-dependent pathways in nonlinear photoemission and provide a possible mechanism of spin-filtering in optical transitions.

DOI: 10.1103/PhysRevB.85.165137 PACS number(s): 79.60.−i, 73.20.−r, 73.21.Fg, 79.20.Ws

The electron spin plays a fundamental role in condensed matter physics. Ranging from the building blocks of spintronics to novel materials such as topological insulators, advanced knowledge of material properties has been gained through studies of the spin dependent electronic structure.[1–3] As a general method to analyze the electronic structure with spin resolution, spin-polarized photoemission has evolved into a powerful technique in combination with femtosecond lasers, allowing the manipulation of spin-polarized electrons at surfaces and interfaces using nonlinear optical transitions in two-photon photoemission (2PPE).[4–7]

However, because of the abundant possibilities in nonlinear photoexcitation between the continuum of electronic bands,[8–12] it remains difficult to recognize the spin-polarized electrons optically injected into specific *bulk* electronic states. Ideal conditions to study the selective optical transitions into bulk-derived electronic states can be offered by ultrathin films. Within a few atomic layers, the electronic states confined within the interior of the film form discrete quantum-well (QW) states, providing an opportunity to study bulk-derived unoccupied states with 2PPE.[13–15] In this study, we provide experimental evidence for the spin selection of optically excited electrons via unoccupied bulk-derived electronic states. Through a comparison to one-photon photoemission (1PPE), we identify an enhanced spin polarization in 2PPE which is due to a majority unoccupied QW state. Moreover, we observe a modified spin-dependent depth sensitivity enforced by the bulk-derived intermediate state in nonlinear photoemission, which leads to the suppression of surface-state minority-spin signals. Our results demonstrate the specific influence of bulk-derived unoccupied electronic states on spin-polarized nonlinear photoemission and illustrate a possibility to selectively steer polarized electrons by nonlinear optical transitions via intermediate spin-dependent electronic states.

We choose the well-known ferromagnetic cobalt films on Cu(001) as our system. In Fig. 1 we show the relevant electronic states of the cobalt films[16,17] together with the excitation scheme of 1PPE and 2PPE. For clarity, we include only the bands with Δ_1 or Δ_5 symmetry that are relevant to our experimental geometry. The six-monolayer- (ML) thick cobalt films exhibit exchange-split QW states originating from the bulk *sp* bands at around 2.1 eV above the Fermi level (E_F)[17,18] and an occupied minority-spin surface resonance (SR) at 0.4 eV below E_F.[16,19] The QW states are shown with qualitative momentum broadening due to the finite film thickness. Possible optical transitions in the electronic structure are marked by arrows, with a length corresponding to the photon energies $h\nu_1 = 6.0$ eV (1PPE) and $h\nu_2 = 3.1$ eV (2PPE). As can be seen in Fig. 1, the occupied SR can be probed in 1PPE as well as in 2PPE, whereas 1PPE is not sensitive to the unoccupied QW state. In addition to the differences in energy, spin, and momentum, SR and QW states have different spatial extension as shown in the inset of Fig. 1.[17] QW states are dominant in the region within the cobalt film, whereas the SR is mostly localized at the surface.

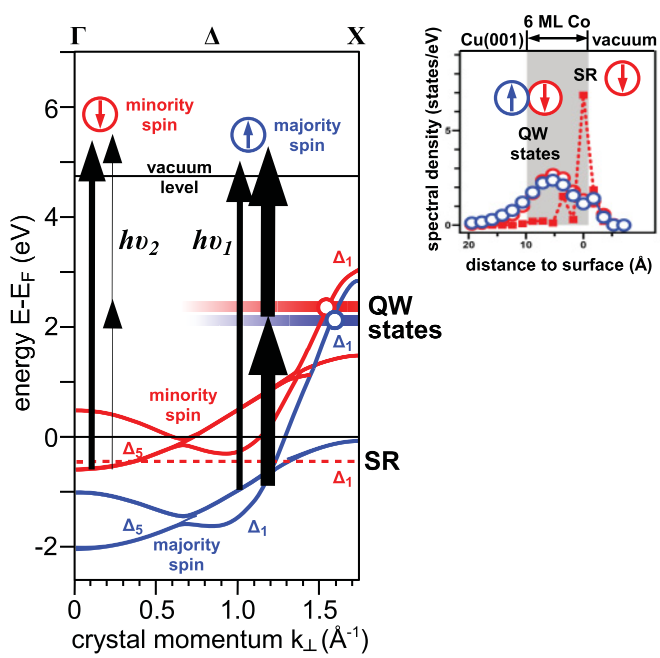

FIG. 1. (Color) The relevant electronic structure of 6-ML cobalt films on Cu(001). The surface resonance (SR) and quantum-well (QW) states are shown with the bulk fcc cobalt band structure.[16,17] Arrows indicate possible transitions for 1PPE with $h\nu_1 = 6.0$ eV and 2PPE with $h\nu_2 = 3.1$ eV. The inset shows the theoretically calculated spectral density of SR and QW states along the surface normal.[17]

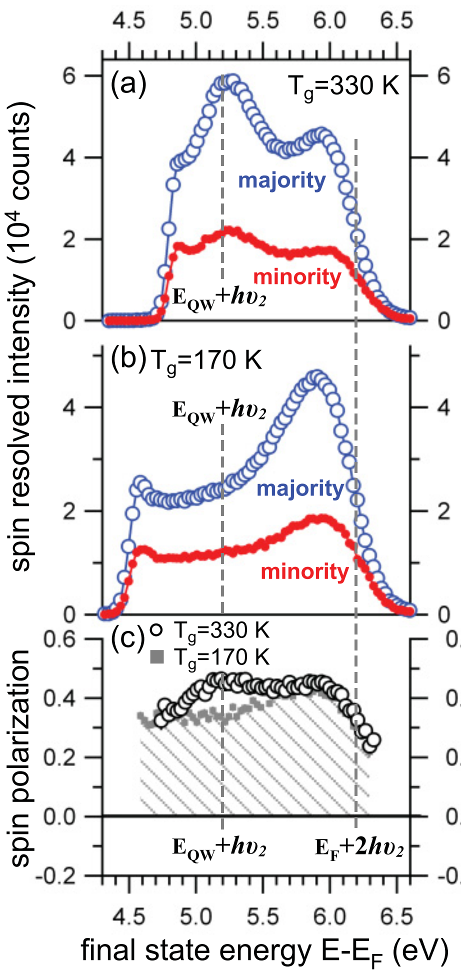

FIG. 2. (Color online) Spin-resolved 2PPE spectra from 6-ML cobalt films grown at (a) 330 K and (b) 170 K. Spin polarization is shown in (c). Features of the majority quantum-well state ($E_{QW} + h\nu_2$) and the Fermi level ($E_F + 2h\nu_2$) are marked. The photon energy is $h\nu_2 = 3.1$ eV.

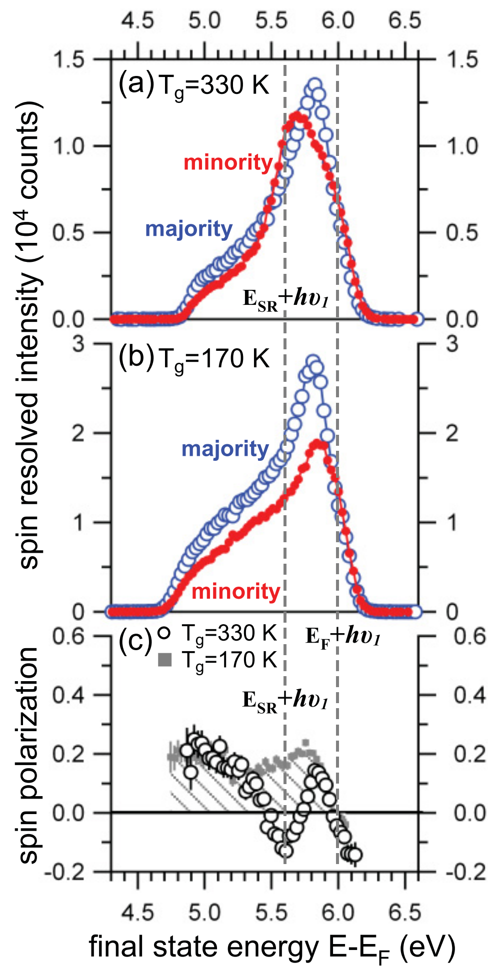

FIG. 3. (Color online) Spin-resolved 1PPE spectra from 6-ML cobalt films grown at (a) 330 K and (b) 170 K. Spin polarization is shown in (c). Features of the minority surface resonance ($E_{SR} + h\nu_1$) and the Fermi level ($E_F + h\nu_1$) are marked. The photon energy is $h\nu_1 = 6.0$ eV.

In the experiments, 1PPE and 2PPE are measured with the fourth and the second harmonics of a Ti-sapphire laser, respectively. Details of the apparatus and sample preparation were published previously.[17,20] The incident light was p polarized for all the experiments reported here. The ferromagnetic cobalt films were magnetized in the optical plane along the [110] crystal direction. Photoelectrons in normal emission were measured by an electrostatic energy analyzer coupled to a spin analyzer.[21] The energy resolution was 100 meV and the spin polarization of the photoelectrons was analyzed along the quantization axis parallel to the sample magnetization. For comparison, we used two different growth temperatures of the 6-ML cobalt films. The cobalt films grown at $T_g = 330$ K and measured at 300 K have good quality of surface and interface, allowing the development of the SR and the identification of QW states in the photoemission spectra.[22,23] To reveal the influence of the SR and QW states on the spin polarization of photoelectrons, we performed experiments with the same excitation conditions for films grown at $T_g = 170$ K and measured at 170 K. The comparison between films with different growth temperature (T_g) can provide us with the differential spin-polarization signals signifying the influence of SR and QW states on photoemission.

Spin-resolved 2PPE spectra from the 6-ML cobalt films, grown at 330 K, are shown in Fig. 2(a). The high-energy cutoff in the majority and minority spectra near 6.2 eV represents 2PPE from E_F. The low energy cutoff at around 4.8 eV is given by the sample work function. In the majority spectrum, the feature of the unoccupied QW state is located around 5.2 eV ($E_{QW} + h\nu_2$), in agreement with previous experiments[15,18] and theoretical calculations.[17] The spin polarization derived from the spectra in Fig. 2(a) is shown with open black circles in Fig. 2(c). The 2PPE spin polarization has a shoulder near $E_{QW} + h\nu_2$ and varies slightly around 0.4 from 4.8 eV to 6.0 eV before decreasing to 0.2 near 6.2 eV.

To check the contributions of SR and QW states in 2PPE, we show for comparison the spin-resolved 2PPE spectra and the spin polarization of 6-ML cobalt films grown and measured at 170 K in Figs. 2(b) and 2(c). In strong contrast to the films grown at 300 K,[15] the 2PPE spectra of the 170 K grown films do not show ML-resolved intensity oscillations during growth and have a lower work function, and the QW state peak is absent. This indicates increased surface roughness of the films grown at 170 K. Comparing the 2PPE spin polarization of the 170 K to the 330 K grown films in Fig. 2(c), we can identify an increase of spin polarization from 0.34 to 0.46 at $E_{QW} + h\nu_2$ due to the unoccupied majority-spin QW state. The appearance of the majority QW state feature in 2PPE spectra and the corresponding increase in the spin polarization provide evidence that the two-photon transition is regulated in a spin-dependent way by the intermediate QW state in the cobalt films grown at 330 K.

To selectively analyze the role of the initial electronic states in 2PPE, we carried out 1PPE measurements with a photon energy of $h\nu_1 = 6.0$ eV, nearly twice the photon energy used in 2PPE ($2h\nu_2 = 6.2$ eV). With our choice of photon energies, the excitation processes in 1PPE and 2PPE share a similar set of initial and final states, allowing us to identify the influence from the additional intermediate states in 2PPE. The spin-resolved 1PPE spectra and the spin polarization from the 170 K and 330 K grown films are shown in Fig. 3. In Figs. 3(a) and 3(c), 1PPE spectra and spin polarization of the 330 K grown films clearly show the signature of the minority SR at about 0.4 eV below the Fermi level ($E_{SR} + h\nu_1$),[16,19] leading to a negative spin polarization around −0.1. The spin polarization increases to +0.2 at the energy further below the SR ($E_{SR} + h\nu_1$). Above the SR, the spin polarization reaches +0.15 and then decreases to −0.17 at 0.1 eV above the Fermi level ($E_F + h\nu_1$). The observed spin polarization can be understood based on the occupied cobalt electronic structure in Fig. 1. The majority d bands are located in the energy range up to E_F and superimpose on the minority SR at E_{SR}. In the vicinity of E_F, the spin polarization decreases because the minority d and sp bands start to contribute to photoemission,[16] giving rise to a negative spin polarization in 1PPE above 6.0 eV. Comparing the 1PPE spectra from films with different growth temperatures (T_g) in Fig. 3(a) and in Fig. 3(b), we observe remarkable variations in the minority spectrum: The maximum near $E_F + h\nu_1$ for the 170 K grown films is shifted with respect to the 330 K grown films and has a much lower intensity relative to the majority spectrum. This change is correlated to the disappearance of the negative spin-polarization dip for the $T_g = 170$ K films at $E_{SR} + h\nu_1$ in Fig. 3(c), indicating a suppression of the minority SR.

The spin-dependent 2PPE and 1PPE measurements are summarized in Fig. 4. The upper axis is the intermediate state energy for 2PPE, and the lower energy axis is the initial state energy for both 1PPE and 2PPE. The overall spin polarization seen in 2PPE is higher than in 1PPE. In addition, there is an obvious change of spin polarization in 1PPE by 0.3 at the SR (E_{SR}), as we compare the films with different growth temperature. In analogy, we can clearly identify the appearance of the cobalt majority QW state in 2PPE, showing a difference in spin polarization of 0.1 at E_{QW}. Moreover, the 2PPE spin polarization at the initial-state energy E_{SR} in Fig. 4 remains fairly unchanged as we go from the 330 K to the 170 K grown films, in strong contrast to the change at the intermediate state energy E_{QW}. This comparison indicates that 2PPE is more sensitive to the QW state in the cobalt film than the SR at the surface, a property which is unique in comparison to previous surface-sensitive 2PPE experiments.[24,25]

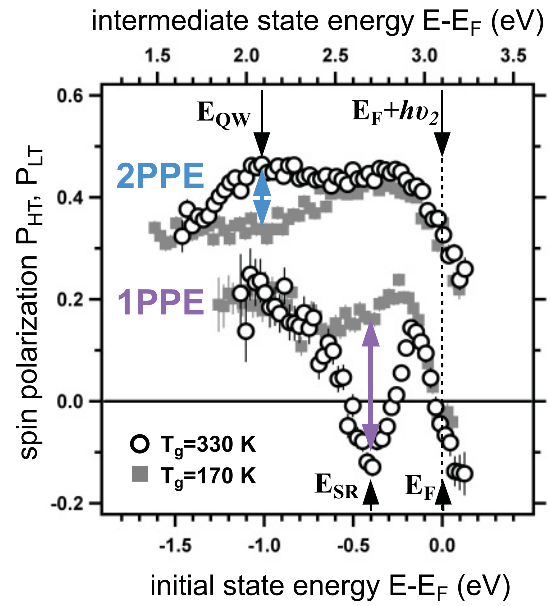

FIG. 4. (Color online) Comparison between spin polarization of 2PPE from Fig. 2(c) and 1PPE from Fig. 3(c). The upper axis shows the energy scale of intermediate states in 2PPE, while the lower axis gives the energy scale of initial states in 1PPE and 2PPE; $h\nu_1 = 6.0$ eV and $h\nu_2 = 3.1$ eV.

In the following, we discuss the possible mechanism for the suppressed surface sensitivity in 2PPE as compared to 1PPE. Since both the 2PPE and 1PPE processes share a similar energy range of initial as well as final states (Fig. 1), the significant difference between 2PPE and 1PPE can only come from the additional intermediate states in 2PPE. Considering the optical transition between the initial and intermediate states, the SR has its dominant weight near the film surface[19] and the QW state is confined within the cobalt film.[17] The different spatial extensions of the SR and QW states (inset in Fig. 1) lead to a smaller overlap between them as compared to the overlap between other bulk-derived cobalt states and the QW states, which would give rise to a lower 2PPE signal from SR via QW states. The optical transitions through the intermediate QW states thus favor 2PPE processes with initial states localized in the interior of the cobalt films.

The overall larger spin polarization seen in 2PPE compared to 1PPE can be explained qualitatively, taking into account the energy and momentum conservation in optical transitions. The most relevant cobalt initial states in 2PPE can be determined from the band structure in Fig. 1. Both the majority and minority intermediate QW states are located near the X point, emphasizing 2PPE transitions starting from initial states with nearly the same crystal momentum around the X point. The strict crystal momentum conservation in bulk optical transitions will be partially relaxed due to (i) the finite cobalt film thickness, which broadens the k-space extension of the QW states and (ii) the many-body interactions which effectively smear out the k vectors of majority states in a single-particle band structure to a larger extent than the minority states.[26] Under these conditions, the bulk optical transitions populating the unoccupied QW states in 2PPE will prefer *majority* initial states near 1.2 Å^{-1}. The minority bulk states in the same initial-state energy region are located farther away from the X point in k space, in the vicinity of Γ near 0.1 Å^{-1}, and, thus, will couple much less efficiently to the QW states due to the larger mismatch in crystal momentum. These arguments explain the dominating majority-spin character of the electrons excited in 2PPE, in contrast to 1PPE, as well as the comparable signals of minority and majority QW states in previous inverse photoemission studies.[18] Although the photoemission features of QW states are suppressed for the low-temperature-grown films due to the increased surface roughness, the corresponding *sp* states, from which the QW states are derived, can serve as intermediate states for 2PPE, leading to a similar selection of initial states. Additionally, the minority contributions in 2PPE will be damped by the shorter lifetime of minority unoccupied states than the majority states,[27–29] including magnon emission for energy relaxation.[4] Spin-flip processes in the intermediate states can be neglected due to weak spin-orbit coupling in the QW states.[17] On the whole, an efficient suppression of the minority channel in the 2PPE compared to the 1PPE is resulting.

To summarize, our results show how the additional transition channels provided by intermediate states modify the production of spin-polarized photoelectrons in nonlinear compared to linear photoemission. In our specific case, we observe an increased spin polarization in 2PPE via intermediate quantum-well states in Co/Cu(001) films. The observed higher spin polarization in 2PPE than 1PPE is attributed to the spin, energy, and momentum selection in the two-photon transitions. Our results also demonstrate that the selection of specific spin-dependent excitation pathways in nonlinear photoemission at the same time can change the sensitivity to the spatial distribution of the states involved. In our case, we go from more surface-specific excitations in 1PPE toward bulk-derived transitions in 2PPE, which is important for mapping *bulk* unoccupied states using angle-resolved nonlinear photoemission.[11,12] The clear spin dependence in 2PPE through quantum-well states may, furthermore, provide a spin filtering mechanism for optical spin injection from ultrathin ferromagnetic films.

We gratefully acknowledge discussions with H. Petek and technical assistance by F. Helbig and M. Schröder.

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