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Letter

Characterization of LSMO/C_{60} spinterface by first-principle calculations

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ABSTRACT

Spinterface between fullerene C_{60} and $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) was studied by means of density functional theory. Co-existence of many different configurations was shown, and probabilities of their appearance were estimated. Dependence of composite properties on configuration and temperature was also investigated. Key role of transition metal atoms in both binding between composite compartments and magnetic ordering in C_{60} molecule was discussed. The latter was suggested to be responsible for spin-polarized charge transport while overall magnetic moment of fullerene molecule is relatively small.

1. Introduction

Organic semiconductors are well-known as promising candidates for spintronics due to weak spin-orbit and hyperfine interaction [1–4]. Both giant magnetoresistance effect (GMR) and tunneling magnetoresistance (TMR) effect were observed in organic-based spin valves with rubrene, pentacene, tris(8-hydroxyquinolino) aluminum (Alq_3) and C_{60} as spacers [3,5–10]. Fullerene C_{60} is considered to be especially promising due to the absence of atoms other than carbon and, hence, weaker hyperfine interaction [10–13]. Half-metallic $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) is widely used in spintronic devices due to its high spin polarization [7,11–14] even though it may vary due to the *k* broadening in direction perpendicular to the surface [15] resulting in reduction of spin polarization observed in experiment [16]. It has a lot of advantages comparing with conventional ferromagnetic materials (e.g. Fe, Co, Ni) being much less spin polarized and suffering from well-known conductivity mismatch problem. One way to solve this problem is to add tunnel barriers between FM electrodes and a spacer at the cost of increasing device complexity. Using half-metallic electrodes (LSMO) allows achieving up to the 95% contact spin polarization in MTJ devices without using any additional layers. Moreover, in contrast to abovementioned transition metals, LSMO is highly resistive against oxidation [1]. These features make LSMO an ideal candidate for using in spintronics. Detailed studies of magnetoresistance in LSMO/C_{60}/Co vertical spin valve [11–14,17] including effects of spacer thickness and surface morphology reveal very complex behavior combining GMR resulted from spin injection and TMR due to the presence of pinholes in organic spacer [12]. Magnetoresistance effect was found to increase drastically when C_{60} layer possesses higher crystallinity and larger grain size with many pinholes. Co then can diffuse through these pinholes reducing the effective thickness of spacer and causing tunneling rather than spin injection [12]. In contrast to that, samples with smoother C_{60} surface demonstrate completely different characteristics corresponding to the spin-polarized injection [12]. In order to prevent Co from diffusing into the pinholes, more complex LSMO/C_{60}/AlO_x/Co devices were fabricated [11]. Aluminum oxide was found to suppress cobalt diffusion into the spacer layer effectively. Surprisingly, magnetoresistance effect changes its polarity in this

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case becoming positive instead of negative for original LSMO/C_{60}/Co. This is explained in terms of competition between positive GMR channel and pinhole channel in latter case while positive MR dominating in former one [11]. Effect of Co/fullerene spinterface is also investigated both experimentally and theoretically by Liang et al. [14]. However, the nature of interface between C_{60} and LSMO is relatively less investigated. Experimental study of its electronic structure by photoelectron spectroscopy was performed very recently [18]. Shift of HOMO and LUMO levels leading to n-p transition was observed when increasing the thickness of C_{60}. This was attributed to p-doping caused by oxygen diffusion from LSMO to the C_{60} layer.

The present work is originally to study spin polarization features of LSMO/C_{60} hybrid structures by means of density functional theory. When performing DFT calculations, we found many possible structures to be stable revealing the existence of microstates continuously transforming to each other by fullerene's rotation along the surface. Thus, this effect is also to be described in details.

2. Computational details

The first-principles density functional theory calculations of LSMO/C_{60} composites were performed using VASP code [19–22]. GGA PBE potential [23,24] with taking into account Hubbard corrections (GGA + U) [25,26] and projector augmented wave [27,28] method (PAW) were implemented. D3 Grimme correction of weak dispersion interactions [29] was used in order to describe the interaction between fullerene molecule and LSMO substrate correctly. The U = 2 and J = 0.7 eV parameters of GGA + U approach are adopted from earlier calculations of LSMO [30–32]. Geometry optimization was performed until the forces acting on atoms were less than 0.01 eV/Å.

First, unit cell of bulk LSMO was optimized, and the a translation vector is found to be equal to 3.886 Å which is in a good agreement with experimental data (a = 3.876 Å [33] and a = 3.87 Å [34]) and previous theoretical calculations (a = 3.89 Å) [30]. Then, LSMO (001) surface was constructed by cutting it along the corresponding crystallographic plane. Mn-O terminated surface was chosen since it was investigated in experimental works [11–13]. 4 × 4 × 1 supercell of LSMO surface was used for calculation of interface with C_{60}. This means that, in periodic boundary conditions, fullerene molecules are distant from each other (distance between them is ~8.6 Å) and can be considered as isolated. We suppose that mainly the topmost Mn-O layer should be responsible for interface properties so one can use an oversimplified model of 1 unit cell along *c* direction without any cost at computational accuracy while considerably increasing the speed of calculation. Artificial interactions in periodic boundary conditions were avoided by setting the vacuum interval of approximately 13 Å in direction normal to the interface. Lattice vectors were then set to be a = b = 15.544 Å, c = 30.000 Å. The Mönkhorst-Pack [35] k-point Brilloin sampling was used. The k-point grid contained 2 × 2 × 1 points along *a*, *b* and *c* directions, respectively. The energy cut-off was specified as 450 eV in all calculations.

Energy of bonding between fullerene and LSMO slab was estimated as:

$$E_b = E_c - E_f - E_{LSMO}, \quad (1)$$

where E_c, E_f and E_{LSMO} are total energies of composite, fullerene and LSMO slab, respectively. Charge and magnetic moment on fullerene molecule were estimated according to the Bader charge analysis [36–38].

3. Results and discussion

Different possible configurations of LSMO/C_{60} nanocomposite were considered (see Fig. 1). Each configuration is denoted as X(η^y), where X = O or Mn, and y stands for the number of carbon atoms surrounding X (see Fig. 1). Five initial configurations with y varying from 2 to 6 were chosen for Mn-coordinated structures, and, similarly, for O-coordinated ones. Since there are two unequal η^2 configurations (with carbon bond between two hexagons or between hexagon and pentagon placed upon corresponding LSMO atoms), they were designated as η^2 and $\eta^{2'}$, respectively. Obviously, there is no way to construct an η^4 configuration with four carbon atoms being equally distant from coordinating atom. Thus, it has been excluded from the scope of our investigation, and so the total number of initial structures became 10. According to our calculations, binding energies of all structures are considerably high and differ from each other in range of 0.3 eV. Such proximity witnesses the co-existence of many microstates that can easily transform from one to another (see Fig. 1). The height of migration barrier is conditioned mainly by the difference in binding energies. Possibility of fullerene's migration along the surface was also recently reported for Au and Fe surfaces [39,40]. The probability of each state appearance was estimated according to the Gibbs distribution:

$$P_i = \frac{e^{-\frac{E_i}{k_B T}}}{\sum_{i=1}^{10} e^{-\frac{E_i}{k_B T}}} \quad (2)$$

in the temperature range of 300–600 K O(η^3) and O(η^5) were found to be the most probable to occur at 300 K. It can be noticed from Fig. 1 that these two structures possess carbon atoms placed upon Mn atom, while structure with C–C bond upon the Mn atom are less favorable, and ones without contact with manganese atom are considerably higher in energy. This reveals the key role of transition metal atom in binding between LSMO and C_{60} molecule. At the same time, the presence of oxygen leads to repulsion with fullerene's π-conjugated system. Supply from O(η^6) and Mn($\eta^{2'}$) configurations becomes valuable as the temperature increases (18 and 10% at 600 K, respectively, see Table 1). Less pronounced are supplies from O($\eta^{2'}$) and Mn(η^2) (6% at 600 K). Probabilities of other configurations appearance are less than 5% even at 600 K. The analysis of composites' electronic structure (see Table 1) shows that charge and magnetic moment on fullerene molecule is virtually the same for all configurations. Spin polarization at Fermi level was calculated as:

$$\xi = \frac{n_\uparrow - n_\downarrow}{n_\uparrow + n_\downarrow}, \quad (3)$$

where $n_\uparrow$ and $n_\downarrow$ are spin-up and spin-down electron densities at Fermi level, respectively. This value varies from 4 to 22% for different configuration. However, it doesn't change its sign (see Table 1) that means that spin-polarized transport is possible even if one configuration moves to another. Averaged properties of fullerene molecule in LSMO/C_{60} composite were calculated taking into account probabilities of microstates' appearance at different temperatures:

$$X = P_i \cdot X_i, \quad (4)$$

where X is the property, i denotes the configuration, and P is the probability of its appearance at the corresponding temperature. All properties discussed here remain stable in the temperature range of 300–600 K (see Table 2). C_{60} molecule gains the charge of