Spintronic and electrochromic device based on Li-intercalated transition-metal doped anatase TiO₂

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We have explored the effects of the Li intercalation on the electronic and magnetic properties of transition-metal (TM) doped anatase TiO₂. By Li intercalation, Mn-doped TiO₂ exhibits the insulator to metal transition. On the other hand, Li-intercalated Fe-doped TiO₂ has the insulating ground state for low concentration of Li/Ti = 0.067, but the metallic ground state for high concentration of Li/Ti = 0.133. We discuss the n-type carrier induced ferromagnetism in Li-intercalated TM-doped anatase TiO₂. Based on the Li-intercalated TM-doped anatase TiO₂, we propose a potential spintronic and electrochromic device controlled by the electric-field.

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Spintronic, namely spin-based electronics, is a new generation of microelectronics which utilizes both charge and spin degrees of freedom of carriers. Dilute magnetic semiconductors (DMSs) are expected to play a vital role in spintronics due to easy integration into existing semiconductor devices. Ideal DMS must satisfy such conditions as high Curie temperature (T_C) above room temperature and easy incorporation of p- and n-type dopants. So far, two types of Mn-doped DMS families have been investigated: II-VI (CdTe and ZnSe) and III-V (GaAs) zinc-blende compounds. Especially, the ferromagnetic (FM) behavior with T_C ~ 110K of Mn-doped GaAs attracts great attention, and it has been suggested that delocalized holes mediate the FM interaction between Mn spins.

It has been recently reported that Co-doped anatase TiO₂ film (Ti₁₋ₓCoₓO₂) shows the ferromagnetism even above room temperature. Ti₁₋ₓCoₓO₂ films were fabricated by means of the pulsed-laser-deposition or the oxygen-plasma-assisted molecular-beam-epitaxy technique. However, still controversial is the issue that the ferromagnetism in this system is an intrinsic DMS property or not. One claim is that Co atoms substitute properly for Ti atoms and the ferromagnetism is caused by the exchange interaction mediated by the vacancy-induced n-type carriers. Another is that Co atoms form nano-clusters, resulting in the high T_C ferromagnet. The other claim is that Co atoms incorporate in the interstitial position or forms Co-Ti-O complexes. It is also reported that the as-grown film has coexisting contributions from Co metal clusters and matrix-incorporated Co, but that the high temperature heat treatment enhances the matrix-incorporated Co contribution drastically.

Independently of the DMS project, Li intercalation in anatase TiO₂ has been studied extensively for possible uses in high energy density batteries, electrochromic, and solar-cell devices. It is possible to intercalate Li atoms in anatase TiO₂ up to the Li/Ti ratio of ∼ 0.7. There is an indication that the intercalation does not occur uniformly throughout each crystallite. Further, there seem to exist two phases: the Li-poor anatase phase and the Li-rich orthorhombic phase. The insulator to metal transition is observed for the Li/Ti ratio of ∼ 0.3. Interestingly, the magnetic susceptibility is observed to be proportional to the Li/Ti ratio in the Li-intercalated anatase TiO₂ with the measured localized moment of ∼ 0.004 μ_B per Ti.

Motivated by the easy Li intercalation into anatase TiO₂, we have explored the magnetic properties of transition-metal (TM) doped TiO₂ with intercalating Li. To this end, we have investigated electronic structures of Li-intercalated Ti₀.₉₃₇₅M₀.₆₆₂₅O₂ (M=Mn, Fe). We have found that both Mn- and Fe-doped TiO₂ with sufficient intercalated Li concentration have metallic and ferromagnetic ground states, implying that n-type carriers produced by Li intercalation induce the ferromagnetism.

We have employed the linearized muffin-tin orbital (LMTO) band method in the local-spin-density approximation (LSDA). The space group of anatase structure is tetragonal I₄₁/amd. The anatase TiO₂ is composed of stacked edge-sharing octahedrons formed by six O anions. Ti atoms are in the interstitial sites of octahedrons that are distorted with different bond lengths between the apical (1.979 Å) and the equatorial (1.932 Å) Ti-O bond and with the Ti-O-Ti angle 156.3°. For Ti₀.₉₃₇₅M₀.₆₆₂₅O₂, we have considered a supercell containing sixteen formula units in the primitive unit cell by replacing one Ti by M atoms (Ti₁₅M₁O₃₂; a = b = 7.570, c = 9.514 Å). Sixteen empty spheres are considered in the interstitial sites to enhance the packing ratio for the LMTO band calculation. To simulate the Li intercalation, we replaced one (corresponds to Li/Ti=0.067) or two (Li/Ti=0.133) interstitial empty spheres by Li atoms.

We have studied before electronic structures of TM doped anatase Ti₁₋ₓMₓO₂ (M=Mn, Fe, Co, Ni) without Li intercalation. Using the LSDA band calculation, we have obtained the half-metallic ground states for Fe- and Co-doped cases with the carrier type of mainly Fe and Co 3d states, respectively. On the other hand, we have obtained insulating ground states for Mn- and Ni-doped cases. Ni-doped TiO₂ was found to be nonmagnetic. We have also studied Li intercalation effects on
the electronic and magnetic properties of both undoped and Co-doped anatase TiO$_2$. What we have found for undoped TiO$_2$ was that the $n$-type carriers produced by the Li intercalation fill Ti 3$d$ conduction band so as to induce small magnetic moments at Ti sites. In contrast, Li-intercalated Co-doped TiO$_2$ becomes nonmagnetic and insulating, because the produced $n$-type carriers fill up the low-spin Co 3$d$ states located in the energy gap region. Hence the Li intercalation was detrimental to stabilizing the magnetic state in Co-doped TiO$_2$. These features, however, suggested that some other TM-doped anatase TiO$_2$ with TM of high-spin configuration would have carrier induced ferromagnetism through the Li intercalation.

Now let us study the Li intercalation effects in Ti$_{0.9375}$Mn$_{0.0625}$O$_2$. Figure 1 provides the LSDA density of states (DOS) for the FM phase of Ti$_{0.9375}$Mn$_{0.0625}$O$_2$ with Li/Ti=0.067. We have obtained metallic ground state, contrary to the non-intercalated Mn-doped TiO$_2$ which has an insulating ground state. The energy band gap between O 2$p$ and Ti 3$d$ states is estimated to be $\sim 3.2$ eV, which is reduced from $\sim 4$ eV estimated for the non-intercalated case. The Mn 3$d$ projected local density of states (PLDOS) indicates the high-spin state of Mn, that is, the exchange splitting between $t_{2g}$ states is larger than the crystal-field splitting between $t_{2g}$ and $e_g$ states. Most of occupied Mn 3$d$ ($t_{2g}$) states are located in the energy gap region, whereas the empty Mn 3$d$ states are shifted up and hybridized with Ti 3$d$ conduction band. Note that, for the non-intercalated case, both the occupied $t_{2g}$ and the empty $e_g$ states were in the energy gap region far below the Ti 3$d$ conduction band. According to the rigid band model, the extra n-type carriers produced by Li intercalation would fill the empty Mn $e_g$ majority spin states first. Figure 2, however, indicates that the extra electrons fill not only Mn $e_g$ majority spin states but also Ti 3$d$ conduction band, indicating that the simple rigid band concept does not work here. It happens because the extra carriers produced by Li intercalation are localized at Ti sites near the intercalated Li. Due to this localization, Mn $e_g$ majority spin states are pushed up above the Ti 3$d$ conduction band bottom and so only slightly filled. The magnetic moment of Mn ion is 3.43 $\mu_B$, and the total magnetic moment is 3.74 $\mu_B$. With Li intercalation, magnetic moments of Ti ions are a bit enhanced as compared to the non-intercalated case.

Figure 2 shows the band structure of Li-intercalated Ti$_{0.9375}$Mn$_{0.0625}$O$_2$ with Li/Ti=0.067 near the Fermi level $E_F$. The size of circle represents the amount of Mn 3$d$ component in the wave function. It is seen that the majority spin states near $E_F$ are mostly of Mn 3$d$ states, while the minority spin states near $E_F$ correspond mainly to Ti 3$d$ conduction band states with fairly large band dispersion. Thus Mn 3$d$ states are nearly half-metallic.
and the flat Mn 3d states suggest that they are rather localized [21]. Half-metallic Mn 3d states near $E_F$ together with the localized Mn $t_{2g}$ states far below $E_F$ suggest that the double-exchange (DE) mechanism would be operative to yield the FM ordering of Mn spins [15].

On the other hand, the localized nature of Mn 3d states and the dispersive Ti 3d conduction band carriers are reminiscent of Mn-doped GaAs in which As 4p hole carriers seem to mediate the Ruderman-Kittel-Kasuya-Yosida (RKKY)-type exchange interaction [22,23,24]. The difference from Mn-doped GaAs is the type of conduction band carriers which is $n$-type in the present case. With the information of the Fermi surface wave vector $k_F$ of the conduction band, one can derive the magnetic ground state of the system in the RKKY formalism, That is, if the relation $2k_F R_{MM} < 4.5$ ($R_{MM}$: nearest distance between Mn spins) is satisfied, the FM ordering of Mn spins would be stabilized [23]. As shown in the inset of Fig. 3, the minority spin band structure has an oblate sphere-like Fermi surface centered at $\Gamma$. One can measure $k_F$'s directed from $\Gamma$ to some symmetry points in the irreducible Brillouin zone [24]. The longest $k_F$ is $k_F^{-1}$, while the shortest one is $k_F^{-2}$. Then, with $R_{MM}=7.57\,\AA$, one obtains $2k_F R_{MM} = 4.63$ and 2.96 for $\Gamma - X$ and $\Gamma - Z$ directions, respectively. However, besides $k_F^{-1}$, all other $k_F$'s give rise to $2k_F R_{MM}$ less than 4.5, suggesting that the FM interaction is dominant in the RKKY interaction mediated by the $n$-type conduction band carriers of Ti 3d states. Therefore, it is expected that, in Li-intercalated Ti$_{0.9375}$Mn$_{0.0625}$O$_2$, the FM interaction between Mn spins is reinforced by the combined effects of the DE and RKKY interactions.

For more Li-intercalated Ti$_{0.9375}$Mn$_{0.0625}$O$_2$ with Li/Ti=0.133, we have also obtained magnetic and metallic ground state. More extra electrons fill both Mn and Ti 3d states. Compared to the Li/Ti=0.067 case, the total magnetic moment is reduced to 3.6 $\mu_B$, while Mn has nearly the same value, 3.41 $\mu_B$. The reduced total magnetic moment originates from lowered Mn 3d DOS at $E_F$ which diminishes the spin-polarized hybridization between Mn and neighboring atoms. As mentioned above, the observed FM state in Co-doped TiO$_2$ is questioned whether it is an intrinsic DMS property or not. Once the FM state is observed in Mn-doped TiO$_2$, it can be considered as intrinsic, because Mn or Mn-oxide clusters, if they were formed in anatase TiO$_2$, would have the AFM ground state. Therefore, to get the direct evidence of DMS property in TiO$_2$, it is desirable to fabricate Mn-doped TiO$_2$ with varying the intercalated Li concentration.

Next we have examined electronic structures of Li-intercalated Fe-doped TiO$_2$: Ti$_{0.9375}$Fe$_{0.0625}$O$_2$ with Li/Ti=0.067 and 0.133. For Li/Ti=0.067 case, we have obtained the insulating and magnetic ground state (see the inset of Fig.3). This is again in contrast to non-intercalated Fe-doped TiO$_2$ which is half-metallic [25]. The electron carriers produced by Li intercalation fill up the Fe $\epsilon_g$ majority spin states which was half-filled for the non-intercalated case. The empty Fe 3d minority spin states are shifted up above Ti 3d conduction band bottom, as in the Mn-doped case (Fig.3). The energy band gap between O 2p and Ti 3d states is estimated to be $\sim 3.0$ eV which is similar to that of Mn-doped case. Total magnetic moment is 5 $\mu_B$, which comes mainly from Fe local magnetic moment of 4.31 $\mu_B$.

Figure 3 presents results for more Li-intercalated Fe-doped TiO$_2$ with Li/Ti=0.133. In this case, we have obtained the metallic and magnetic ground state. The metallic ground state results from more electron carriers produced by more intercalated Li concentration. The states near $E_F$ are mostly of Ti 3d character. This feature is different from the Mn-doped case having both Ti and Mn 3d characters near $E_F$. It is expected that the RKKY-type interaction works here too, that is, $n$-type carriers of Ti 3d states mediate the magnetic interaction between Fe local magnetic moments. Note, however, that the Ti conduction band shows little spin polarization at $E_F$ ($\sim 20\%$), and so this case is different from Mn-doped GaAs which has the 100% spin polarization at $E_F$. Total magnetic moment is a bit reduced to 4.85 $\mu_B$, but Fe local moment 4.31 $\mu_B$ is nearly the same. The reduced total magnetic moment seems due to metallic phase, which results in the enhanced AFM interaction between Fe and oxygen ions.

On the basis of above findings, we propose a new spin-
tronnic ground state for Li-intercalated Fe-doped TiO$_2$ and 0.133, respectively. We have also obtained magnetic ground state for Li-intercalated Ti$_{0.875}$Mn$_{0.125}$O$_2$ with Li/Ti=0.143. The energy differences between two configurations are found to be negligible within the numerical precision. But, for Fe-doped case, the insulating state prefers the AFM configuration of Fe spins.

The LSDA+U ($U = 3.0$ eV) band calculation yields the further splitting in the majority spin $e_g$ states near $E_F$. But the lower pinned states at $E_F$ are not changed much.

In this way, an electric-field controlled spintronic and electrochromic device can be realized in the Li-intercalated TM-doped anatase TiO$_2$ system.

In conclusion, we have obtained ferromagnetic ground state for Li-intercalated Mn-doped TiO$_2$ with the $n$-type carriers of Ti 3$d$ states. Mn ions have the high spin states with 3.43 and 3.41 $\mu_B$ spin moments for Li/Ti=0.067 and 0.133, respectively. We have also obtained magnetic ground state for Li-intercalated Fe-doped TiO$_2$. As the intercalated Li concentration increases, the electronic structure changes from insulating to metallic nature. Fe ions have the high spin states with 4.31 $\mu_B$ spin moment for both cases. Our results suggest that the DMSs of Mn- and Fe-doped anatase TiO$_2$ can be synthesized by Li intercalation. Based on our findings, we propose a novel non-volatile spintronic and electrochromic multifunctional device which can be controlled by the electric-field.

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