Vol 17 No 11, November 2008
1674-1056/2008/17(11)/4305-07

Chinese Physics B

© 2008 Chin. Phys. Soc.
and IOP Publishing Ltd

Interface dipole induced by asymmetric exchange effect in Mott-insulator/Mott-insulator heterojunction*

Hao Lei(郝 雷)[a)†] and Wang Jun(汪 军)[b)]

[a)] *National Laboratory of Solid State Microstructures and Department of Physics, Nanjing University, Nanjing* 210093, *China*
[b)] *Department of Physics, Southeast University, Nanjing* 210096, *China*

(Received 16 June 2008; revised manuscript received 25 June 2008)

We study theoretically the interfacial electronic property of a heterojunction made from two Mott insulators (MI) with different magnetic structures. By means of unrestricted Hartree-Fock calculations in real space, we find that a charge dipole can form spontaneously near the interface of the MI/MI heterojunction. The magnitude of this charge dipole depends strongly on the magnetic states of both sides of the heterojunction. Combining with the result from an exactly solvable two-site toy model, we argue that the interface dipole arises from exchange effects as well as its asymmetry intrinsic to the heterojunction near the interface. Our study may shed light on the fabrication of ultrathin ferroelectric and magnetoelectric devices.

Keywords: Mott insulator heterojunction, interface dipole, asymmetric exchange
PACC: 7320D, 7530E, 7127

1. Introduction

The delicate balance between competing interactions in transition metal oxides (TMOs) results in a great many of peculiar phases,[1] such as the Mott insulator,[2] the high T_C cuprate superconductors,[3] and the various magnetic and charge-ordered or orbital-ordered states in manganites.[4] The fine tuning of a certain external stimulus, such as magnetic field or external pressure can change the system from one phase to another. This extraordinary sensitivity makes TMOs an ideal candidate for the next generation of functional electronic devices.[5] In semiconductor science, the combination of semiconductors of different doping types (p- or n-type) and/or different materials into heterostructures has bloomed out into a mature subject and produced various devices with novel functions not seen ever in any of their constituents. Following this line of research, a recent concern in TMO studies is to combine different TMO materials into heterojunction or superlattice structures.[6−12] One example is the conducting quasi-two-dimensional electron gas (q-2DEG) that is formed near the interface between two band insulators (BI), i.e. $LaAlO_3$ and $SrTiO_3$;[8,9] another example is the ferromagnetic metallic interface region between a typical Mott-insulator (MI) $LaTiO_3$ and a BI $SrTiO_3$.[6]

In the theoretical aspect, the interface-induced electronic reconstructions in the $LaTiO_3/SrTiO_3$ (MI/BI) heterostructure have been successfully investigated in the literatures.[13−15] Lee and MacDonald[5] investigated the possibility of modulation doping and electronic interface reconstruction in an MI/MI heterojunction (HJ), and showed in the case of electron doping that the modulation doping could be attained in a wide range of dopant densities for both antiferromagnetic (AF) and ferromagnetic (F) states.

A comparison between the BI/BI and the MI/BI HJs leads to the question whether an interfacial q-2DEG could form if zero doping is taken to either side of the MI/MI HJ. This issue is also fundamental to other electronic/magnetic properties and practical applications of the MI/MI HJ. In order to answer this question, we study in this work a model of MI/MI HJ similar to that considered by Lee and MacDonald in Ref.[5], in which the MIs are described by using the single-orbit Hubbard model with different on-site Coulomb correlations and/or site energies. Long-range Coulomb interactions accounting for possible electron redistribution are also taken into account. The on-site Coulomb interactions are treated in the unrestricted Hartree–Fock approximation (UHFA),[5,13] and the long-range Coulomb in-

*Project supported by the National Natural Science Foundation of China (Grant Nos 10574021, 90403011, and 10704016).
†E-mail: hi549063@sina.com

teractions are treated in the Hartree approximation. Though not so accurate for excitation state properties and finite-temperature behaviour, the UHFA has been shown to be able to give a reliable picture of the ground-state properties,[5,13] and so it is to be studied here. By considering various possible combinations of magnetic states of the two sides of HJ, our calculations show that a sheet of interface charge dipole usually forms spontaneously in the MI/MI HJ. The dipole region is extremely sharp and involves only one-to-two layers on either side of the junction. The charge densities of the dipole layers exhibit strong dependence on magnetic states of the two sides. The generic picture is that the charge density increases with the increase of the interfacial AF bond density, and it is attributed to the exchange coupling of electrons between two sides of the HJ, which can reduce the overall energy of the system though involving high-energy states associated with double occupation of a single site by two electrons of opposite spins. The key point is that the two kinds of high-energy states with double occupation occurring to the left and the right of the interface have different probabilities due to the intrinsic left-right asymmetry of the HJ, which results in a net transfer of charge from one side of the HJ to the other, as well as the formation of the interface dipole. A similar mechanism has been proposed to explain the interface dipole observed for atoms and molecules physisorbed on metal surfaces.[16] To confirm the above mechanism and gain more insights, we further consider an exactly solvable two-site toy model with two electrons of opposite spins, which is a minimal model of our system. Calculations based on this toy model indicate that the results are consistent with our 3D real-space UHFA calculations.

In contrast to the cases observed in both the BI/BI and the MI/BI HJs, the interfacial dipole in our studying MI/MI HJ is usually insulating. This can be seen from the calculated layer-resolved density of states (DOS) of the HJ, which indicates that the exchange process mainly induces some mid-gap states in one MI and an energy gap persists throughout the whole HJ. The mid-gap states are similar to the interface-induced gap states (IFIGS) in the context of a metal (semiconductor)/semiconductor junction due to a finite extension of the electronic wave functions from one side to the other,[17−20] except that now both sides of the junction are insulators and the mid-gap states are induced corresponding not to occupied states such as the Fermi surface of a metal (or, filled valence band of a semiconductor) but to the empty upper Hubbard band of the other MI.

In the next section we describe the single-orbit Hubbard model used to study the MI/MI HJ as well as the mean-field approximation and also present the two-site toy model. In Section 3, we give our results of interface dipole and discuss its properties, physical origin and possible applications. A brief conclusion drawn from the present study is given in Section 4 finally.

2. Model

Typical Mott-Hubbard type MIs,[2] such as $YTiO_3$ and $LaTiO_3$, which have respectively F and AF ground states, can be generically expressed as ABO_3 in which A denotes a trivalent rare-earth ion while B refers to a trivalent ion derived from group IVB or VB elements. In the case of TMOs, B represents either a Ti ion or a V ion.

In order to investigate qualitatively the interfacial electronic properties of an undoped MI/MI HJ, we employ the single-orbit Hubbard model to describe the two MIs making up of the junction.[5] When the anisotropic crystal field is strong enough to fully lift the orbital degeneracy, the single-orbit Hubbard model becomes a reasonable representation of the system. Besides the usual hopping and on-site Coulomb repulsion terms, the model Hamiltonian also includes a site-energy term reflecting the possible d-band offset between the two MIs and a long-range Coulomb interaction term that will take effect when the nonuniform space charge emerges near the interface. The model Hamiltonian reads $H = H_{\rm t} + H_{\rm U} + H_0 + H_{\rm C}$, where

$$H_{\rm t} = -t \sum_{i,\delta,\sigma} d^{\dagger}_{i\sigma} d_{i+\delta,\sigma}, \tag{1}$$

$$H_{\rm U} = \sum_i U(z_i) \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}, \tag{2}$$

$$H_0 = \sum_i E(z_i) \hat{n}_i, \tag{3}$$

$$H_{\rm C} = \frac{1}{2} \sum_{i \neq j} \frac{e^2 \hat{n}_i \hat{n}_j}{\epsilon |\boldsymbol{R}_i - \boldsymbol{R}_j|}. \tag{4}$$

$\hat{n}_{i\sigma} = d^{\dagger}_{i\sigma} d_{i\sigma}$ is the number operator for spin σ electron on the i-th site, and $\hat{n}_i = \hat{n}_{i\uparrow} + \hat{n}_{i\downarrow}$. For simplicity, a cubic structure and an ideal lattice parameter matching between the two-compositional MIs are assumed, so that the hopping amplitude t is identical everywhere. The index i labels the position of a transition

metal ion (B), so $\boldsymbol{R}_i = (x_i, y_i, z_i)a$ in a perovskite unit cell with lattice constant a. The index δ labels one of the displacements connecting the i-th site with its at most six nearest-neighbouring sites. We denote the direction perpendicular to the interface of the HJ and running from the left side to the right side as the positive z direction. The x and y axes are parallel to the interface of the HJ, thus the z coordinates are conveniently used to label the layers. We will consider a system with $2N_3$ layers (each with $N_1 \times N_2$ sites) labelled sequentially from the left to the right and define $U(z_i)(E(z_i)) = U_1(E_1)$ for $z_i = 1$ to N_3 and U_2 (E_2) for $z_i = N_3 + 1$ to $2N_3$. The $H_{\rm C}$ part of the Hamiltonian is treated in the Hartree approximation and only the contribution from the extra charges due to possible charge redistribution near the interface is considered.[5] As a result, the long-range Coulomb interaction reduces to

$$H_{\rm C}^{\rm eff} = \sum_{i \neq j} \frac{e^2(\rho_j - 1)\hat{n}_i}{\epsilon |\boldsymbol{R}_i - \boldsymbol{R}_j|}, \tag{5}$$

where $\rho_j = \sum_\sigma \langle \hat{n}_{j\sigma} \rangle$ is the electron density on site j. The on-site Coulomb interaction $H_{\rm U}$ is treated in the Hartree-Fock approximation so that

$$H_{\rm U} \longrightarrow H_{\rm U}^{\rm eff} = \sum_i U(z_i)(\langle \hat{n}_{i\uparrow} \rangle \hat{n}_{i\downarrow} + \langle \hat{n}_{i\downarrow} \rangle \hat{n}_{i\uparrow}), \tag{6}$$

where the constant terms are neglected.

In this work, an exactly solvable two-site model is also taken into account as a minimal realization of the problem to illustrate the mechanism of the interface dipole formation. The model Hamiltonian is given by

$$\begin{aligned} H' = & -t \sum_\sigma (d_{1\sigma}^\dagger d_{2\sigma} + \text{h.c.}) + \frac{e^2}{\epsilon a} \hat{n}_1 \hat{n}_2 \\ & + \sum_{i=1,2} (E_i \hat{n}_i + U_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}), \end{aligned} \tag{7}$$

where the various operators and parameters are the same as those in Eqs.(1)–(4) except the difference in system size. Following the 3D case, we will consider a half-filled system with two electrons of opposite spins.

3. Results and discussion

In the following, all the presented calculational results are based on a finite-sized 3D lattice with $N_1 = N_2 = 6$ and $N_3 = 5$, and they are confirmed by the calculations on larger systems (e.g. $N_1 = N_2 = 13$ and $N_3 = 5$). Open boundary condition is employed in the calculations, for the periodic boundary conditions in the x and the y directions have no qualitative effect on the results. Calculations on this lattice for the case of electron doping have reproduced quite well the earlier results[5] for both the F state and the AF state.

We consider in the following only magnetic ordered states of F and/or bipartite AF types as the basic building blocks of the two sides of the HJ. There are then six unequivalent combinations of magnetic states labelled as 1) P–F, 2) AP–F, 3) AP–AF, 4) P–AF, 5) F/AF, and 6) AF/F, where P and AP denote parallel and antiparallel relative magnetic orders between the two sides at the interface, respectively. Cases 1) and 3) are the usual F state and the AF states throughout the 3D lattice. In case 2), the left and the right MIs are both F but polarized antiparallel to each other. Case 4) is obtained by shifting one side of the AP–AF junction by a lattice constant a along any one of the four possible directions lying in the layer. In cases 5) and 6), one material has an F magnetic order while the other has an AF magnetic order. The results of the last two cases are almost identical, thus only the first five cases need studying. We first neglect the d-band offset and take typical parameters as $U_1 = 24t$, $U_2 = 15t$ and $E_1 = E_2 = 0$. For the long-range Coulomb interaction part of the Hamiltonian, parameters are the same as those adopted in earlier study,[13] i.e. $a \approx 0.4\,\text{nm}$, $\epsilon \approx 15$, and $t \approx 0.3\,\text{eV}$. By multiplying an additional factor of $1/4\pi\epsilon_0$ (ϵ_0 is the vacuum permittivity), we can obtain $U_{\rm C} = e^2/\epsilon a \approx 0.8t$[5,13] which will be used throughout this paper.

The calculated layer-averaged electron density distributions for the five cases are shown in Fig.1(a). The curves for P–F and P–AF are further replotted in Fig.1(b). It is clear that except the P–F combination, an interface dipole emerges prevalently in the other four cases. A general trend is that the amount of charge transfer increases with the increase of interfacial AF bonds. However, there are also two small deviations from this simple relationship. One is that the charge transfer of AP–F is larger than that of AP–AF. The other is that the charge transfer of P–AF is small but nonzero while that of P–F is exactly zero. In either of these two exceptions, the numbers of interfacial AF bonds for the two magnetic configurations involved are identical. We have verified that the above results are insensitive to the choice of N_3: this is related to the fact that the charge dipole is restricted to the neighbourhood of the interface as can be seen

from Fig.1.

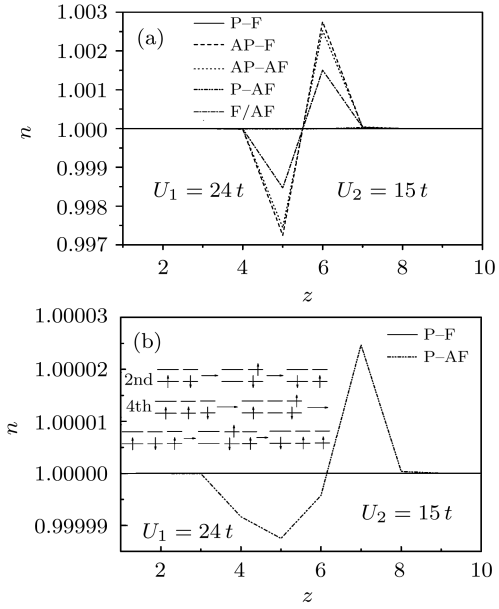


Fig.1. Electron density distribution from UHFA calculations on the $6 \times 6 \times 10$ lattice for five different magnetic configurations described in text (a) and the P–F and P–AF configurations enlarged (b), with $U_{\rm C} = 0.8t$. The typical second (2nd) and fourth (4th) order exchange processes of electrons are shown in the inset of (b), with longer and shorter lines indicating sites on the left side and the right side of the heterojunction respectively.

We argue that the above interface charge dipoles emerge as a result of asymmetric exchange processes between the two MIs through the interface. The asymmetry of the exchange arises from intrinsic differences between the two MIs making up of the HJ which are indicated by the parameters defining them, and we will illustrate its meaning further. This mechanism is similar to the one put forward to account for the interface dipole in the system of atoms and molecules physisorbed on metal surfaces.[16] The exchange processes occur because they can lower the overall energy of the HJ though involving high energy states with double occupation of a single site by electrons of opposite spins. The exchange through direct interfacial AF bonds is a second-order process. Other higher-order exchange processes may also exist, the most important of all these is of course the fourth-order process. A schematic illustration of typical second- and fourth-order exchange processes is shown in the inset of Fig.1(b), and other similar processes can be obtained in the same way. Although the fourth-order exchange process is smaller by the factor $(t/U)^2$ than the second-order one, it is just the fourth-order exchange process which results in the two small exceptions mentioned above. By comparing case 1) with case 4) and case 3) with case 2), both case 4) and case 2) have extra contributions from fourth-order exchange processes and hence show bigger interface dipoles. In case 1), exchange process to any order cannot happen so that the charge transfer is exactly forbidden and no dipole forms near the interface.

The above UHFA calculations indicate the importance of antiferromagnetic bonds in mediating the exchange processes and inducing the interface dipoles. In order to confirm the mechanism further and gain more insights, analysis which can be done based on more analytical calculations is highly desirable. In our case, a two-site system containing two electrons of opposite spins is the minimum realization of the antiferromagnetic bond and is exactly solvable. In the following, we make comparative calculations based on the two-site model defined by Eq.(7) and the 3D lattice model. For the half-filled two-site system with two electrons of opposite spins, the Hilbert space is four-dimensional with its basis written as $|1\rangle = |\uparrow,\downarrow\rangle$, $|2\rangle = |\downarrow,\uparrow\rangle$, $|3\rangle = |\uparrow\downarrow,\phi\rangle$, $|4\rangle = |\phi,\uparrow\downarrow\rangle$, where $\uparrow$ / $\downarrow$ denotes a spin up/down electron, ϕ refers to an empty site. The occupation status of the left/right site is represented by the left/right side of the basis. The Hamiltonian is then written in a matrix form as

$$[H'] = \begin{bmatrix} \epsilon_{12} & 0 & -t & -t \\ 0 & \epsilon_{12} & t & t \\ -t & t & \epsilon_{11} & 0 \\ -t & t & 0 & \epsilon_{22} \end{bmatrix}, \qquad (8)$$

where ϵ_{12}=$E_1 + E_2 + U_{\rm C}$, $\epsilon_{11} = 2E_1 + U_1$, and $\epsilon_{22} = 2E_2 + U_2$ are the expectation values of Eq.(7) with respect to the states $|1\rangle$ (and $|2\rangle$), $|3\rangle$, and $|4\rangle$. For all values of E_i (U_i) $(i = 1, 2)$ employed in this work, it holds that the ground-state energy is always smaller than ϵ_{12}, which is the energy of the system if every site is singly occupied and no exchange process can happen. From this two-site model we can make a perturbative analysis to clarify the asymmetric exchange. The initial state is set as state $|1\rangle$ (the case of state $|2\rangle$ is similar). Processes involving states $|3\rangle$ and $|4\rangle$ will make corrections to state $|1\rangle$. Denoting the unnormalized first-order perturbation-corrected wave function as $|0\rangle$, it is written as

$$|0\rangle = |1\rangle + \frac{-t}{\epsilon_{12} - \epsilon_{11}}|3\rangle + \frac{-t}{\epsilon_{12} - \epsilon_{22}}|4\rangle. \qquad (9)$$

It is clear that there will be a charge transfer between the two sites whenever $E_1 + U_1/2 \neq E_2 + U_2/2$.

When going from the two-site model to a 3D MI/MI HJ, $E_1 + U_1/2$ and $E_2 + U_2/2$ will correspond to the chemical potentials of the left and the right MIs, respectively. So the meaning of the asymmetry in the "asymmetric exchange" is a difference in chemical potential between the two MIs.[14,21] When the exchange process happens, this asymmetry will result in a net charge transfer from the side with higher chemical potential to the other side so that a dipole can appear in the interface layer. It is then expected that the charge transfer can reverse its direction when $\Delta\mu = E_1 - E_2 + (U_1 - U_2)/2$ changes its sign, and vanishes as $\Delta\mu = 0$. We take the AP–F configuration of the finite 3D lattice as an example to compare its result with that from exact calculation based on the two-site model. One situation with fixed $U_1 = 24t$, $U_2 = 15t$, and $E_2 = 0$ as a function of E_1 is shown in Fig.2(a), another with fixed $U_2 = 24t$, $E_1 = E_2 = 0$ and varying U_1 is shown in Fig.2(b). The results for P–F are also shown as reference. It is clear that the behaviours coincide qualitatively with the above expectations, which further indicates that the interface dipole results from asymmetric exchange processes intrinsic to the MI/MI HJ.

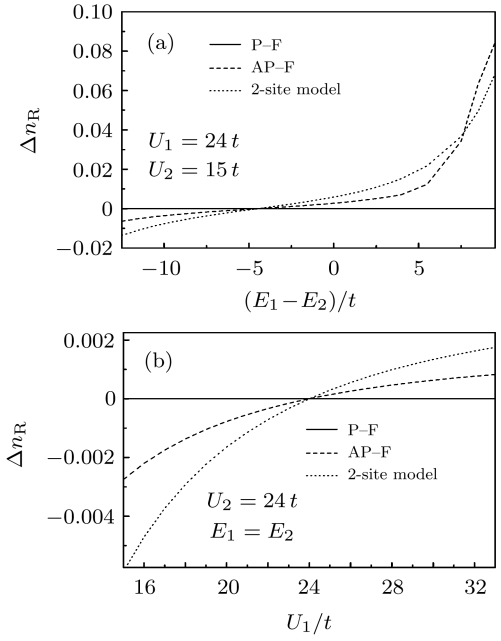


Fig.2. The deviation of electron density for the right site in the two-site model from one and for the sites on the right interface layer of the 3D lattice as a comparison. Two cases are considered (a) $U_1 = 24t$, $U_2 = 15t$, and $E_2 = 0$; (b) $U_2 = 24t$, $E_1 = E_2 = 0$, and $U_C = 0.8t$.

If we set $a = 0.4\,\text{nm}$, the interface charge density in the case of AP–F with parameters the same as those taken in Fig.1(a) is about $1.7\times10^{12}\,\text{cm}^{-2}$, which is analogous to that of the 2DEG in the GaAs/AlGaAs HJ interface.[22] One may naturally ask whether it can similarly form a 2DEG. We will calculate the layer-resolved DOS (L-DOS) of the heterojunction to answer this question. Our tentative calculations show that for the parameters $U_1 = 24t$, $U_2 = 15t$, and $E_1 = E_2 = 0$, the effect of U_C is negligibly small, which is similar to the case of electron doping,[5] so we drop it here and make a partial Fourier transformation in the xy plane. We still consider a $5 + 5\,\text{HJ}$. The L-DOSs for the 4, 5, 6 and 7 layers are shown in Fig.3. The L-DOSs for the 1−3 and 8−10 layers resemble those of the 4th and 7th layers, respectively. The horizontal axis is the energy relative to the Fermi energy. It is clear that a finite energy gap persists in each layer between the Fermi level and the lowest unoccupied states so that the interface dipole layers are insulators. This result is qualitatively different from those observed in both the BI/BI[8,9] and the MI/BI[6] HJs. Besides the change in occupied DOS up to the Fermi energy reflected by the layer-averaged electron density distributions, the exchange processes resulting in the interface dipole only give rise to some mid-gap states in the interface layer of the wide-gap MI and some states higher than the upper Hubbard band in the interface layer of the narrow-gap MI (hardly seen on the figure because of smallness in magnitude). Both of them correspond to a redistribution of the DOSs. This is similar to the interface-induced gap states (IFIGS) in a metal(semiconductor)/semiconductor HJ[17−20] but with a significant difference that the extra states here correspond to empty bands in contrast to the Fermi surface of a metal (or, filled valence band of a semiconductor) and no electrons actually occupy them. But we do not exclude the possibility that a conducting 2DEG may form in the MI/MI HJ if other factors such as interface chemical bonds[17,22,23] or coexistence of several orbits[13] are taken into account which may possibly enhance the magnitude of the charge transfer across the interface.

Finally, we discuss possible applications of our findings. An ongoing effort on integrating TMOs into multifunctional devices is to design devices with combined ferroelectric and ferromagnetic properties.[24,25] In bulk samples ferroelectricity and ferromagnetism are usually mutually exclusive.[26,27] So researchers have paid their attention to the composites of two materials with ferroelectric and ferromagnetic order separately and coupled by ferroelastic effects.[28] Our

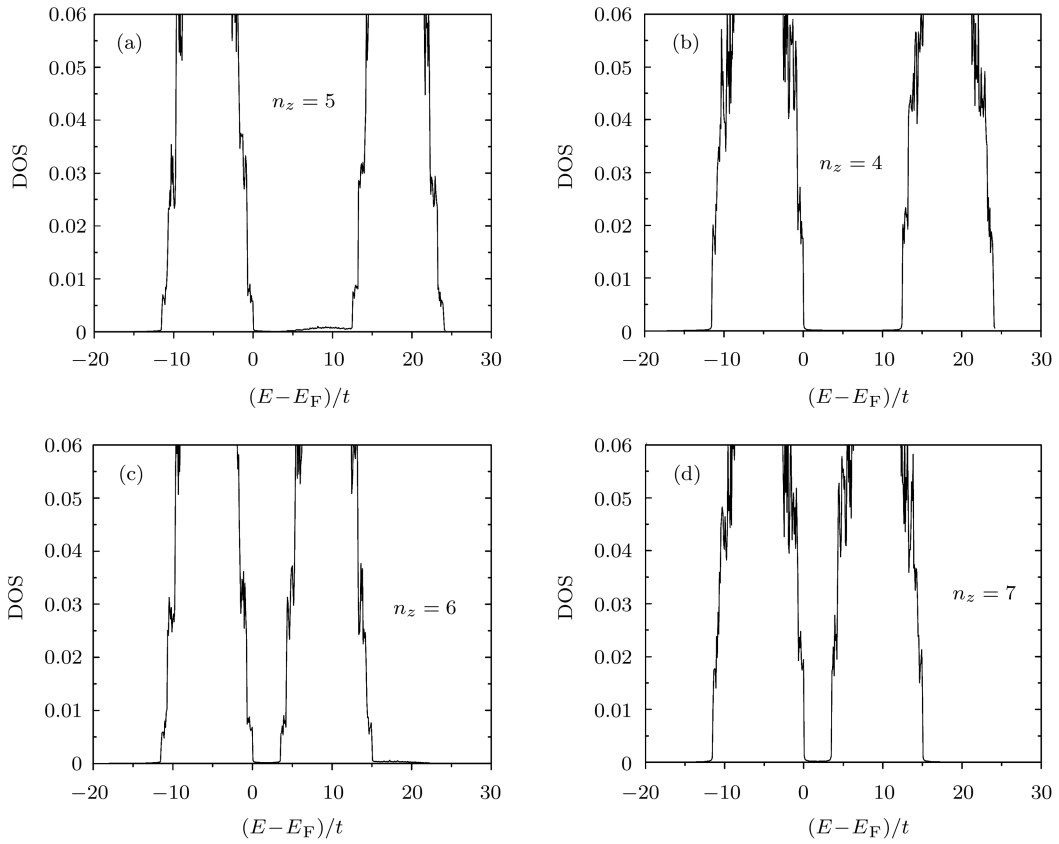


Fig.3. The layer-resolved DOSs for the (a) fifth, (b) sixth, (c) fourth, and (d) seventh layers in the $6 \times 6 \times 10$ lattice under the AP–F configuration. Parameters are taken as $U_1 = 24t$, $U_2 = 15t$, $E_1 = E_2 = 0$, and $U_C = 0$. The half width half maximum is taken as $0.01t$.

results give another possibility of obtaining devices with similar magnetoelectric properties by combining two MIs with antiparallel F-type magnetic order into an HJ. When the magnetization of one MI is fixed and that of the other MI is flexible, the ferroelectricity obtained in the AP–F configuration can be conveniently turned off and turned on again by a magnetic field. Our calculation shows that this kind of device can form even when there are only two layers that can be no more than 1 nm thick.[29] We find that the magnitude and direction of the ferroelectricity obtained in the MI/MI HJ can also be tuned by a voltage difference between the two materials.[9] The above effect is similar to the electronic interface reconstruction observed at polar-nonpolar MI heterojunctions,[5] in light of the equivalence between polarity and electric field in producing a linear variation of the on-site energies between consecutive layers of the polar MI or the MI to which an electric field is applied except for the tunability of the electric field.

4. Conclusions

We have studied a model of MI/MI heterojunction in which the MIs are described by the single orbit Hubbard model. It is found that a dipole layer usually emerges near the interface. We have shown that the dipoles emerge due to the asymmetric exchange processes with their magnitude depending strongly on the density of interfacial antiferromagnetic bonds. Our study may shed light on the fabrication of ultrathin ferroelectric and magnetoelectric devices.

Acknowledgement

We thank Professors Xing Ding-Yu and Shen Rui for helpful discussions.

References

[1] Elbio Dagotto 2005 *Science* **309** 257

[2] Masatoshi Imada, Atsushi Fujimori and Yoshinori Tokura 1998 *Rev. Mod. Phys.* **70** 1039

[3] Lee P A, Nagaosa N and Wen X G 2006 *Rev. Mod. Phys.* **78** 17

[4] Elbio Dagotto, Takashi Hotta and Adriana Moreo 2001 *Phys. Rep.* **344** 1

[5] Lee W C and MacDonald A H 2006 *Phys. Rev.* B **74** 075106
Lee W C and MacDonald A H 2007 *Phys. Rev.* B **76** 075339

[6] Ohtomo A, Muller D A, Grazul J L and Hwang H Y 2002 *Nature* (London) **419** 378

[7] Ahn C H, Triscone J M and Mannhart J 2003 *Nature* (London) **424** 1015

[8] Ohtomo A and Hwang H Y 2004 *Nature* (London) **427** 423
Ohtomo A and Hwang H Y 2006 *Nature* (London) **441** 120

[9] McGuire J A and Shen Y R 2006 *Science* **313** 1942

[10] Chakhalian J, Freeland J W, Srajer G, Strempfer J, Khaliullin G, Cezar J C, Charlton T, Dalgliesh R, Bernhard C, Cristiani G, Habermeier H U and Keimer B 2006 *Nature Phys.* **2** 244

[11] Koinuma H 2005 *Thin Solid Films* **486** 2

[12] Jin K J, Lu H B, Zhou Q L, Zhao K, Cheng B L, Chen Z H, Zhou Y L and Yang G Z 2005 *Phys. Rev.* B **71** 184428

[13] Satoshi Okamoto and Andrew J Millis 2004 *Nature* (London) **428** 630
Satoshi Okamoto and Andrew J Millis 2004 *Phys. Rev.* B **70** 075101
Satoshi Okamoto and Andrew J Millis 2004 *Phys. Rev.* B **70** 241104(R)

[14] Satoshi Okamoto, Andrew J Millis and Nicola A Spaldin 2006 *Phys. Rev. Lett.* **97** 056802

[15] Kancharla S S and Dagotto E 2006 *Phys. Rev.* B **74** 195427

[16] Paul S Bagus, Volker Staemmler and Christof Wöll 2002 *Phys. Rev. Lett.* **89** 096104

[17] Livia Giordano, Fabrizio Cinquini and Gianfranco Pacchioni 2006 *Phys. Rev.* B **73** 045414

[18] Alexander A Demkov 2006 *Phys. Rev.* B **74** 085310

[19] Winfred Mönch 1996 *J. Appl. Phys.* **80** 5076

[20] Winfred Mönch 2005 *Appl. Phys. Lett.* **86** 122101

[21] Kourkoutis L F, Hotta Y, Susaki T, Hwang H Y and Muller D A 2006 *Phys. Rev. Lett.* **97** 256803

[22] Leroy L Chang and Klaus Ploog 1985 *Molecular Beam Epitaxy and Heterostructures* (Martinus Nijhoff Publishers)

[23] Hirose K, Sakano K, Nohira H and Hattori T 2001 *Phys. Rev.* B **64** 155325

[24] Nicola A Spaldin and Manfred Fiebig 2005 *Science* **309** 391

[25] Evgeny Y Tsymbal and Hermann Kohlstedt 2006 *Science* **313** 181

[26] Hill N A 2000 *J. Phys. Chem.* B **104** 6694

[27] Hans Schmid 1994 *Ferroelectrics* **162** 317

[28] Manfred Fiebig 2005 *J. Phys.* D: *Appl. Phys.* **38** R123

[29] Javier Junquera and Philippe Ghosez 2003 *Nature* (London) **422** 506