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Thickness dependence of structure stability of Co/Cu(100) superlattices

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Abstract

The electronic structures and stability of Co/Cu(100) superlattices have been investigated by a first-principles method based on density functional theory. The models 3Co/xCu (x = 1–8 monolayers) with different Cu layer thicknesses are investigated. The result shows that the stability increases with an increase in Cu layer thickness for odd (or even) Cu layer models. The charge transfer is prominent at the Co–Cu interface; the magnetic moment of atoms at the interfaces is larger than that of the interior Co layers, and the nonmagnetic Cu layer at the interface is slightly spin polarized under the influence of the ferromagnetic Co layers in the neighborhood. Finally, the Fermi energy, densities of states and structural energy are also discussed.

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

1. Introduction

The giant magnetoresistance (GMR) effect observed in multilayers consisting of ferromagnetic layers separated by a nonmagnetic spacer has been studied intensively since its discovery [1], in which the Co/Cu system is an example of particular interest because of the large magnetoresistance at room temperature [2]. It was observed by inverse-photoemission experiment [3] that the density of states near the Fermi surface for a Co/Cu(100) superlattice oscillates with the thickness of the Cu layers, and that the oscillation had a period of about six atomic layers, which was consistent with the oscillating period of spin polarization [4], the saturation magnetic field [5] and GMR [2, 6]. A great deal of theoretical work has been done to explore the nature of the oscillation, and much progress has been made [7–10]. As we know, the GMR effect can exist in very thin-film systems and has been used in electronic devices. As electronic device miniaturization continues, it becomes increasingly imperative to comprehend the quantum physics that dominates the properties. As the thickness of a film decreases to the atomic scale, the confinement of the film's electrons by its boundaries gives rise to discrete electronic states, known as quantum well states [11]. For electronic devices, the stability of the structure is of special importance, since it is related to the stability of the device's properties. In this paper, the electronic structure and the thickness dependence of the structural stability for 3Co/xCu (x = 1–8 monolayers) superlattices are investigated by a first-principle method.

2. Computational method and models

A common face-centered cubic (fcc)-based structure consisting of three atomic layers Co and x (x = 1–8) atomic layersof Cu stacked along the [001] direction was constructed to simulate the 3Co/xCu (001) superlattice. Considering Co and Cu to have fcc structure in very thin films (x-ray-diffraction data show that both Cu and very thin Co layers $\leqslant$20 Å have fcc structure [6]) and a lattice mismatch of about 2% for Co and Cu [11, 12], the initial structures shown in figure 1 are constructed by adopting the average lattice constant of the fcc structures of Co and Cu. Then the structures are fully optimized until the force for each atom is less than 0.03 eV Å^{-1}. The electronic structure of the system being considered is calculated self-consistently by a first-principles method within the framework of density functional theory (DFT) [13]. In our calculation, ultrasoft pseudo-potentials were expanded within a plane-wave basis set with an energy cutoff of 280 eV. Integrations in the Brillouin zone were

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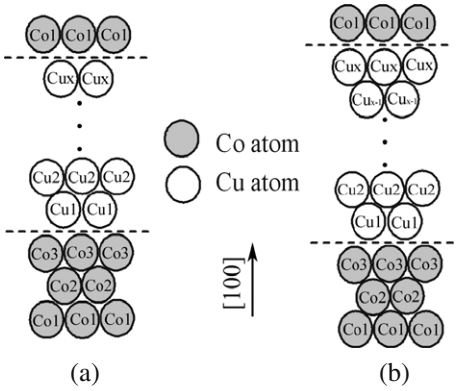

Figure 1. Sketch of 3Co/xCu models: (a) Cu thickness x is an odd number of layers and (b) Cu thickness x is an even number of layers. Dashed lines represent the interfaces between Co and Cu.

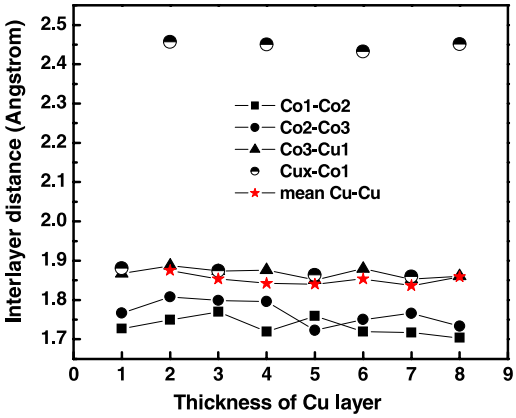

Figure 2. Interlayer distance for the 3Co/xCu models (x = 1–8).

performed using a special k-point generated with a 8 × 8 × 1 mesh parameter grid. The exchange and correlation potential is described by Perdew–Wang parameterization [14] in the generalized gradient approximation (GGA).

3. Results and discussion

3.1. The atomic structure and stability

Considering the limit of computation capability, we only calculated eight models: 3Co/xCu (x = 1–8). Full optimization is performed until the force for each atom is less than 0.03 eV Å^{-1}. The layer distances for the 3Co/xCu models are shown in figure 2. The layer distances Co1–Co2 and Co2–Co3 are the smallest; the average distance for the Cu–Cu layer is larger than that for Co–Co; the Co–Cu interface distance is the largest due to the immiscibility of Co and Cu in the bulk phase. At first glance, some strange phenomena are found: namely, the very large layer distances (about 2.45 Å) for Cux–Co1 for the even Cu layers model of 3Co/xCu. This can be explained since the Co layer is odd (three layers): for the even Cu layers 3Co/xCu model, the interface Co3–Cu1 is stable; the interface Cux–Co1 is less stable because the Cux atom is opposite the Co1 atom along the [100] direction,

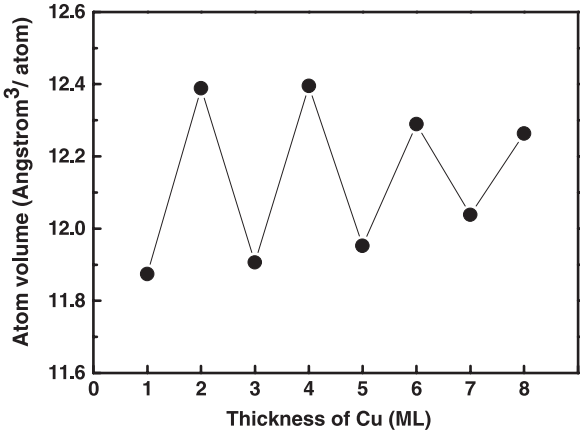

Figure 3. Average atom volume as a function of Cu layer thickness for 3Co/xCu models (x = 1–8).

which can be seen clearly in figure 1(b). Therefore, the Cux–Co1 distance must maintain a suitable distance, resulting in the large Cux–Co1 layer distance, which is the reason for the different behavior of the two different interfaces. The average atom volumes of different models are also shown in figure 3. We can see that the average atom volume of the system increases with an increase in Cu thickness for the odd number Cu layer model and decreases with an increase in Cu thickness for the even Cu layer model. This means that a suitable average atom volume can be arrived at by an increase in the Cu thickness. To study the stability of the structure of 3Co/xCu, we have calculated the formation energy. The formation energy per atom is defined as

$$E_{\mathrm{f}} = \frac{1}{n+m}\left[E_{\mathrm{T}}(n\mathrm{Co}\,/\,m\mathrm{Cu}) - nE_{\mathrm{T}}^{\mathrm{bulk}}(\mathrm{Co}) - mE_{\mathrm{T}}^{\mathrm{bulk}}(\mathrm{Cu})\right] \quad (1)$$

where $E_{\mathrm{T}}(n\mathrm{Co}/m\mathrm{Cu})$, $E_{\mathrm{T}}^{\mathrm{bulk}}(\mathrm{Co})$ and $E_{\mathrm{T}}^{\mathrm{bulk}}(\mathrm{Cu})$ are the total energies of the nCo/mCu superlattice, per bulk Co and per bulk Cu atom, respectively; and n and m are the Co and Cu atom numbers in an nCo/mCu superlattice, respectively.

The formation energy per atom is a measure of the phase stability in the solid state. The lower the formation energy is, the more stable the phase is. A positive formation energy means that the superlattice is not stable compared with the bulk Co and bulk Cu. The formation energies per atom of the 3Co/xCu models are shown in figure 4. The stability of the structure increases with an increase in Cu thickness for x odd (or even), which can be explained by more energy being needed to create more interfaces for a given thickness of material. The large formation energies of even Cu thickness indicate that the instability of even Cu thickness for 3Co/xCu models is because of the larger layer distance for Co–Cu. For odd Cu thickness models, the formation energies are negative for $x \geqslant 5$, which means that these systems are stable compared with bulk Co and bulk Cu. But for $x < 5$, the formation energies are positive. This is why it is difficult to obtain very thin superlattices in experiments.

Table 1. Charge transfer, and magnetic moment of interface and interior atom layers for 3Co/xCu (x = 1–8) models.

	Models	Interface Co Co3 (Co1)	Interior Co	Interface Cu Cu1(Cux)	Interior Cu
Charge (e)	3Co/Cu	0.19(0.19)	−0.03	−0.35	—
	3Co/2Cu	0.19(0.11)	−0.04	−0.18(−0.07)	—
	3Co/3Cu	0.17(0.17)	−0.04	−0.18(−0.18)	0.06
	3Co/4Cu	0.18(0.12)	−0.06	−0.17(−0.09)	−0.01
	3Co/5Cu	0.17(0.18)	−0.03	−0.19(−0.19)	0.00
	3Co/6Cu	0.19(0.12)	−0.06	−0.18(−0.09)	0.00
	3Co/7Cu	0.18(0.19)	−0.04	−0.19(−0.19)	0.00
	3Co/8Cu	0.18(0.12)	−0.06	−0.18(−0.01)	0.00
Magnetic moment (μ_B)	3Co/Cu	1.78(1.78)	1.72	−0.08	—
	3Co/2Cu	1.72(1.74)	1.62	−0.04(0.00)	—
	3Co/3Cu	1.74(1.74)	1.70	−0.04	0.02
	3Co/4Cu	1.78(1.80)	1.66	−0.02(0.02)	0.02
	3Co/5Cu	1.78(1.78)	1.70	−0.02	0.02
	3Co/6Cu	1.78(1. 84)	1.70	−0.02(0.02)	0.00
	3Co/7Cu	1.72(1.72)	1.68	−0.04	0.00
	3Co/8Cu	1. 68(1.74)	1.62	−0.06(−0.02)	−0.02

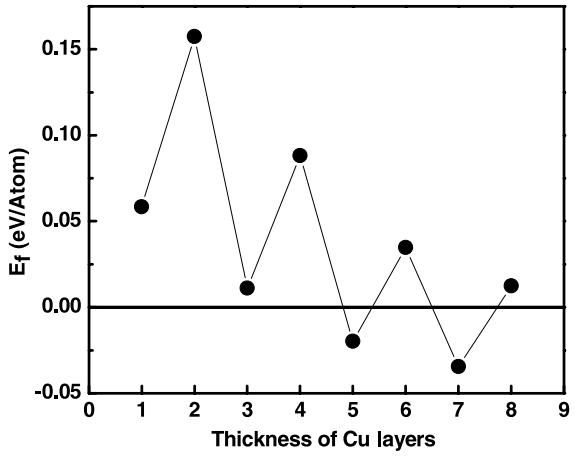

Figure 4. Formation energy per atom of 3Co/xCo systems (x = 1–8).

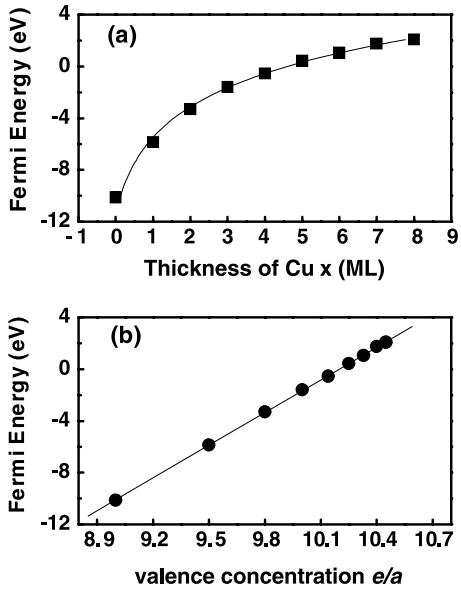

Figure 5. (a) The change in Fermi energy with thickness of the Cu layer x in 3Co/xCu. (b) The change in Fermi energy with valence concentration e/a in 3Co/xCu.

3.2. Charge transfer and magnetic moment

The charges and magnetic moments are obtained by Mulliken population [15] analysis, as shown in table 1. Positive charge means that the atom loses electrons; negative charge means that the atom gains electrons. From table 1, we find that charge transfer is prominent at the Co/Cu interface, but there is little in the interior. For the even Cu atomic layer model, charge transfer for the Co1–Cux interface is smaller than that for the Co3–Cu1 interface. This means that the interaction for the Co1–Cux interface is weaker than for the Co3–Cu1 interface for even Cu layer model 3Co/xCu, which is consistent with the result of formation energies. Furthermore, at the interface the Cu layers gain electrons and the Co layers lose electrons. It is reasonable that electrons flow from Co to Cu at a Co/Cu interface due to the Fermi level of bulk Cu being below that of bulk Co. The interface atom Co1 (or Cux) in the even Cu layer model loses (or gains) less charge than that for the odd Cu layer 3Co/xCu models. The magnetic moment for the Co layer in the interior is about 1.6–1.7 μ_B, which is similar to the values for bulk Co. However, the magnetic moments of Co layers at the interface are larger than those of the middle Co atom layers. This phenomenon can be explained from the free volume effect [16]. Because the distance of Co and Cu atom layer is larger than that of their internal layer distance, the magnetic moment of the Co layer in the Co–Cu interface is larger that of the internal Co layer. In addition, we notice that the nonmagnetic Cu layers at the interface are slightly spin polarized under the influence of the ferromagnetic Co layers in the neighborhood.

3.3. Fermi level

The Fermi level changes as a function of the Cu thickness in 3Co/xCu (x = 1–8) superlattices, as shown in figures 5(a).

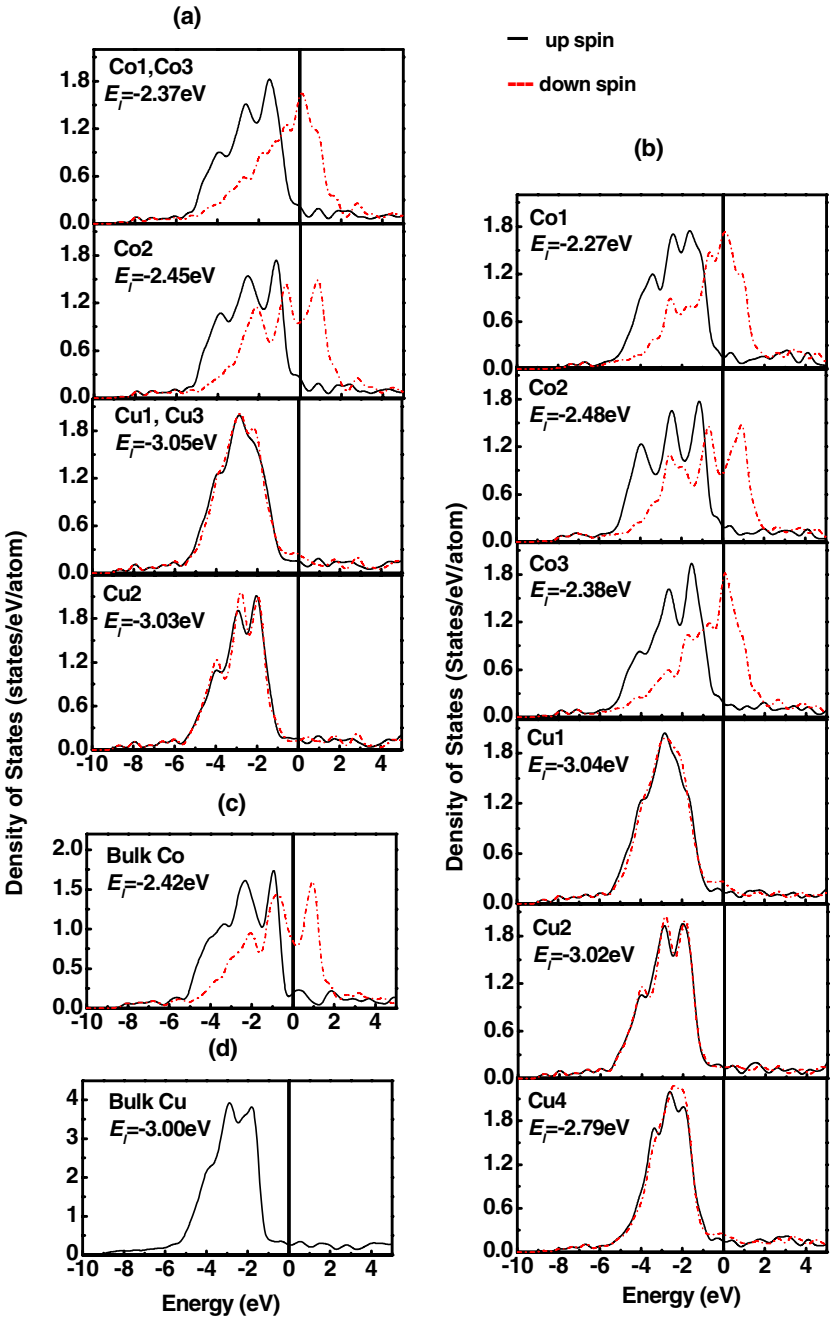

Figure 6. Density of states and structural energy E_l: (a) 3Co/3Cu; (b) 3Co/4Cu; (c) bulk HCP Co; (d) bulk FCC Cu. The Fermi level is set to zero.

The Fermi level increases exponentially as a function of Cu layer thickness. This is due to the change in valence concentration e/a (valence electrons per atom). The change in thickness of Cu can alter the electron concentration, e/a, of the system. The Fermi energy increases with electron concentration e/a linearly, as shown in figure 5(b). The valence band width increases from about 8.95 eV for the 3Co/Cu model to 9.52 eV for the 3Co/8Cu model, which means that the extra valence electrons fill the higher energy level. Consequently, the filling of the bonding orbital increases the bond strength and thereby the stability.

3.4. Density of states and structural energy

In order to understand better why the odd atomic layer Cu displays very different properties from those of even atomic layer Cu in 3Co/xCu superlattices, we calculate the projected density of states (PDOS) for 3Co/Cux, bulk Co and bulk Cu. From the PDOS, we can calculate the structural energy of each atom in the model. The structural energy E_l of an atom is defined as [17]

$$E_l = \frac{\int_{-\infty}^{E_F} E\rho \, dE}{\int_{-\infty}^{E_F} \rho \, dE} \quad (2)$$

where ρ is the PDOS of an atom, E is the eigen-energy, and E_F is the Fermi energy. The smaller the structural energy E_l is, the more stable the atom is in the system.

The projected density of states and the structural energy E_l for 3Co/3Cu, 3Co/4Cu, bulk hcp Co and bulk fcc Cu are shown in figure 6. We can see in figure 6(c) that the density of state (DOS) for bulk Co near the Fermi level has a valley for spin-down states, while the DOS for bulk Cu has two peaks below the Fermi level. Comparing the DOS for 3Co/3Cu and 3Co/4Cu models with those for bulk Co and bulk Cu, we find that the 3Co/3Cu and 3Co/4Cu models have similar features: the peak spin-down DOS for the interface Co lies near to the Fermi level, which means that the interface Co atom has a higher energy and is unstable, while for the interior Co, there is a valley near the Fermi level in the spin-down DOS, which is similar to that for bulk Co; the spin-up (spin-down) DOS of the interfacial Cu has one peak, but two peaks exist in the DOS for the interior Cu, which is a feature of bulk Cu. The peak of the spin-down DOS for the interfacial Cu4 lies at a higher energy compared with that for Cu1 in the 3Co/4Cu model, which means that the Cu4 atom has a higher energy and that the system 3Co/3Cu is more stable than 3Co/4Cu. We see from the structural energy that for the 3Co/3Cu model the interfacial Co atoms have a larger value than that of the interior Co atoms, but that Cu atoms in both the interface and the interior have almost the same structural energy as bulk Cu. For the 3Co/4Cu model, the interfacial Co1 and Co3 atoms have a larger value (-2.27 eV for Co1, -2.38 eV for Co3) than that for the interior Co2 atom (-2.48 eV) and the interfacial Cu1 and interior Cu2 atoms have almost the same structural energy as bulk Cu, which is similar to the case for the 3Co/3Cu model, but the interfacial Cu4 atom has a much larger (-2.79 eV) structural energy than that for other Cu atoms. The structural energy for Co1 (-2.27 eV) is a little larger than that for Co3 (-2.38 eV), which shows that the Co1 atom is less stable that the Co3 atom for the 3Co/4Cu model. The structural energy result shows that the high-energy Co1–Cux interface is the main cause of the lower stability for the 3Co/4Cu model than for the 3Co/3Cu model. A similar analytical result is true for the other models.

The calculation method that is used is a self-consistent first-principles method within the framework of density functional theory (DFT) [13]. The method is precise for calculating the electronic structure and the total energy, is free of any experimental parameters, and is widely used in study of the solid state. However, the first-principles method is time-consuming. So we chose just the 3Co/xCu superlattice models for simulating the Co/Cu multilayer, in which the Co layer includes three atomic layers and the Cu layer includes between one and eight atomic layers. Structural imperfections such as disorder, interfacial roughness, interdiffusion, which are all known to be important in real Co/Cu multilayer systems, have an important influence on stability as well as the magnetic properties. Because of the limited calculational capability, structural imperfections such as disorder and interfacial roughness could not be considered in our models. Previously [18] we studied the influences of one kind of interfacial imperfection by exchanging the position of perfect interfacial Co and Cu layers to simulate interdiffusion in the electronic structure and giant magnetoresistance. The results showed that interdiffusion can enhance the charge transfer and magnetoresistance ratio; interdiffusion models are a little higher in energy (less stable) than perfect interfacial models.

4. Conclusions

Based on a first-principles method within the framework of density functional theory, we studied the electronic structure and stability of 3Co/xCu (x = 1–8) superlattices. The calculated results show that stability increases with the Cu spacer thickness for Cu odd (or even) layer thicknesses. The density of states and structural energy results show that the high-energy Co1–Cux interface is the main cause of the lower stability of the even Cu layer models compared to the odd Cu layer 3Co/xCu models. The change in thickness of Cu alters the electron concentration, e/a, of the models. The Fermi energy increases linearly with electron concentration e/a, and the valence bandwidth increases from about 8.95 eV for the 3Co/Cu model to 9.52 eV for the 3Co/8Cu model, which means that the extra valence electrons fill the higher energy level. Therefore, the filling of the bonding orbital increases the bond strength and thereby the stability.

Acknowledgments

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