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2010 J. Phys.: Condens. Matter 22 052203

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FAST TRACK COMMUNICATION

Quantum-well states in a double-well system: an example of Cu/Co(Ni)/Cu

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Received 30 November 2009

Published 15 January 2010

Online at stacks.iop.org/JPhysCM/22/052203**Abstract**

The quantum-well (QW) states in the Cu/Co double-well system are studied by first-principles calculations. We have shown that the monolayer Ni or Co as a heterogeneous spacer in Cu QW can not only disturb the QW states extending into the whole structure, but also create new QW states because of the interfaces introduced, resulting in sub-well-confining electrons. If the QW state energy in two sub-wells is close to each other, these two sub-well QW states can couple together. We have also demonstrated that monolayer Co and Ni spacers play different roles for modulating QW states at different energy levels, which also result in a complicated distribution of QW states. The obtained results are in good agreement with experiment data.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In an ultra-thin film with nanometer-scale thickness, it is well known that the electrons can be confined in the direction normal to the film, resulting in quantum-well (QW) states. QW states in metallic films, such as Ag/Fe(001) [1, 2], Cu/Co(100) [3–14], Ag/Ge(111) [15, 16] and Pb/Si(111) [17, 18], have attracted considerable interest. QW states can remarkably influence the physical properties through changing the density of states (DOS) at the Fermi level. Therefore, QWs provide a great possibility to modulate the physical properties with film thickness, which is essential to the application of thin films. The modulation effect of QW states on variable physical properties has already been discovered, like the modulation of thin metallic film stability [2, 19], work function [20], magnetic interlayer coupling [7], superconducting transition temperature [21], surface chemical reactivity [22, 23], etc.

Usually the energy of QW states in metallic thin films depends on the film thickness, and the quantization

condition can be well understood by the phase accumulation model (PAM) [7, 24, 25]. The Cu/Co(001) system is one of the model systems to study QW states in metallic thin films, and the nature of the single QW states has been widely studied by experiments [7–10] and theoretical calculations [11, 26–28]. Besides the film thickness, the film structure can also modify the QW states through the interaction between different quantum confined systems. Such an effect has been demonstrated in the stacks of Cu/Co(Ni)/Cu grown on a Co(001) substrate [9, 10]. In the Cu/Ni/Cu system, the Ni monolayer can be used as a probing layer to detect the envelope modulation of QW states. In the case of symmetric double QWs with equal well widths separated by a 1 ML Ni spacer layer [9], it has been demonstrated that each QW state splits into two for high energies (that is, energies closer to the Fermi level). The interaction between two QWs also exhibits a state-crossing effect near the degenerate energy levels of the corresponding two separated Cu QWs in the Cu/Co/Cu system [10]. Moreover, by replacing the middle Ni (or Co) barrier layer with an Ni/Cu/Ni QW to tune the

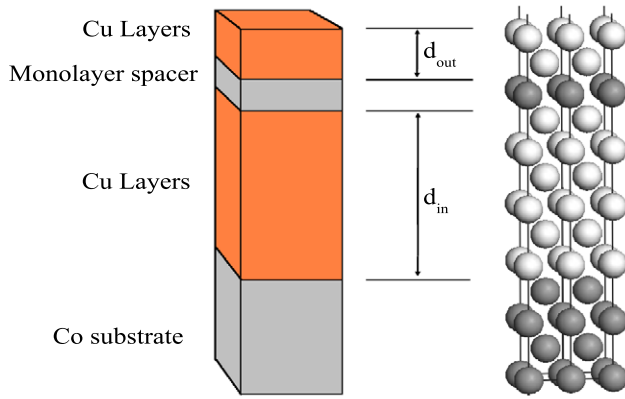


Figure 1. Schematic drawing of the calculated sample Cu/Co(or Ni)/Cu/Co(4 ML) structure. The total thickness has been fixed and only the Co (or Ni) spacer layer would be changed.

middle layer energy levels, a resonant interaction of two Cu QWs can occur at the energy levels of the middle Ni/Cu/Ni QW [8]. All these experimental studies clearly proved that QW states in metallic thin films can be influenced by the film structure. However, there was very little theoretical effort in understanding the interaction between the Cu QWs in the Cu/Co/Cu system and in the Cu/Ni/Cu system, and it still needs to be answered whether the QW states in these systems can spread into the whole stack, which is hardly identified only by the experimental study.

In this paper, we studied the QW states in the multi-layer stack of Cu/Ni(Co)/Cu by first-principles calculations, and investigated the effect of the Ni or Co monolayer on the QW states. We found that the monolayer Ni or Co in a Cu stack cannot only disturb the QW states of the whole stack, but also creates new QW states simultaneously. Due to the different electronic structures of the monolayer Co and monolayer Ni layer, they show different modulation effects on QW states at high energy close to the Fermi surface.

2. Theoretical methods

Our calculations are based on the density functional theory (DFT) implemented in the Vienna *ab initio* simulation package (VASP) [30]. The generalized gradient approximation (GGA) is used for the exchange–correlation functional [31]. Only the valence electrons are treated explicitly, and their interactions with ionic cores are described by the projector augmented-wave (PAW) pseudo-potentials [32, 33]. The film is modeled by periodically repeated Cu(001) slabs or stacks (see figure 1) on 4 ML Co(001), separated in between by a vacuum region thicker than 25 Å. Here the 4 ML Co layer can be considered as the Co(001) substrate and it is thick enough for energy convergence of QW states, consistent with previous calculations [11]. In the Cu/Co/Cu(001) system, the energies of the Cu QW states do not change with Co film thickness for $d_{\text{Co}} > 3$ ML [14]. The lattice vectors of the supercell used to model the film structures are $\vec{a}_1 = (\sqrt{2}/2)a\vec{i}$, $\vec{a}_2 = (\sqrt{2}/2)a\vec{j}$ and $\vec{a}_3 = c\vec{k}$, where a is the calculated lattice constant of bulk Cu and c is the repeat period perpendicular to the film.

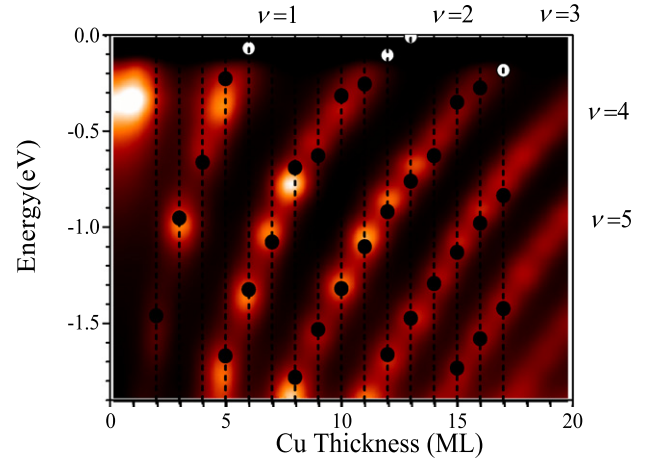


Figure 2. The comparison between the experimental measurements and the calculated results on the Cu/Co(001) system. The contour shows the normal photoemission intensity as a function of Cu thickness and binding energy. Solid circles (white and black) represent the energies of QW states at the surface Brillouin zone center calculated by using GGA for different Cu thickness.

It is known that experimentally all the film structures were grown pseudomorphically on a bulk Cu substrate along the [100] direction [7]. The calculated lattice constant of Cu of 3.64 Å is well consistent with the experimental value of 3.61 Å. Given such a supercell, a $23 \times 23 \times 1$ k -point grid of k -space integration and an energy cutoff of 400 eV are set up for all the calculations. Both a quasi-Newton algorithm (a pre-converged starting guess for better convergence) and a conjugate gradient algorithm are used to optimize the atomic structures. In the calculation, the interlayer spacing is relaxed until the highest residual force is less than 0.01 eV \AA^{-1} . Tests have been performed to make sure that all the results are fully converged with respect to energy cutoff, system size and k -point sampling.

To investigate the influence of the Co (or Ni) monolayer spacer on QW states, we calculated the QW states in 9 ML thick Cu/Co(Ni)/Cu stacks on 4 ML Co(001), with the Co(Ni) spacer located at different positions in the whole stack, as shown in figure 1. Here the Cu/Co(Ni)/Cu stack can be considered as when the i th Cu atomic layer is replaced by a Co(or Ni) layer in the 9 ML Cu stack. Then the Cu/Co(Ni)/Cu stack can be considered either as a whole QW system or a system with two sub-wells separated by a 1 ML Co (or Ni) potential barrier [7]. The thickness of the inner sub-well is $d_{\text{in}} = i - 1$ and the thickness of the outer sub-well is $d_{\text{out}} = 9 - i$.

3. Results and discussion

Figure 2 shows the high quality photoemission measurement from the Cu/Co(001) system; the experimental procedure is the same as [8–10]. The thickness-dependent energies of Cu QW states can be determined from the intensity contour plot as functions of Cu thickness and binding energy. The discrete intensity peaks indicate the energies of the Cu QW states with

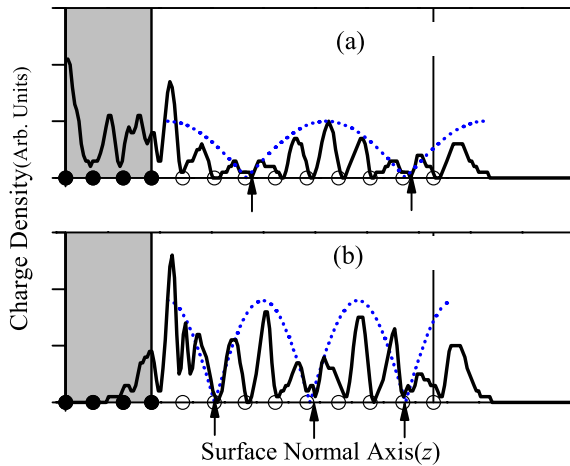


Figure 3. Calculated plane-averaged charge densities of single QW states in Cu(9 ML)/Co(4 ML) films. The nodes of the envelope wavefunctions are marked by the arrows. The position of Co and Cu atoms are marked by solid and open circles, respectively, and the gray shaded layer indicates the position of the Co substrate. The dotted line is a guide for the eyes to show the envelope function. (a) $\nu = 2$, $E = -0.63$ eV; (b) $\nu = 3$, $E = -1.53$ eV.

the integer number of layer thickness. The QWs energy can be well described by the phase accumulation method [7, 24, 25], in which the quantization condition is given by

$$2k_{\perp}(E)d_{\text{Cu}} + \phi_B + \phi_C = 2\pi n, \quad n = \text{integer} \quad (1)$$

where ϕ_B and ϕ_C are the phase gains of the electron wavefunction upon the Cu/vacuum and the Cu/Co interfaces, respectively, d_{Cu} is the Cu layer thickness and $k_{\perp}(E)$ is the momentum of the Cu sp band along the normal [001] direction (Δ_1 symmetry). However, if considering that the Cu thickness can only take integer multiples (m) of the atomic spacing a , then equation (1) can be rewritten in terms of a new index ν [24]:

$$2(k_{\text{BZ}} - k_{\perp}(E))d_{\text{Cu}} - \phi_B - \phi_C = 2\pi\nu \quad (2)$$

with the Brillouin zone (BZ) vector $k_{\text{BZ}} = \pi/a$ and the new index $\nu = m - n$. From figure 2, it can be seen that ν is an appropriate quantum number for classification of QW states.

We first performed the calculation on the single Cu QWs. In the Cu/Co(001) system the QW states only exist in the minority sp band [4–8], so in this paper we only present the calculated results on the QW states of the electron with minority spin. The calculated thickness-dependent energy of QW states along the $\bar{\Gamma}$ - \bar{X} direction was plotted in figure 2. The energies of the QW states show a close agreement with the experimental data, and most of the calculated values fall within the peaks of photoemission intensity. It should be noted that the QW states show a slightly different evolution trend above and below -0.5 eV, which does not agree well with the experimental result. This disagreement also existed in the previous theoretical studies on QW states in Cu/Co(001) [11, 28] and it may be attributed to the band structure of the Co substrate, since the minority sp band along the $\bar{\Gamma}$ - \bar{X} direction only exists above -0.5 eV for fcc Co.

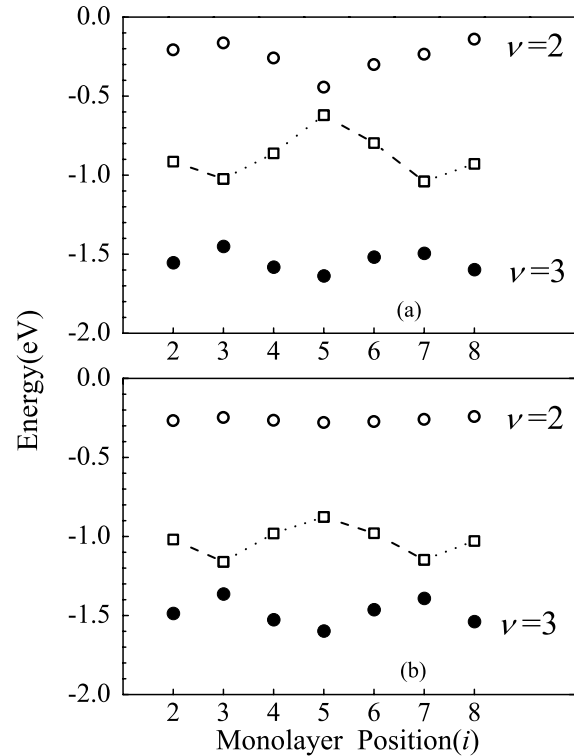


Figure 4. Energies of the $\nu = 2$ (empty circles) and $\nu = 3$ (solid circles) QW states and new sub-well QW states (squares) as a function of the position of (a) Co and (b) Ni monolayer spacer.

Figure 3 shows the plane-averaged charge densities of QW states of the 9 ML Cu layer. The charge density is defined as $|\psi(z)|^2$, where z is the coordinate in the direction normal to the film. Therefore, the plane-averaged charge density can reflect the envelope shape of the wavefunction of QW states [24] and the number of nodes of the wavefunction can be determined by the index ν . For the QW states with the energy -0.63 eV ($\nu = 2$), the charge density is not fully confined in Cu layers, but extends into the Co substrate. This indicates that the $\nu = 2$ QW state is a resonance QW state [34]. However, for the $\nu = 3$ QW state with energy -1.53 eV, the electron can be truly confined in the Cu film and the charge density decays very fast in the Co region. All these phenomena are consistent with previous theoretical studies [11]. These two states will be taken as typical examples of high energy states and low energy states, respectively, to explore how the Ni (or Co) monolayer spacer affects the Cu QW states.

Next, we will show how the Co or Ni spacer layer affects the QW states in 9 ML Cu/Co(Ni)/Cu stacks. Figure 4 shows the dependence of the QW state energy on the position of the spacer layer in each Cu/Co(Ni)/Cu stack. Three QW states have been found in each 9 ML Cu/Co(Ni)/Cu stack, different from the QW states in the 9 ML pure Cu slab. For the QW states with energies at ~ -0.3 and ~ -1.5 eV, their charge densities are found spreading over the whole Cu/Co(Ni)/Cu stack, as shown in figure 5. If we disregard the detailed charge density around the Co (or Ni) layer position, the overall charge densities have two nodes for the QW states at ~ -0.3 eV and three nodes for the QW states at ~ -1.5 eV, which are very

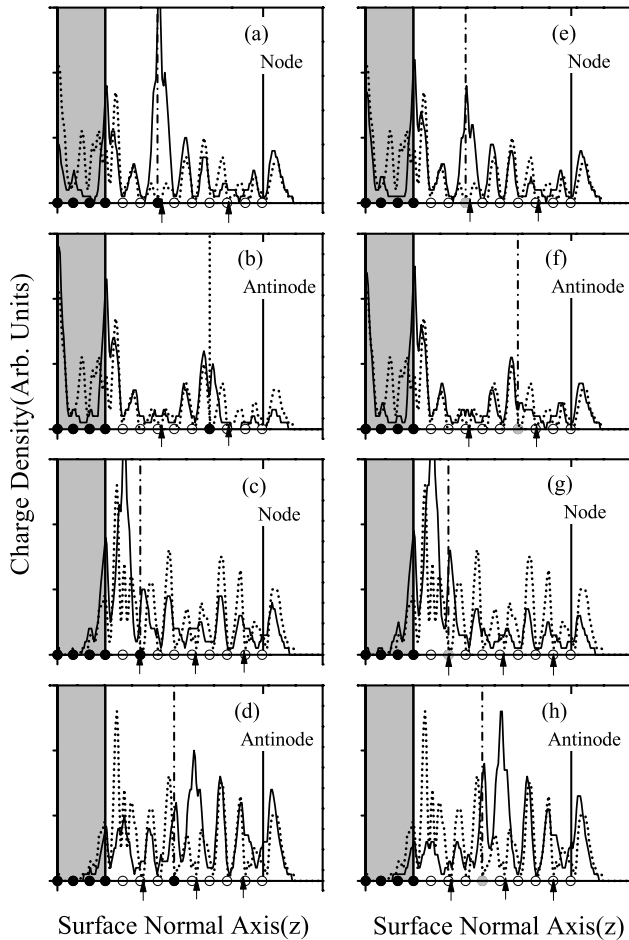


Figure 5. Plane-averaged charge densities of $\nu = 2$ and 3 QW states (solid line) in the whole stack with the monolayer of Co ((a)–(d)) and the monolayer of Ni ((e)–(h)). For comparison, the plane-averaged charge density distribution of QW state in 9 ML Cu film is also plotted as the dotted line in each figure. The black, open and gray circles indicate the position of the Co, Cu and Ni atoms. The arrows mark the node position of the envelope wavefunction. (a), (b), (e) and (f) $\nu = 2$. (c), (d), (g) and (h) $\nu = 3$.

similar to those of the QW states of a 9 ML single Cu quantum well. So our calculation indicates that the QW states of overall Cu/Co(Ni)/Cu stacks can still exist after replacing a Cu layer by an Ni or Co layer. However, the QW states with energy ~ -1.0 eV are new QW states confined in one of the Cu subwells, which will be discussed later.

We will first discuss how the Co (or Ni) layer at different positions influences the QW states in the whole stack with the energy at ~ -0.3 and ~ -1.5 eV. For convenience, those QW states will be denoted as high energy QW state ($\nu = 2$) and low energy QW state ($\nu = 3$). In figure 4, clearly the energies of those QW states oscillate with the Co (or Ni) position in the stack. For the low energy state, the Co and Ni position has a similar modulating effect on the QW state. However, for the high energy state, the energy of the QW state is not sensitive to the position of the Ni spacer, while it strongly depends on the position of the Co spacer. The different effect may be

associated with the different bandgaps of bulk Co and bulk Ni. It is known that [35] the bottom edge of the sp band with the minority spin is at -1.0 eV for bulk Ni and -0.5 eV for bulk Co. Then the Ni sp band is closer to the Cu sp band of Cu, so the electron reflection should be smaller above the bandgap, which may be the reason that the Ni layer has much less effect on the high energy QW states. At low energy, the QW states are located within the bandgap of both Co and Ni, so both of them will have a strong effect on the energy position of the lower energy QW states.

The calculated results indicate that the inserted spacer layer can modulate the QW energy, but this effect has not been clearly proved by experiments. In the Cu/Co/Cu [8] and Cu/Ni/Cu [9] systems, the photoemission results only show that the photoemission intensity instead of the energy of QW states varies with the position of the spacer layer. Since the photoemission only probes the local electron density of states, which is assumed to be proportional to the charge density, we can compare the photoemission results with the calculated charge densities. To reveal how the Co (or Ni) layer at different positions influences the charge density of the QW states, we present plane-averaged charge densities of QW states in the stack with the spacer at the node position and the antinode position. In figure 5, the plane-averaged charge densities are shown to explain the spacer effect on the Cu QW states which spread into the whole stack. For comparison, the plane-averaged charge densities of the QW states in the pure Cu slab (dotted line) with the same thickness are also presented in the figures. The monolayer spacer has a stronger modulation effect on the low energy state than the high energy state. If disregarding the detailed charge density around the Co (or Ni) layer position, the plane-averaged charge density of the high energy state, as shown in figures 5(a), (b), (e) and (f), is very similar to that of the corresponding QW states in the Cu slab, while the plane-averaged charge density of the low energy state shown in figures 5(c), (d), (g) and (h) is more different from that of the corresponding QW state in the Cu slab. This phenomenon may be attributed to the fact that the low energy states are located within the energy gap of the Co (or Ni) minority sp band, so the spacer serves as a larger barrier at this energy level.

Due to the limited electron mean free path, only the electronic density of states in the three outermost layers can be measured by the photoemission experiments. Then we will discuss the quantitative change of the charge densities in the three outer layers [7]. We calculated how the charge densities in the three outer Cu layers change with the different positions in the Cu/Co(Ni)/Cu stacks to the total charge densities of the QW states. Since the charge density at the Co or Ni position is very different with the Cu sites, we excluded the stacks with $i > 6$, in which the inserted Co (or Ni) monolayer is within the three outer layers. For the Cu/Co/Cu system, the largest variations of the total charge densities in the three outer layers of different stacks are 19.2% for the high energy QW states and 18.3% for the low energy QW states, respectively. However, the results are very different for the Cu/Ni/Cu system. For the low energy QW state, the maximum variation of charge density is 22.4%, but for high energy states, the maximum is only

0.4%. Consistent with the present calculation in the Cu/Co/Cu system [8], the photoemission intensity oscillates with Co layer position in Cu QW for both high energy and low energy states. In Cu/Ni/Cu systems [9], the observed photoemission intensity also oscillates with Ni position for both the high and low QW states, which is contradicted by the present calculation. However, in a recent photoemission measurement on the Cu/Ni/Cu system, if the electron binding energy is higher than -0.3 eV and the emitted electron emits exactly along the normal direction, the photoemission intensities are almost constant with the different Ni layer positions. This new experimental result [29] fully agrees with the present calculation.

Now we turn our attention to discuss the QW states at ~ -1.0 eV as shown in figure 4. Figure 6 shows the charge densities of those QW states in the Cu/Co/Cu stack with different inserting layer position. Those QW states in the Cu/Ni/Cu stack have a similar charge density distribution. From the charge density distribution of those QW states, those QW states can be identified as located in one of the Cu layers in both Cu/Co/Cu and Cu/Ni/Cu stacks, so those QW states will be called the sub-well QW states in the later discussion. Figures 6(a) and (e) show the QW states in the outer sub-well of the stack with $i = 2$ and 6, and figures 6(c) and (g) show QW states in the inner sub-well of the stack with $i = 4$ and 8. For these sub-well QW states, the charge densities are totally confined in one Cu sub-well, and decay very fast to zero in the other Cu sub-well. Meanwhile, the charge density distribution of these sub-well QW states has a similar nodal structured envelope function as that of the corresponding QW states in the pure slab. However, if the QW state energies in two sub-wells are close to each other, those two sub-well QW states can couple together to form a degenerated state, and the charge densities of this degenerated QW state should distribute into both Cu sub-wells. Figures 6(b), (d) and (f) show coupled sub-QW states of the stack with $i = 3, 5$ and 7, whose charge density distributes in both inner and outer sub-wells. Experimentally, the coupling of two isolated sub-well states has been studied systematically by Ling *et al* [10].

From our theoretical results, it is clear that inserting a spacer Co(Ni) layer into a Cu film can not only modulate the QW states, but also bring about a new QW state. The electrons can have a certain probability to transmit through the middle Ni or Co monolayer. Therefore the electrons are reflected at the surface and the bottom Co/Cu interface, then form the QW states in the whole stack, so those QW states should have a similar energy to the single QW states in the pure Cu slab with the same total thickness. However, the Co(Ni) spacer also creates a new Co(Ni)/Cu interface. Then the electrons would be reflected by one Co(Ni)/Cu interface. If the Bohr-Sommerfeld quantization condition in the sub-well can be satisfied, then the new QW state can form in the sub-well and its energy mainly depends on the thickness of the sub-well. Experimentally, by performing photoemission measurements on the sample structure with the total thickness fixed and the Co (or Ni) spacer layer position varied, as shown in figure 2, it is expected to prove the coexistence of these two kinds of QW states, but such measurements have not been presented in the previous studies.

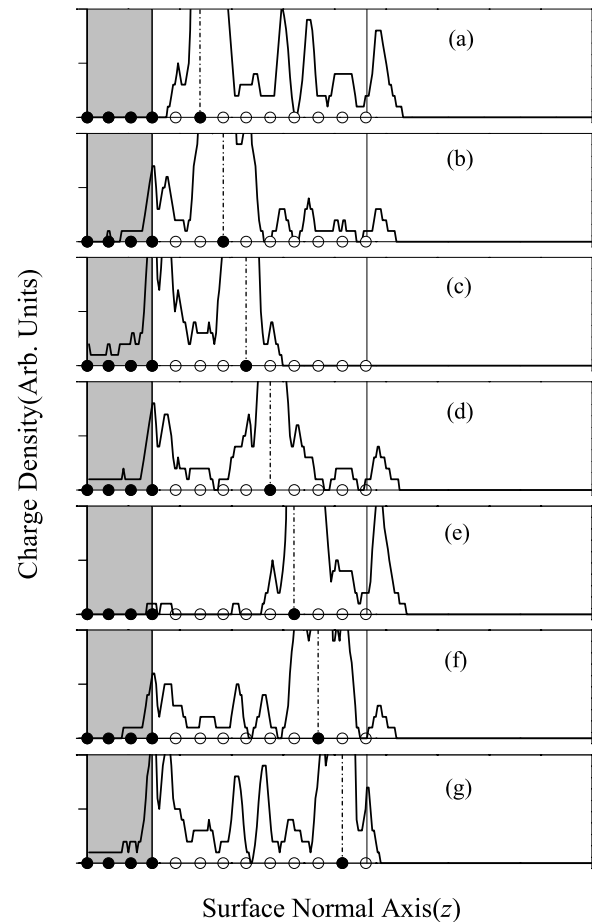


Figure 6. Plane-averaged charge densities of the sub-well QW states of the Cu/Co/Cu stack with the different positions of Co spacer layer. The black and open circles under each figure indicate the position of the Co and Cu atoms, respectively. Outer QW state (a) $i = 2$, (e) $i = 6$. Coupled state (b) $i = 3$, (d) $i = 5$, (f) $i = 7$. Inner QW state (c) $i = 4$, (g) $i = 8$.

4. Conclusion

The QW states in a series of sandwiched structures of Cu/Co(Ni)/Cu stacks are calculated and the effect of the monolayer spacer on the QW states is investigated. From first-principles calculations, it is found that both Ni and Co monolayer spacers can modulate QW states of the whole stack and form new sub-well QW states, so the QW states of the whole stack and the sub-well QW states could coexist. Due to the different electronic structures of Co and Ni spacer layers, the Ni spacer has less effect on the QW states near the Fermi level.

Acknowledgments

The authors thank Professor Z Q Qiu and Professor Z Zhang for critical discussions. This work was supported by the National Science Foundation of China, the Special Funds for Major State Basic Research, MOE and the Shanghai Project for the Basic Research. The computation was performed at the Fudan supercomputer center.

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