Co and Phthalocyanine Overlayers on the Quantum-Well System Co(001)/Cu: Spin-Polarized Electron Reflection Experiments

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Abstract
The influence of a Co or phthalocyanine (Pc) molecular overlayer on the properties of quantum-well resonances (QWR) in Cu layers atop Co(001) is studied by means of spin-polarized electron reflection. For Co atoms and Pc molecules, an energy shift of the QWR-induced signal is observed with increasing coverage and is attributed to a variation of the electron reflection phase at the Cu/Co and Cu/Pc interface. For Co we find a linear energy shift in the Cu QWR energy position with increasing coverage down to the sub-monolayer regime. This shows that the phase accumulation model remains accurate within the sub-monolayer regime of a discontinuous interface. An opposite sign in the energy shift between Co and Pc overlayers could reflect an opposite impact on the Cu surface work function of overlayer adsorption.

Keywords
Quantum-Well Resonances, Spin-Polarized Electron Reflection

1. Introduction
Quantum confinement in thin metallic films gives rise to discrete quantum-well states (see Ref. [1] and references therein) that are known to lead, as the film thickness is varied, to variations in different physical quantities such as surface energy [2], thermal stability [3], work function [4], electrical conductivity [5] and surface adsorption [6] [7]. This confinement can become spin-dependent if ferromagnetic layers are considered. This accounts for the oscillatory behavior of the indirect exchange coupling between two ferromagnetic layers separated by a
non-magnetic spacer layer [8], the magneto-optical response [9], the induced magnetic moment [10], the magnetic anisotropy [11], and the Curie temperature [12].

While there is a lot of literature concerning quantum confinement in systems such as Fe(001)/Ag or Co(001)/Cu (for instance Refs. [1] and [13]), only little work exists on how quantum well states (QWS; below the vacuum energy) or resonances (above the vacuum energy) are influenced when such a system is covered. Scanning tunneling spectroscopy measurements on QWS in Cu and Pb studied the behavior of the Kondo resonance of Co for Co overlayers [14] [15] and of Mn for a molecular overlayer coverage of Mn-phthalocyanine (MnPc) [16]. As the Kondo resonance can only be seen for isolated atoms or molecules only very small coverage of about 0.01 monolayer (ML) could be studied. Interestingly, quite different results were obtained for Co coverage on Cu [14] and on Pb [15]. While the Kondo resonance of Co atoms on Cu shows QWS-induced oscillatory modulations of its line width, Co atoms adsorbed atop Pb destroy the QWS within the Pb film. On the other hand, the QWS in the Pb layer are not destroyed by adsorption of MnPc molecules which is proven by the presence of strong line width modulations of the Kondo resonance of Mn [16]. The effect on QWS in Ag(111) layers by a very similar molecule, namely CuPc, has been studied by photoemission spectroscopy [17]. Interestingly, neither the intensities of the QWS (after consideration of the signal attenuation due to the CuPc layer) nor their energy positions change with increasing CuPc coverage (up to 1 ML).

The goal of this work is to shed more light on the question of how the presence of an additional interface affects the quantum confinement, in particular as the above cited results are somewhat contradictory. In the following we examine the behavior of QWR by spin-polarized reflection of electrons in Co(001)/Cu layers when covered by metallic Co or by semiconducting Pc molecules.

Information on QWS are mostly obtained via photoemission experiments [13]. One of the major results of such experiments is that the appearance of QWS as a function of film thickness is explained very well by the so-called phase accumulation model [18]. Consequently, if the electron system is confined to a thin film of thickness \(d\) deposited onto a substrate, constructive interference, \(i.e.\) maximum in intensity, requires the wave vector component \(k_\perp\) perpendicular to the surface of the electrons in the thin film to fulfill the standard quantization condition:

\[
2k_\perp d + \theta = 2\pi n \quad (1)
\]

with \(\theta\) a phase shift due to the reflections of the electrons at the film/vacuum and the substrate/film interface and \(n\) an integer. As a consequence, the difference between two neighboring \(k_\perp\)-values fulfilling the above interference condition decreases with increasing film thickness. Thus, the number of QWS increases with increasing film thickness.
2. Experiment

The experimental set-up is shown schematically in Figure 1. A spin-polarized electron-source based on a GaAs photocathode produces a spin-polarized electron beam with 25% spin polarization [19]. By switching from right- to left-circularly polarized light, the direction of the initial spin polarization of the photoexcited electrons can be inverted. The electron beam impinges onto the sample at an angle of 45° with respect to the surface normal [001] of the Cu(001) single crystal. The surface projection of the incident electron wave vector is along the [110]-direction of the Cu substrate. The spin polarization vector $P_0$ of the incident electrons is oriented either parallel or antiparallel to the magnetization vector $M$ of the ferromagnetic material. The specularly reflected electrons are energy analyzed by a retarding grid analyzer that has an energy resolution of 0.3 eV FWHM. The broad distribution of inelastically scattered electrons is suppressed by applying a retarding field to the retardation grid. Subsequently, the intensity of the specularly reflected electron beam is measured. To get rid of any experimental asymmetry, the direction in space as well as the relative alignment of $P_0$ and $M$ is interchanged.

Due to exchange interactions at the surface of the ferromagnetic sample, which are essentially an outcome of the Pauli principle, the reflection properties of the electron beam depend on the relative orientation of $P_0$ and $M$. In fact, the reflectivities for electrons with $P_0$ parallel to $M$, $R_{\uparrow\uparrow}$, and antiparallel to $M$, $R_{\uparrow\downarrow}$, are in general different, such that one obtains a non-vanishing exchange asymmetry:

$$A_{ex} = \frac{1}{P_0} \frac{R_{\uparrow\uparrow} - R_{\uparrow\downarrow}}{R_{\uparrow\uparrow} + R_{\uparrow\downarrow}}$$

which is normalized by the polarization value $P_0$ of the incident electron beam.

In a first step a Co film of 10 ML thickness was deposited onto a single crystalline Cu(001) substrate at room temperature from a Co rod heated by electron beam bombardment. Prior to deposition, the Cu substrate was cleaned by several
cycles of Ar-ion sputtering and annealing at 800 K. Co on Cu(001) exhibits an easy axis of magnetization in the film plane along the [110] direction. The Co films are magnetized remanently by applying magnetic field pulses along this direction. We note that the system Cu(001)/Co has extensively been investigated in the past (see for instance Refs. [20] [21] [22] [23]). In a second step Cu films of different thicknesses (3, 6, and 10 ML) are deposited onto the Co film at room temperature. This overlayer system, namely Co(001)/Cu, has as well extensively been studied in the past and shows the existence of QWS and QWR [24] [25]. Both Co and Cu thicknesses could be determined within an accuracy of about ±10%. The evaporation rate was controlled by a quartz microbalance. In a third step either Co or H₂-phthalocyanine (H₂Pc) molecules are deposited at room temperature successively onto the Co/Cu stack during the electron reflection experiments. For detailed information about the growth of Pc molecules on Cu(001) in the monolayer range see Ref. [26]. The thicknesses of the molecular layers are determined by Auger electron spectroscopy [27] and by the study of the work function change with increasing Pc thickness [27]. We emphasize that our X-ray photoemission spectroscopy measurements on H₂Pc molecules deposited onto Cu(001) at room temperature do not indicate any Cu-metalation of the H₂Pc molecules (i.e. replacement of the two central protons by Cu²⁺; data not shown).

3. Results and Discussion

It has already been shown by Egger et al. [28] that the very pronounced structures of $A_{ex}$ as a function of Cu thickness in the system Co(001)/Cu are directly related to the presence of QWR in the Cu film. In a later work [25] the Cu-thickness dependent behavior of the spin motion angle $\phi$, which is directly related to the quantity $A_{ex}$ [29], has been studied. Most importantly, the energy positions of the extrema in $\phi$ and thus in $A_{ex}$ shift with varying Cu film thickness and are in good agreement with those of the extrema in reflectivity. This shows that the existence of QWR is at the origin not only of the reflectivity oscillations but also of the oscillations in $A_{ex}$. Moreover, the extrema in $A_{ex}$ usually are much more pronounced than those of the reflectivity [25] [30] such that $A_{ex}$ is an ideal quantity to study the behavior of QWR.

We present in Figure 2 the dependence of $A_{ex}$ on the kinetic electron energy (i.e. the incident energy with respect to the vacuum level) as the thickness of the Co and Pc overlayer is increased. In both cases, we concentrate on the energy variation of the $A_{ex}$ minimum between 6 and 7 eV kinetic energy. While an energy shift in the $A_{ex}$ minimum to lower kinetic energies is observed with increasing Co coverage, the energy shift is positive for Pc coverage. We emphasize that the observed energy shifts of the QWR-induced structure is related to a phase shift. However, we cannot extract phase shifts directly from the measured energy shifts as the phase change $\Delta \theta$ is proportional to the change $\Delta k_\perp$ of the electron wave vector, $\Delta \theta = -2d \cdot \Delta k_\perp$, and not of the energy difference (see...
Figure 2. $A_{\text{ex}}$ vs. kinetic electron energy for different Co (top) and Pc coverages (bottom) on 6 ML Cu on Co(001). The inset shows a schematic electronic band structure with two bands and a band gap in-between (see text).

Equation (1)). In order to obtain the corresponding $k_{\perp}$ values one needs thus the unoccupied band structure of Cu above the vacuum level. This, however, is not available for our particular measuring geometry in which the incident electron wave vector is not normal to the sample surface (see section “Experiment”) so that we have to refrain from a calculation of the phase shifts and show only the energy shifts.

We plot in Figure 3 the energy shift of the QWR-induced $A_{\text{ex}}$ minimum for both Co and Pc coverage on Co(001)/Cu with varying Cu thickness. We first discuss the case of the Co overlayer. This energy shift is linear within the Co thickness range studied, with a slope that decreases when going from 3 to 10 ML Cu thickness. This is understandable since, with increasing Cu thickness, the QWS features become denser in energy [1], such that a given phase shift corresponds to a smaller energy shift. The observation that the energy position of the QWR shifts to lower kinetic energy is consistent with ab initio calculations of a
Figure 3. The energy shift of the QWR-induced $A_{ex}$ structure for Co coverage (full symbols) and Pc coverage (open symbols) on Co(001)/Cu with varying Cu thickness. The inset shows the amplitude of the $A_{ex}$ structure as a function of both Co and Pc coverage.

Co overlayer on top of the Co(001)/Cu quantum-well system [31]. In fact, these calculations of the density-of-states below $E_F$ show that with increasing Co coverage the QWS disperse smoothly upwards in energy. This is due to the fact that the wave vector of the QWS which lie on the lower band (see the schematic band structure as inset of Figure 2 (top)) shifts to higher values such that the QWS come closer to the boundary of the Cu Brillouin zone. In the case of QWR which lie above the band gap (see inset of Figure 2 (top)) this wave-vector shift closer to the Brillouin zone boundary leads thus to a downward dispersion in energy of the QWR with increasing Co thickness as observed.

Our result is particularly interesting in view of recent calculations concerning the effect of Co ad-atoms on the quantum confinement in the Co(001)/Cu system [32]. These calculations show that the density-of-states of the Cu surface is drastically modified by a sub-ML fraction of Co ad-atoms, such that an analysis within the phase accumulation model proves to be inadequate. This failure of the phase accumulation model suggests that the QWS are substantially perturbed by the presence of Co ad-atoms, which, in contrast to a complete monolayer, do not constitute a smooth interface. However, within our study we observe a linear increase of the energy shift between 0 and 2 ML Co coverage. There is thus no experimental indication that the behavior of an incomplete Co layer might be very different from that of a complete Co layer. The lateral inhomogeneity of the Co film for sub-ML coverage does not seem to be important at least for the energy shift and thus the phase shift. Moreover, a strongly perturbed QWR would result in a strongly modified amplitude of the $A_{ex}$ signal. However, this is not observed in our measurements. In fact, the inset in Figure 3 shows only a monotonous decrease of the $A_{ex}$-amplitude whose value is mainly determined by the limited
mean free path of the electrons.

The behavior of the energy shift as a function of Pc coverage is quite different from that of Co coverage. The most important difference concerns the amplitude of the $A_\alpha$ signal as the latter is rapidly decreasing with increasing Pc coverage and almost disappears for coverages well below 1 ML (see inset in Figure 3). We emphasize that a similar behavior, which we called breakdown phenomenon and which results in a spin-independence of the electron reflection (i.e. $A_\alpha$ becomes zero), has been found recently by some of us for many metal-organic interfaces [27] [33]. It is important to note that this breakdown phenomenon is only observed in experiments in which the reflection of electrons is studied and is not yet understood. Thus, a rapid decrease of the $A_\alpha$ signal with increasing Pc coverage is indeed expected. Within the Pc coverage range for which the $A_\alpha$ signal can be studied as a function of energy, we observe an energy shift that is much stronger than that of Co. Moreover, it does not exhibit a linear behavior as for Co and seems to saturate. This behavior of the energy shift thus resembles that of the breakdown phenomenon and is as such without explanation at the moment.

The other significant difference between the case of Co and Pc overlayers is the opposite sign in the QWR energy shifts. However, this does not seem to us very surprising. As the electronic density-of-states of Co and Pc are completely different one can expect as well quite different electron reflection properties at the interfaces Cu/Co and Cu/Pc, including opposite sign of the phase shifts. Moreover, the change of the work function at the overlayer surface might also have a certain influence on the reflection properties of the standing electron waves [1], in particular if the overlayer is extremely thin, as it is the case in our measurements, such that the overlayer/vacuum interface can have an important influence on the Cu/overlayer interface. Since the work function differences $\Delta \phi$ in the two cases are in particular of opposite sign (Cu/Co: $\Delta \phi = +0.3$ eV, Cu/1 ML Pc: $\Delta \phi = -0.8$ eV [34]) they could be responsible for the different sign in phase shift.

4. Conclusion

In conclusion, the spin-dependent electron reflection at the Cu/Co or Cu/Pc top interface within the Co(001)/Cu quantum-well system has been studied. A clear energy shift of the QWR-induced signal was observed both for Co atoms and Pc molecules with increasing overlayer coverage. The linearity of this energy shift for increasing Co coverage, both below and above the monolayer, suggests that the phase accumulation model remains valid below the monolayer regime for the quantum well considered. A comparison with the literature suggests that the inferred variation of the electron reflection phase at the Cu/Co and Cu/molecule interface appears to depend on the exact quantum well resonance considered. The opposite sign of the energy shift for Co and Pc overlayers could reflect the opposite impact on the Cu surface work function of these overlayers. This work
establishes guidelines to better understand the physics of spin-polarized quantum confinement using both metallic and molecular layers.

References


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