Tuning Interlayer Exchange Coupling of Co-Doped TiO$_2$/VO$_2$ Multilayers via Metal-Insulator Transition

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(Received 24 July 2013; published 4 September 2013)

Reversibly switching interlayer exchange coupling (IEC) of magnetic semiconductor multilayers between ferromagnetic (FM) and antiferromagnetic (AFM) modes is a difficult but key issue for fabricating semiconductor giant magnetoresistance devices. Here, we show that such tunable IEC is achievable around room temperature in Co-doped TiO$_2$/VO$_2$ dilated magnetic semiconductor multilayers. On the basis of first-principles calculations of electronic structure and fermiology, it is clarified that, associated with the metal-insulator transition (MIT) of nanosized VO$_2$ spacers, exotic short-range magnetic orders are developed in the multilayers so that the IEC can be tuned reversibly from FM mode to AFM mode by varying temperature crossing the MIT ($\sim$ 340 K).

DOI: 10.1103/PhysRevLett.111.107203

PACS numbers: 75.50.Pp, 71.30.+h, 75.70.Cn, 85.75.–d

Interlayer exchange coupling (IEC) plays an important role in manipulating transport properties of magnetic multilayers because the spin-dependent carrier scattering can be changed greatly by switching the IEC between ferromagnetic (FM) and antiferromagnetic (AFM) modes. Although the AFM IEC of the semiconductor multilayers is rather difficult. Although the AFM IEC and the oscillatory IEC have been predicted based on the general Ruderman-Kittle-Kasuya-Yosida (RKKY) theory [10–12], experimental observations have mostly shown the FM IEC [3–5]. Only very recently, direct evidence of the AFM IEC was reported in [13,14], was employed for the magnetic layers.

DMS material of room-temperature ferromagnetism [13,14], was employed for the magnetic layers.

The DMS multilayers were simulated by using slab supercells. As illustrated in Fig. 1, the supercell of each model DMS multilayer consists of two rutile TiO$_2$ layers (with a fixed thickness of $m = 4$ slabs) separated by a VO$_2$ spacer ($n$ slabs). The Ti atoms near two interfaces in the model multilayer were substituted by Co atoms so that two Co-doped TiO$_2$ DMS layers were obtained. An R-phase VO$_2$ spacer of thickness $n$ was trivially constructed by stacking $n$ building blocks of $1 \times 2 \times 1$ rutile VO$_2$ unit cells along the $c$ axis. An $M1$-phase VO$_2$ spacer of thickness $n$ (Fig. 1) was obtained by dimerizing and distorting the V–V pairs along the $c$ axis in the corresponding $R$-phase spacer [19].

It is well-known that a Peierls-like phase transition results from the pairing distortion of atoms in the neighboring unit cells so that the unit cell doubles after the phase transition. For VO$_2$, it is noticed that in addition to the pairing along the $c$ axis, the twisting of the V ions after the MIT is actually equivalent to another pairing of the V ions along the prolonged V–O bond direction (the distorted octahedron of the rutile VO$_2$ has four shorter V–O bonds of 1.92 Å and two longer V–O bonds of 1.93 Å). Therefore, the $M1$-phase VO$_2$ spacer can be obtained as shown in Fig. 1.

Our first-principles calculations were performed by using the L(S)DA + U scheme implanted in the
FIG. 1 (color online). Structure of Co-doped TiO$_2$/VO$_2$ multilayers and their variations in metal-insulator phase transition. Top (a): the multilayer with an $R$-phase VO$_2$ spacer. The combination of two building blocks of the rutile VO$_2$ layer (black and red rectangles) forms a large orthogonal unit cell matching well the Co-doped TiO$_2$ layers. Middle [(b) and (c)]: distorting the atoms in the building blocks of the $R$-phase VO$_2$ spacer following the arrows (b) results in the monoclinic unit cells of the $M1$-phase VO$_2$ (c). Bottom (d): the multilayer with the $M1$-phase VO$_2$ spacer.

QUANTUM-ESPRESSO package [20]. Details about the calculations can be found in the Supplemental Material [21]. By careful tweaking of the pseudopotentials and the on-site Hubbard parameters U and J, the calculations well reproduce the band structures of bulk VO$_2$ in both the $R$ and $M1$ phases: as shown in Fig. S1 of the Supplemental Material [21], a semiconductor band structure is obtained for the $M1$ phase and the calculated band gap is 0.25 eV, about half of the experimental value ($\sim$ 0.6 eV) [15]. We focus on the perpendicular magnetization of the DMS multilayers, i.e., the magnetization directions aligned either parallel (FM ordering) or antiparallel (AFM ordering) to the $c$ axis. The total energies of these two magnetic configurations were calculated, and the IEC was obtained as the energy difference, $\Delta E = E_{FM} - E_{AFM}$.

In the present model multilayers, three kinds of magnetic interactions may contribute to the calculated $\Delta E$, namely, indirect IEC $\Delta E_1$ and $\Delta E_2$ through the middle VO$_2$ spacer and through the side TiO$_2$ layers, respectively, and a possible direct magnetic interaction between the DMS layers (which is negligible when the spacer is thick enough). By replacement of the middle VO$_2$ spacer by an undoped TiO$_2$ layer with different thickness, $\Delta E_2$ of the present model multilayers is estimated to be only about 3.0 meV and thereby is negligible (Supplemental Material [21]). Figure 2 presents the calculated IEC through the $M1$-phase VO$_2$ spacer as a function of thickness $n$. It is observed that, for all the calculated $M1$-phase VO$_2$ spacers, the FM configuration of the two DMS layers is always energetically favorable (i.e., $\Delta E < 0$) and from $n = 2$ to 12 $|\Delta E|$ rapidly decreases from 207.1 to 6.3 meV. As a matter of fact, a similar monotonic decrease in $|\Delta E|$ with increasing $n$ is also observed when the $M1$-phase VO$_2$ spacers are replaced by the undoped TiO$_2$ spacers (Fig. S2 of the Supplemental Material [21]), indicating that it is common for the semiconducting spacers.

The conventional RKKY theory predicts a FM-AFM oscillatory IEC with increasing the spacer thickness in metallic multilayers. Nevertheless, on the basis of a two-band model Abrikosov [22] and Narita and Kasuya [23,24] studied the RKKY interaction mediated by valence-conduction band excitations in intrinsic semiconductors in the 1980s and later Litvinov and Dugaev [25] studied the one originated from impurity-valence band excitations in Mn-doped GaAs. It has been shown that because of the imperfect spin screening effect the indirect RKKY interaction in gapped systems is ferromagnetic and its amplitude decays exponentially as $|J(R) | \propto e^{-\beta R}/R^2$ in the two dimensions [26,27], where $\beta = 2\sqrt{m^* E_g}$ is an exponential decay prefactor depending on the effective mass of the carriers ($m^*$) and on the energy gap ($E_g$) and $R = nc$ is the distance between the magnetic layers. Taking $\beta$ as a fitting parameter, we obtain the thickness-dependent IEC as $\Delta E$ (eV) = $-1.344e^{-0.30n}/n^2$ and $\Delta E$ (eV) = $-2.010e^{-0.102n}/n^2$ for the TiO$_2$ and $M1$-phase VO$_2$ spacers, respectively. As shown in Fig. S2 of the Supplemental Material [21], these model functions indeed describe reasonably the trends of $\Delta E$. As the calculated band gap of the $M1$-phase VO$_2$ (0.25 eV) is smaller than
that of TiO$_2$ (2.41 eV), a slower decay in $\Delta E$ is expected for the VO$_2$ spacers (Supplemental Material [21]).

So far, the calculations indicate that the ferromagnetic IEC of the semiconductor multilayers originates from the spacer’s band gap so that if an intrinsic (or a low doped) semiconductor spacer is employed, only the ferromagnetic IEC can be obtained. To obtain an antiferromagnetic IEC, heavy doping in the spacer layers is necessary to produce “metalliclike” carrier bands to mediate the IEC, as supported by the recent theory [10,11,25–27] and experiment [6]. This mechanism reminds us that the MIT may be an alternative way even more effective to manipulate the IEC of the DMS multilayers. For this reason, we next study the IEC mediated by the metallic rutile VO$_2$ spacers.

It is found from the calculations that in the magnetic multilayer environment, the unpaired 3$d^6$ electrons of V$^{4+}$ in the rutile VO$_2$ not only make the spacer metallic [15,18] but also exhibit considerable magnetic response to the magnetic DMS layers, which in combination with the spin interaction among the V$^{4+}$ ions leads to abundant features in the magnetic structures of the DMS multilayers. To demonstrate this, we compare in Fig. 3 the calculated spin-density distributions in the multilayers with $n = 5$ (odd) and 6 (even) with the two magnetic DMS layers in both the FM and AFM configurations.

Although the four spin-density distributions shown in Fig. 3 are different from each other, there are two important common characteristics: (1) around the interfaces, the local magnetic moments of the V ions tend to align parallel to those of the nearby magnetic DMS layers, indicating a ferromagnetic interaction between them, and (2) no matter what the interface magnetic structures are, the V ions in each one-dimensional (1D) chain along the $c$ axis always couple antiferromagnetically. As a result, in the cases of the two DMS layers in the FM configuration, the magnetic orders of the whole multilayers are $\uparrow$ (111) $\uparrow$ and $\parallel$ (111) $\parallel$ for the spacer thickness $n = 5$ and even, respectively (here $\uparrow$ and $\downarrow$ denote, respectively, the magnetic moments of the DMS layers and of the V ions). Whereas in the cases of the AFM configuration, the overall magnetic orders are either $\downarrow$ (111) $\uparrow$ or $\parallel$ (111) $\parallel$ (odd) or $\parallel$ (111) $\parallel$ (even).

The calculated total energies show that, for $n = 5$ (odd) (even), the FM (AFM) configuration of the two DMS layers has the lower energy, i.e., the magnetic structures having more ferromagnetically coupled layers around the interfaces are energetically favorable ($\uparrow$ (111) $\parallel$ for $n = 5$ and $\parallel$ (111) $\parallel$ for $n = 6$). As a result, when $n \geq 3$, the calculated $\Delta E$ oscillates between FM and AFM modes with an oscillatory period of $\lambda = 2c$ (Fig. 3). Furthermore, we performed a discrete Fourier transform for the calculated $\Delta E$ to resolve quantitatively the IEC period (Fig. S4 in the Supplemental Material [21]). A dominant peak at $q = 1.005\pi/c$ is observed, indicating that the calculated oscillatory period is 1.99$c$. To explain

![FIG. 3 (color online). Calculated spin-density distributions in the Co-doped TiO$_2$/VO$_2$ multilayers with the VO$_2$ spacer thickness $n = 5$ [(a) and (b)] and 6 [(c) and (d)]. In (a) and (d) [(b) and (c)], the two DMS layers are in the antiferromagnetic (ferromagnetic) configuration. (b) [(d)] is the ground state for $n = 5$ (6), and its magnetic structure is sketched in (b') [(d')].](image)
satisfy the above condition so that these singular vectors non or a spin-density-wave excitation with antiferromagnetic ordering of the 1D V chain (i.e., a phonon or a spin-density-wave excitation with \(q_1, q_2\)). The latter is not expected in the VO\(_2\) bulk but is possible in the VO\(_2\) spacers of a few nanometers thickness because it had been shown early \([29,30]\) that the 1D long-range magnetic order is unstable to thermal fluctuations so that only nano-sized 1D magnetic domains exist. Moreover, as the rutile VO\(_2\) unit cell contains two equivalent V ions, there are two kinds of nearly independent 1D V chains along the c axis. Their spin-density-wave excitations have either the same phase factor or a phase difference of \(\pi\), corresponding to two distinct magnetic orders in the spacers as (||\(1\)\ldots) or (\|\(1\)\ldots), respectively. Depending on the configurations of the magnetic DMS layers, they result in the exotic short-range magnetic structures of the multilayers shown in Fig. 3 and consequently in the oscillatory IEC different from the ferromagnetic IEC of the M1-phase VO\(_2\) spacers. These significant differences show that, for the VO\(_2\) spacer with \(n = \text{even}\), varying the temperature crossing the MIT can reversibly switch the IEC between FM and AFM modes (Fig. 2). The exotic magnetic structures may also indicate that the present DMS multilayers are insensitive to the interface roughness, which has been proven to play a critical role in metallic magnetic multilayers \([28,31]\). Because the V ions around the interfaces always couple ferromagnetically to the nearby DMS layers, eventually the interface roughness reduces the effective thickness of the VO\(_2\) spacer but may not change the oscillatory period.

To fabricate the temperature-controlled semiconductor GMR devices discussed above, the structural stability of the epitaxial multilayers has to be taken into account. For this reason, we calculate the cleavage energies of the interfaces between the Co-doped TiO\(_2\) and the VO\(_2\) layers based on various optimized multilayer structures (Supplemental Material \([21]\)). It is observed that the saturated value of the interface cleavage energies is about 6.4 J/m\(^2\), stronger than the surface or interface adhesions of most typical element or compound semiconductors such as Si, GaAs, CdTe, etc., whose surface cleavage energies are usually about 1.0 J/m\(^2\) (Supplemental Material \([21]\)). These results indicate that there are rather strong adhesions for both the rutile-rutile and rutile-monoclinic Co-doped TiO\(_2\)/VO\(_2\) interfaces despite the different magnetic orders. Moreover, the midinfrared near-field image observations \([32]\) have shown that the MIT of VO\(_2\) starts from nanopuddles of coexisting R- and M1-phase VO\(_2\), indicating that both the thickness and the interfaces of the sandwiched VO\(_2\) layer play a less important role in its MIT. Indeed, high-quality VO\(_2\) layers (\(\sim 10\) nm) grown on the TiO\(_2\) (001) single-crystal substrates were found to be fairly stable and were not damaged after many circles of the MIT \([33]\). Therefore, both theory and experiment evidence the stability of the multilayer devices discussed in this work.

In summary, the IEC of Co-doped TiO\(_2\)/VO\(_2\) DMS multilayers is studied theoretically. It is clarified that the electronic-structure instabilities of the VO\(_2\) spacers subject to the phonon and magnon excitations of \(q \sim \pi/c\) lead to
an exotic phenomenon that the IEC can be reversibly switched between FM and AFM modes via the MIT of VO₂. The unique effect paves a way to fabricate a class of temperature-controlled DMS GMR spintronic devices operating at around room temperature.

The work is supported by the National Science Foundation of China (Grants No. 61076089, No. 61227902, No. 11175066, and No. 11074075), the State Key Basic Research Program of China (Grant No. 2013CB922300), and the Ministry of Education of China (SRF for ROCS, SEM).

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