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Full Length Article

Suppressed and enhanced spin polarization in the 1ML-Pb/Ge(1 1 1)-1 × 1 system

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ABSTRACT

It is shown, based on the density functional theory (DFT), that the spin splitting of surface electronic states induced by a Pb monolayer on the Ge(1 1 1)-1 × 1 surface depends on the bonding structure of the Pb/Ge interface and may be either significant, ~0.8 eV, (H_3/T_4) or completely suppressed (T_1). It is also shown that for the former the bonding configuration facilitates an emergence of unquenched orbital angular momentum ***L*** along Γ-*K*-*M* direction, which then lifts the spin degeneracy of the electronic states through the spin-orbit coupling (SOC) of electrons in Pb. Along with the DFT data, we present a complementary analysis conducted withing the orbital Rashba framework, which provides an additional insight into the SOC-induced splitting.

1. Introduction

Spin angular momentum (SAM, or simply spin) polarized electronic states induced on surfaces of elemental semiconductors by monolayers of metallic, nonmagnetic adatoms with large intra-atomic spin-orbit coupling (SOC) have attracted much attention due to possible spintronic application [1–7]. The latter requires that the spin polarized states are located within a semiconductor bulk energy gap to prevent mixing with the unpolarized states of the bulk. Also, the spin split of at least 100 meV is desirable to minimize the effect of thermal fluctuations and enable room temperature operations.

Experimentally observed spin splitting of electronic states at semiconductor surfaces are well reproduced by first principle calculations and the phenomenon is usually associated within a Zeeman-like effect described by the Rashba-Bychkov (RB, or simply Rashba) model. This approach, however, lacks predictive power to quantitatively account for spin split, as experiments and the original Rashba theory show large discrepancy in the energy scales reported. A number of proposals had also been put forward to amend the energy of the putative Zeeman-type splitting of the original Rashba model [7–11], however, no universal solution has yet been recognized. On the other conceptual side, recent observations of a direct correlation between unquenched orbital angular momentum (OAM) and the emergence of SAM splitting has led to the formulation of the so-called orbital Rashba model [12–15]. In this approach the unquenched OAM explicitly contributes to the spin-split pattern through both the atomic SOC and the surface electric-dipole/electric-field interaction at the surface. It was also shown that this model quantitatively accounts for the scale of the spin splitting in a variety of systems [14,16,15,17].

In this paper we investigate, based on the density functional theory (DFT), the spin and electronic structure of the Pb/Ge(1 1 1)-1 × 1 adsorption system. We observe that the predicted spin-split pattern depends on the bonding configuration at the Pb/Ge interface, and may be large (~0.8 eV) or completely suppressed in vicinity of the *K* point of the surface Brillouin zone (SBZ). The observed difference is also shown to be correlated with the magnitude of the unquenched adatomic OAM calculated for the SAM-split bands. Our DFT data indicate that the spin split in vicinity of *K* originates form the atomic SOC of Pb adatoms, which we further discuss within the orbital Rashba framework.

2. Methods

Total-energy and electronic structure calculations, were performed using Quantum Espresso [18] (QE), a DFT plane-waves code, employing ultrasoft pseudopotentials [19], local density approximation (LDA) for exchange and correlation of Perdew-Zunger [20], energy cutoffs of 544 and 3400 eV for wave functions and densities, respectively, and SOC. The SBZ was sampled using 12 × 12 × 1 Monkhorst–Pack [21] *k*-point grid scheme. The Pb/Ge(1 1 1) system was modeled by repeated asymmetric slab consisting of six Ge layers, Pb monolayer on one side of

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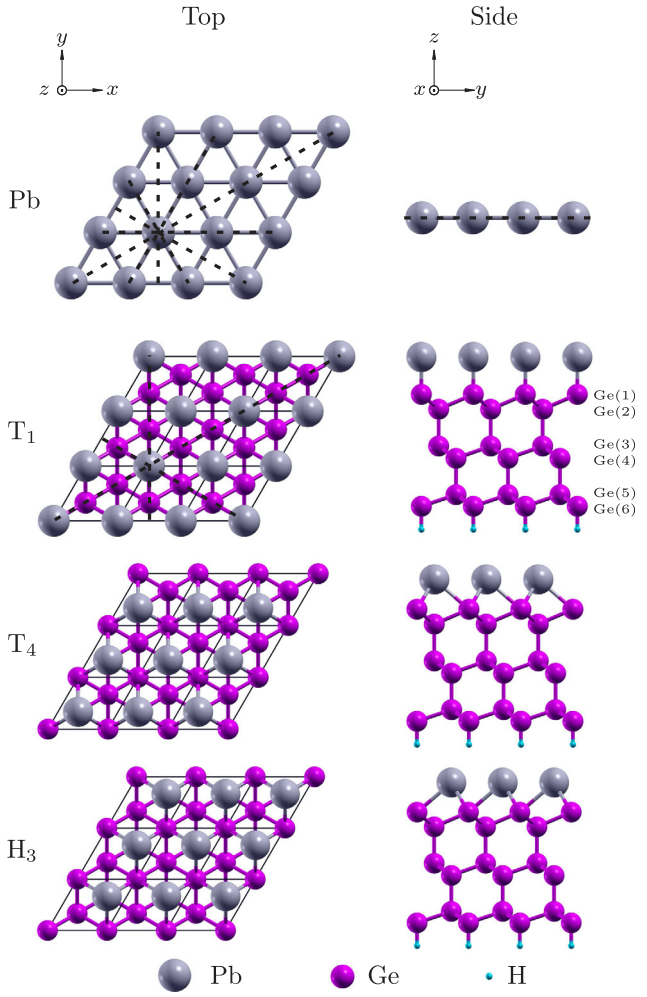

Fig. 1. Schematics of atomic structures of isolated Pb monolayer and configurations T_1, T_4 and H_3 of the Pb/Ge(1 1 1) adsorption system. Black dashed lines indicate mirror symmetry planes. Black lines in the top views indicate surface unit cell borders.

the slab and the hydrogen atoms on the other. The atomic positions, except for H and two bottom Ge layers of the slab, were fully optimized to an assumed criterion for atomic forces (<$1.36{\cdot}10^{-4}$ eV/a.u.). All calculations were performed with the optimized bulk Ge lattice constant of 5.658 Å(experimental value for bulk Ge is 5.64 Å[22]), and the spatial separation between the slabs of 20 Å. The spin-orbit interaction has been reported to have a considerable (~30 meV) impact on the stability of the surface configurations of the Pb-decorated surfaces of Ge (1 1 1) and Si(1 1 1) in the $\sqrt{3} \times \sqrt{3}$ surface reconstruction, and therefore the investigated configurations of Pb/Ge(1 1 1)-1 × 1 were relaxed in presence of SOC. The SAM and OAM projections for specific *k*-points were obtained with the use of the linear combination of pseudo-atomic orbitals (LCPAO) [23] coefficients of local atoms calculated in OpenMX code [24–27], with norm-conserving pseudopotentials [28].

3. Results

The calculations were carried out for three distinct atomic configurations of the Pb monolayer (ML) on a Ge(1 1 1) surface shown in Fig. 1. In the H_3 and T_4 geometries each Pb atom is located at the hollow sites of the Ge(1 1 1)-1 × 1 surface and interacts with three, first layer Ge atoms. The difference between these geometries is that in T_4 the Pb atoms are located above the second layer Ge atoms, while in H_3, above the fourth layer Ge atoms. In configuration T_1, the Pb atoms are placed directly above the topmost layer Ge atoms and each Pb interacts with one surface Ge atom.

Table 1
Calculated atomic distances and interlayer spacings (Δz) within the Pb/Ge (1 1 1) interface in configurations T_1, T_4, and H_3. The enumeration of Ge atoms is shown in Fig. 1.

Atom	Distance			Δz		
	T_1	T_4	H_3	T_1	T_4	H_3
	(Å)					
Pb-Ge(1)	2.754	3.129	3.053	2.754	2.109	1.996
Ge(1)-Ge(2)	2.462	2.530	2.516	0.851	1.030	0.997
Ge(2)-Ge(3)	2.453	2.487	2.466	2.487	2.487	2.466

The surfaces of configurations H_3 and T_4 are of p3m1 symmetry (the Pb adlayer and the first Ge layer being considered). In geometry T_1 the Pb atoms are directly on-top of the first Ge layer resulting in the p6mm symmetry of the two-layer structure. However, in this case first three atomic layers are to be included. It has been shown, that for the symmetry-equivalent surface T_1-Br/Ge(1 1 1)-1 × 1 the quasi-2D structure consists of the Br adlayer and two top atomic layers of the substrate, which give the surface a p3m1 symmetry [29,30] (compare the top views of the configurations shown in Fig. 1).

Geometry T_1 was found to be energetically the most favourable which agrees with experimental data [31]. This configuration is 0.178 and 0.213 eV lower in energy than geometries H_3 and T_4, respectively. The structural parameters of the calculated geometries are summarized in Table 1 and the corresponding electronic structures are shown in Fig. 2. The electronic structure of an isolated two-dimensional (2D) monolayer of Pb atoms (1ML-Pb) arranged in a hexagonal geometry with the lattice constant compatible with that for 1ML-Pb/Ge(1 1 1)-1 × 1 is also shown in the figure.

The electronic structures of 1ML-Pb with and without SOC are shown in Fig. 2a and b, respectively. In the structure without SOC (Fig. 2b), the states within the bands in the vicinity of the Fermi level (E_F) have $l = 1$ character (p type). Only one band, however, can be distinguished by the magnetic quantum number m_l (p_z) as the remaining two result from the in-plane interaction between the electrons in the p_x and p_y orbitals (denoted as p_x/p_y); see Fig. 2b, and also Table 2. The 2D crystal field (non-SOC case) does not couple the p_z and p_x/p_y orbitals so that the corresponding bands remain degenerate at the crossing points. By contrast, in the structure with SOC (Fig. 2a), the spin-orbit interaction couples the p_z and p_x/p_y states and the degeneracy at the crossing points is lifted, however, no spin-split bands are observed as the inversion symmetry of the isolated layer is preserved. When SOC is present, it would be customary to expand the electronic states around an atomic center with total angular momentum (j, m_j), rather than orbital angular momentum (l, m_l). As all the states within the bands of Fig. 2a are of $l = 1$ character, j and m_j can take the values of $\frac{1}{2}$ and $\frac{3}{2}$, and $\pm\frac{1}{2}$ and $\pm\frac{3}{2}$, respectively. As a result there are six possible (j, m_j) bands, however, due to lack of spin splitting, the bands in Fig. 2a are doubly degenerate with respect to m_j and are: $(\frac{1}{2}, \pm\frac{1}{2})$, $(\frac{3}{2}, \pm\frac{1}{2})$ and $(\frac{3}{2}, \pm\frac{3}{2})$ (see the color code in Fig. 2).

The electronic structures of the most stable configuration, T_1, with and without SOC, are shown in Fig. 2c and d, respectively. It is observed that in the band structure without SOC (Fig. 2d), the dispersion and binding energies of the bands of the Pb p_x/p_y character (16 and 17) located in the projected bulk band gap are essentially identical to that of the isolated Pb monolayer (Fig. 2b). This shows that these states are not part of the bonding structure of the Pb/Ge interface and that inversion asymmetry imposed by the Pb/Ge has little impact on the symmetry of these states. Fig. 3a and b, where the corresponding partial charge density are shown, illustrate this effect. Only the band of the Pb p_z character (18 in Fig. 2d) is affected by the interaction with the Ge dangling bonds (see Fig. 3c). As a result this band flattens and its binding energy is shifted down below the Fermi level. Analogous