Spin-Polarized Tunneling Spectroscopy of Co(0001) Surface States

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Spin-polarized tunneling was studied on Co surfaces of exchange coupled Co/Cu/Co samples, using an Fe tip. A spin-polarized surface state of Co(0001) was found to exist at −0.43 eV relative to E_F, with FWHM of 0.23 eV in the spectra. The state exhibits negative magnetoresistance with an effective spin polarization of less than −23%, suggesting negatively high spin polarization of the surface state. Our first-principles calculations have supported the existence of the surface state. From the calculation, the state is identified as a minority spin $\bar{\Gamma}$-centered d_z^2-like surface state.

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A new class of electronics, called spin electronics, exploits spin-polarized transport such as tunneling magnetoresistance (TMR) [1]. TMR emerging between two ferromagnets separated by an insulating barrier, has recently attracted attention because of its promising device application in magnetic information technology. The performance of the TMR devices is governed by the spin polarization of electrons tunneling from or into the ferromagnetic electrode. Although the spin polarization was thought to primarily reflect a characteristic spin polarization of the density of states (DOS) in the ferromagnetic electrode, recent experiments have revealed that the degree of spin polarization, its sign, and their energy dependence differ depending on the insulating barrier material, even for the same electrode material [2,3]. For instance, the polarization of Co adjacent to an Al_2O_3 barrier is +35%, with a maximum TMR at zero bias voltages [3,4]. On the other hand, Co with $SrTiO_3$ shows negative polarization with a TMR maximum at around +0.4 V (Co sample bias voltages) [3]. These results suggest the electronic states formed at the electrode-insulator interface are crucial to determine the spin polarization of the tunneling electrons.

As an insulating barrier material, vacuum is fundamental to the tunneling. The spin-polarized tunneling through a vacuum has been investigated by using scanning tunneling microscopy or spectroscopy [5–9]. The direct measurements of the spin polarization, using GaAs as a spin detector, have shown the polarization of the tunneling electrons near the Fermi level (E_F) of Ni bounded on a vacuum is negative [6], opposite to that on Al_2O_3 [4]. Further, the strong barrier thickness dependence of the polarization was observed, which was explained by the different inverse decay length of the highly polarized *d* electrons and the low-polarized *s* electrons [6].

In this Letter, we report the spin-polarized tunneling of Co through a vacuum, measured by scanning tunneling spectroscopy (STS) with an Fe tip. We show that the spin-polarized tunneling from the Co(0001) surface through a vacuum barrier is featured by a highly spin-polarized surface state of the Co surface. The origin of the state is traced by our first-principles calculations using the full-potential linearized augmented plane wave (FLAPW) method. The result suggests that the spin-polarized tunneling through a vacuum is dominated by the $\bar{\Gamma}$-centered d_z^2-like surface state, which is now becoming a general feature of the vacuum tunneling of the magnetic transition metal surfaces. The polarization of the state does not show the apparent barrier thickness dependence within our distance change.

The experiments were performed on Co(0001) films and Co/Cu/Co sandwich samples using W and Fe tips in an ultrahigh vacuum system with base pressures of less than 3×10^{-9} Pa. The Co films were epitaxially grown on Au(111) at room temperature with the thickness of 4.0–8.0 nm, and also grown on $SrTiO_3(111)$ at 570 K. The structural studies using surface x-ray absorption spectroscopy have revealed that Co on Au(111) has hexagonal close-packed (hcp) stacking with the film thickness of more than 0.8 nm [10]. The low energy electron diffraction patterns for Co grown on $SrTiO_3(111)$ showed the sixfold symmetry characteristic of hcp structure. These Co films were used for the experiments without controlling the magnetization direction. For the spin-polarized experiments, we utilized the Co/Cu/Co sandwich samples with a step-shaped Cu layer, in order to control the magnetic alignment of the sample [Fig. 1(a)]. In such samples, the oscillatory exchange coupling acts between two adjacent Co layers across the Cu layer [11,12], providing the controlled magnetic alignment of the sample surface determined by the Cu thickness. By forming a step-shaped Cu layer [13], two opposite magnetic alignments of ferromagnetic (FM) and antiferromagnetic (AFM) are obtained in one sample. The sandwich samples were grown on Au(111) at room temperature. Two types of sandwich structures were prepared: Co(1.0 nm, top)/Cu(x nm)/Co(1.6 nm, bottom) with $x =$ 1.0 and 1.6 (sample I), and Co(1.0 nm, top)/Cu(y nm)/Co(1.6 nm, bottom) with $y = 0.2$ and 1.0 (sample II). These Cu thicknesses were chosen after examining the coupling behavior for several samples with different Cu thicknesses (0.2, 0.9, 1.0, 1.1, and 1.6 nm). The sandwiches with the Cu thickness of 1.0 nm showed AFM coupling with the saturation field (H_s) of 2200 Oe, and the sandwiches with 0.2 or 1.6 nm Cu layers showed FM or zero coupling with the square-shaped hysteresis with H_s of 30 Oe. The spin-polarized tunneling measurements were

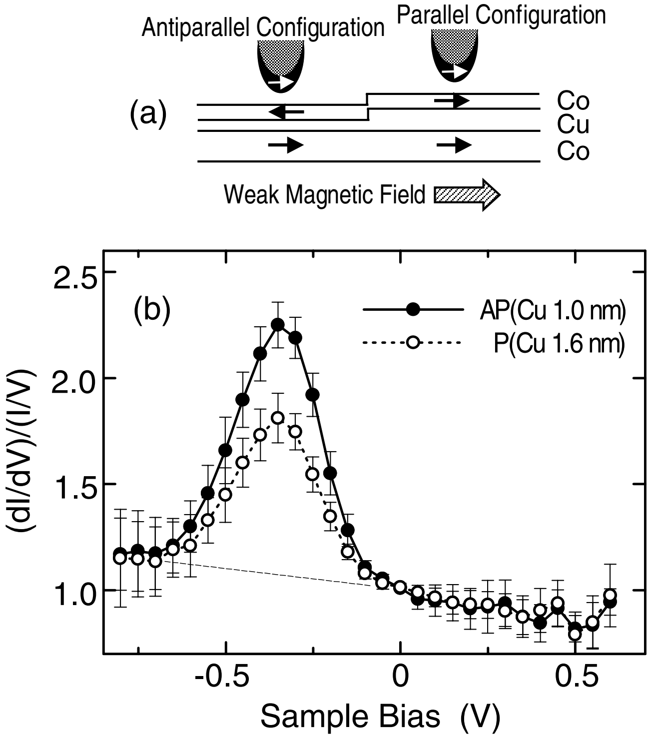

FIG. 1. (a) Schematic illustration of spin-polarized tunneling experiments using Co/Cu/Co sandwich structure with a step-shaped Cu layer and Fe-coated W tip. (b) Normalized tunneling conductance versus sample voltage for Co(1.0 nm)/Cu(x nm)/Co(1.6 nm) with $x = 1.0$ and 1.6 (sample I) measured with an Fe tip. The curves are the averages of more than 30 curves taken over atomic terraces for each Cu thickness region. For both configurations, the tip-sample distance is adjusted at $V_{\mathrm{sample}} = +1.0$ V and $I = 0.4$ nA.

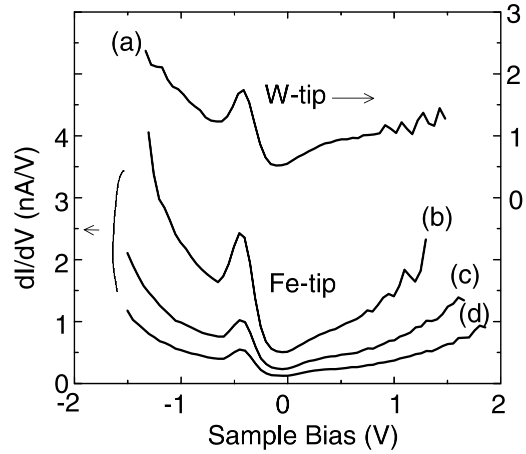

FIG. 2. Tunneling conductance versus sample voltage of Co(0001) surfaces measured on (*a*) Co 8 nm film surface grown on Au(111) taken with a W tip, and (*b*)–(*d*) Co 8 nm film surface grown on $SrTiO_3(111)$ taken with an Fe tip, at different tip-sample separations corresponding to the stabilizing current of (*b*) 0.8, (*c*) 0.4, and (*d*) 0.2 nA. The measurement position is the same during (*b*)–(*d*).

performed by using an Fe tip under a magnetic field of 150 G. This weak magnetic field aligns the magnetizations of the bottom thick Co and the tip parallel to the field, resulting in the antiparallel (AP) and the parallel (P) magnetic configurations between the sample surface and tip for the surfaces of the AFM and FM coupled regions, respectively, as illustrated in Fig. 1(a). This experimental setup allows us to measure both magnetic configurations with a tip, alternately. The electrochemically etched polycrystalline W tips with and without Fe cover layers were used for the measurements. The W tips were cleaned *in situ* in a field ion microscope, and then the Fe layers were deposited onto the tip topmost at a temperature of 550 K. All the tunneling measurements were performed at room temperature.

The tunneling spectra of the Co(0001) surface measured with a W tip and an Fe tip are shown in Fig. 2. The magnetization directions of the tip and sample are not controlled in these measurements. A sharp feature is found in Fig. 2 at around -0.43 eV relative to E_F of Co, with the full width at half maximum (FWHM) of 0.23 eV. This peak appeared independently of the tip materials, and was reproducibly observed in measurements on a large number of Co films with numerous tips. Therefore, it does not arise from the electronic states specific to the tip material nor from the shape of the tip topmost [14], but arises from the Co sample surface. Since the tunneling conductance is roughly proportional to the local DOS of the sample at the tip position multiplied by the tunneling probability [15], the sharp peak indicates the surface state or resonance state of Co(0001) extending outside the surface. The strength of the peak shows strong dependence on the tip-sample distance as shown in the curves (*b*)–(*d*) in Fig. 2, due to the exponential distance dependence of tunneling probability. These curves collapsed into a single curve by normalizing the tunneling conductance by dividing it by conductance, similar to the case of the nonmagnetic surfaces [16–18].

Figure 1(b) shows the normalized tunneling conductance versus bias voltage for the Co(1.0 nm)/Cu(x nm)/Co(1.6 nm) sandwich with $x = 1.0$ and 1.6 (sample I) measured with an Fe tip. The closed circles correspond to the normalized conductance obtained from the surface with Cu 1.0 nm, which yields an AP magnetic configuration between the tip and sample, and the open circles are from the surface of Cu 1.6 nm, yielding the P magnetic configuration. The reproducibility was checked by the measurements for both AP and P configurations, alternately. There is a distinct difference in the peak intensity between AP and P configurations. Since Fig. 1(b) is expressed as the normalized tunneling conductance in which the exponential dependence on the tip-sample distance is canceled out, as discussed later, we can directly compare the peak intensity of these two configurations in spite of the possible distance change between the two configurations. The peak intensity is stronger at AP configuration and weaker at P configuration, indicating negative tunneling MR. The peak position in Fig. 1(b) deviates from that in Fig. 2. It is mainly caused by the normalization procedure for the state having a certain amount of FWHM [17].

The Cu segregation to the surface and face-centered cubic stacking at the initial stage of the growth [19] may affect the peak feature.

The Cu thickness dependence of the peak intensity of samples I and II is shown in Fig. 3(a), together with the coupling behavior estimated from the measured H_s [Fig. 3(b)]. The peak intensity changes corresponding to the coupling behavior; with increasing Cu thickness, the peak intensity of sample I decreased, whereas for sample II, the intensity increased. Moreover, the peak intensities at AFM coupling and FM coupling of sample I are in good agreement with those at the same configurations of sample II, despite the different Cu thickness for the FM coupling. These results indicate that the peak intensity in the normalized conductance is apparently determined by the magnetic alignment between the tip and sample.

Here we discuss the normalized tunneling conductance of the spin-polarized tunneling. In the spin-polarized case, taking into account the two currents of up-spin and down-spin electrons, the normalized tunneling conductance at small bias voltages is given by

$$\frac{dI/dV}{I/V} \cong \frac{N_s(eV)N_t(0)\{1 + p_s(eV)p_t(0)\cos\theta\}}{\frac{1}{eV}\int_0^{eV} N_s(E)N_t(0)\{1 + p_s(E)p_t(0)\cos\theta\}\frac{T(E,eV)}{T(eV,eV)}\,dE} - \frac{1}{2}\frac{eV}{\overline{E_\kappa}},$$

where $N_s(E)$ and $N_t(E)$ are the DOS of the sample surface and the tip, respectively, $p_s(E) = [n_s\uparrow(E) - n_s\downarrow(E)]/N_s(E)$ and $p_t(E) = [n_t\uparrow(E) - n_t\downarrow(E)]/N_t(E)$ are spin polarizations of the sample and tip, respectively, and θ is the angle between the two magnetic directions of the tip and sample. $T(E, eV) = \exp(-2\kappa d)$ is the transmission probability of the electron, where d is the tip-sample distance and $\kappa = \kappa(E, eV)$ is the inverse decay length. $\overline{E_\kappa}$ is the averaged E_κ over $0 < E < eV$, where $E_\kappa = (\hbar^2/2m)(\kappa/d)$. Since the electronic fine structure of the tip was not found in the spectra, we assume a uniform tip DOS and spin polarization, i.e., $dN_t/dV \sim 0$ and $dp_t/dV \sim 0$. The first term in the equation expresses the "normalized" DOS of the sample surface modified by the spin polarization of the system and the angle between two magnetic directions. In this term, $T(E, eV)$ and $T(eV, eV)$ appear as ratios; therefore, the exponential dependence on the distance tends to cancel out [18]. For the spin-polarized tunneling, the tip-sample distance itself varies depending on the magnetic configuration, while the distance is adjusted at the same voltage and current [5]. This distance change changes the peak intensity given in dI/dV. Therefore, the cancellation of the dependence on the distance by the normalization procedure is crucial to compare the peak intensities of two different magnetic configurations. The second term in the equation is the background term, which increases with decreasing bias voltages in negative bias voltages [18]. The estimation using $\kappa = 0.1\ \text{nm}^{-1}$ and $d = 1$ nm yields a relatively large background of 0.53 at bias voltages of -0.4 V. The observed normalized tunneling spectra of Fig. 1(b) contain this background and also contain the featureless electronic states of the sample whose polarization is negligibly small. Eliminating these two components [20], the net peak intensity ratio (Int $\uparrow\downarrow$ − Int $\uparrow\uparrow$)/Int $\uparrow\uparrow$ becomes 61%. For the net surface state, the ratio is simply given as $-2p_sp_t/(1 + p_sp_t)$ when $|p_sp_t| \ll 1$, from the equation. Therefore, the effective spin polarization of the whole tunneling system, which is defined as the product of the sample and tip spin polarizations p_sp_t, is estimated to be less than -23% [21]. If we assume the Fe tip has the highest spin polarization reported for tunneling: $p_t = 44\%$ [4], for convenience, then p_s of the surface state becomes less than -52%, and if $p_t = 23\%$, p_s gives the upper limit of the polarization, -100%, suggesting the high spin polarization of the surface state of Co(0001).

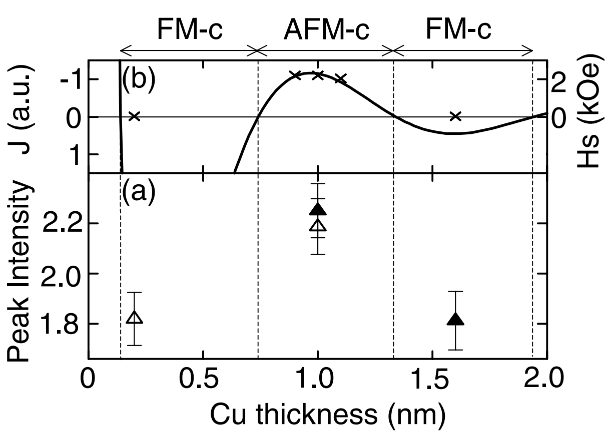

FIG. 3. (a) Peak intensity in normalized tunneling conductance versus Cu thickness obtained from sample I(▲) and sample II(△). (b) Oscillatory behavior of the interlayer exchange coupling (J) derived from the measured saturation field (H_s) (×). At AFM coupling, the negative coupling strength is proportional to H_s. The curve was obtained by fitting using the parameters of the oscillation period of 6 ML and the decay factor of -2 [11].

In our experiments, the peak intensity in normalized conductance for the same magnetic configuration remained the same within the experimental error, during the tip-sample distance change of 0.09 nm. It indicates the polarization is insensitive to the barrier thickness, which seems contradictory to the results of Ref. [6], in which the polarization doubled with decreasing barrier thickness by 0.18 nm. It may be due to the lower contribution of the s electrons to the intensity at the surface state.

In order to identify the spin-polarized surface state observed, we performed the band structure calculations of a seven-layer Co hcp(0001) thin film using the FLAPW method [22]. The calculated band structure of the whole layers, shown in Fig. 4(a), agrees well with that reported previously [23]. At tip position above the surface, the states decay extremely faster with increasing parallel wave

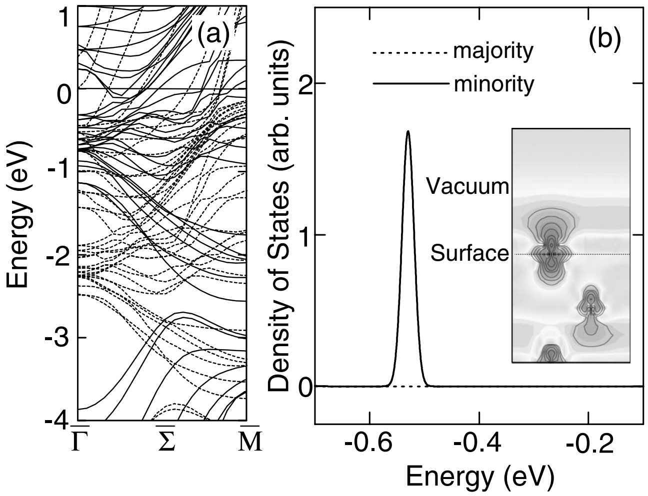

FIG. 4. (a) Band structure of a seven layer Co(0001) film along $\bar{\Gamma}$-$\bar{M}$. (b) Density of the states (DOS) at 0.5 nm above the Co(0001) surface arising from the $\bar{\Gamma}$ point. Inset shows charge density distribution of minority spin $\bar{\Gamma}$-centered surface state showing peak in DOS on the $(11\bar{2}0)$ plane through outermost atoms. Contours start from 67.5 electrons/nm^3 and increase by a factor of 2.

vector $\mathbf{k}_{\parallel}$ [24]. Hence, we discuss here the states at the $\bar{\Gamma}$ point surviving above the surface. Figure 4(b) shows the DOS at 0.5 nm above Co(0001) arising from the $\bar{\Gamma}$ point. A minority state exists at the almost corresponding energy to the observed peak position. It has a typical d_z^2 character (z is normal to the surface), as shown in the inset of Fig. 4(b). Therefore, the origin of the observed spin-polarized state is considered to be this minority band $\bar{\Gamma}$-centered d_z^2-like state. Because the state has negative spin polarization, the negative MR is explained by assuming the positive spin polarization of the Fe tip [8].

The surface state of Co(0001) has been observed in the early spin-integrated photoemission study, at -0.3 eV [25]. Although it was considered to be an sp-like surface state, it might be the same state as that observed in the present tunneling study. The identified origin, $\bar{\Gamma}$-centered d_z^2-like surface state, coincides with those clarified for the states found on Fe(001) [24], Cr(001) [24], Gd(0001) [8], and Tb(0001) [9]. This symmetry might be a general feature for the highly spin-polarized surface states that appear on magnetic transition metals in vacuum tunneling.

In conclusion, we have investigated the spin-polarized tunneling between Co(0001) and the Fe tip through vacuum and found the spin-polarized surface state at -0.43 eV relative to E_F of Co. The intensity of the state exhibited negative TMR with the effective spin polarization of less than -23%. We pointed out that the normalization of the tunneling conductance is crucial in discussing the spin-polarized tunneling in STS. Our first-principles calculation revealed that the state originates from the minority spin d_z^2-like surface state at the $\bar{\Gamma}$ point of the hcp(0001) surface. This highly spin-polarized state on Co will become a useful state for magnetic imaging of the ultrafine Co elements using spin-polarized STS [26].

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