Search and realization of novel electronic properties of solid surfaces and interfaces and of small particles

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We mention two subjects which we addressed this year.

The Ni(110)-(2x1)O surface is known to have a missing-row reconstruction structure, as is shown in Fig. 1 [1]. Oxygen (O) atoms are adsorbed at bridge sites to form Ni-O-Ni atomic chains in the *y*, namely, [001] direction. The O-derived bands exist near the upper and lower edges of the substrate Ni bands. The bands around the lower edge have already been studied well by means of first-principles calculations using small-scaled slabs and some experimental studies.

This year, using a large-scaled slab composed of 21 Ni atomic layers and adsorbed O atoms at both surfaces, we investigated the upper O-derived bands, and identify them with surface states when separated up from the upper edge of the substrate bands.

We employed the program package 'Vienna Ab initio Simulation Package' (VASP) [2,3] on systems B and C.

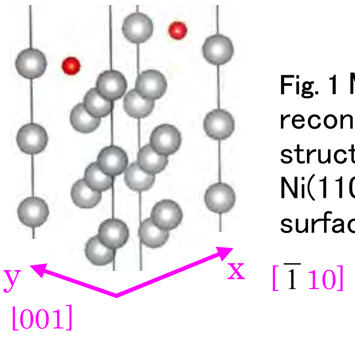

Fig. 1 Missing- row reconstruction structure at the Ni(110)-(2x1)O surface

Graphene is a very popular single-layer structure of carbon (C) atoms arranged in a hexagonal lattice. The band structure of this material is characterized by a so-called Dirac cone, and predicts an extremely high electron mobility. When this material takes a form of nanoribbons, the band structure due to π orbitals around the Fermi level depends on edge shapes. Nanoribbons with zigzag edges have localized edge states, while those with armchair edges possess no edge states.

We consider the electronic structure of graphene systems of finite area. By means of the tight-binding method, we examined if edge-localized states can be formed in finite graphene systems, and how the electronic structure of these systems depends on system shapes or areas.

(1) Identification of surface states at the Ni(110)-(2x1) O surface [4]

Assuming a slab of 21 Ni-atom layers with O atoms adsorbed at each surface and using the generalized gradient approximation, we obtained the optimized ground state structure. Figure 2 (a) shows the band dispersion on the $\bar{\Gamma}-\bar{Y}$ line for majority spin. As is displayed by an arrow, there exist a pair of nearly degenerate bands that lie above the densely distributed substrate bands due to Ni *d* orbitals. Figure 2 (b) exhibits electron-density isosurfaces of the higher energy one of the above paired states at the

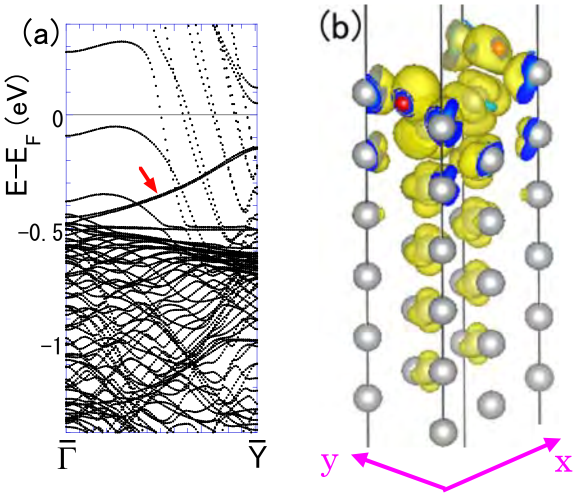

Fig. 2 (a) Band dispersion on the $\bar{\Gamma}-\bar{Y}$ line for majority spin and (b) electron density isosurfaces of the state on the midpoint of the $\bar{\Gamma}-\bar{Y}$ line, as is arrowed in (a).

middle point of the $\bar{\Gamma}-\bar{\mathrm{Y}}$ line. Isosurfaces of the lower one are almost the same. This isosurface map clearly indicates that this state is localized near the surface, and that the p_x orbital of an O atom, which extends in the x, namely, $[\bar{1}10]$ direction, plays a major role, and it bonds to d_{xy} orbitals of a surface Ni atom. We can recognize this tailed localization at the surface only in such a large-scaled slab as ours. However, we still have to verify that these surface states really exist even in a semi-infinite substrate. We consider that bulk which can be obtained in the limit of increasing the slab thickness, and evaluate the upper edges of those bands which correspond to the substrate bands of the slab. We find that these upper bulk-band edges are below the paired nearly degenerate bands. Through this analysis, we concluded that the surface states are really present in the semi-infinite substrate.

We made the same analysis of the O-derived bands around the upper edge of the substrate bands on the $\bar{\Gamma}-\bar{\mathrm{X}}$ line as well. We identified the surface states in which the p_y orbital of an O atom bonds to the d_{yz} orbitals of a surface Ni atom.

(2) π-band structure of finite graphene systems [5]

We examined the electronic structure of finite graphene systems for various shapes and areas. Each eigenstate is expressed in a form of a linear combination of p_z orbitals of C atoms extending in a plane-normal direction, and each component of its eigenvector represents the p_z orbital coefficient of the corresponding C atom.

As an example of the results, figure 3 displays the p_z-orbital coefficients in color scale of (a) the lowest-energy state (n=1), (b) the highest-occupied state (n=23) and (c) the highest energy state (N=46) for a parallelogram graphene with 46 C atoms. This parallelogram is quite special in having only zigzag edges.

As is shown in Fig. 3 (a), the p_z orbital coefficients in the lowest-energy state are coherent in sign. On the other hand, figure 3 (c) indicates that, in the highest-energy state, the coefficient alternates in sign along each hexagonal atom ring. In either of these states (a) and (c), the coefficient amplitude tends to decrease as we move from the center to the edge. These features are common to various shapes of finite graphene.

Figure 3 (b) shows that the highest occupied state has edge localization. Red and blue circles indicate atoms with large positive and low negative coefficients, respectively. These coefficients with large amplitudes alternate in sign along the edge line. The electron density distribution is localized around the acute-angle vertices, namely, at those edges farther away from the center. Generally, edge localization occurs at zigzag edges in specific states at or just near the Fermi level.

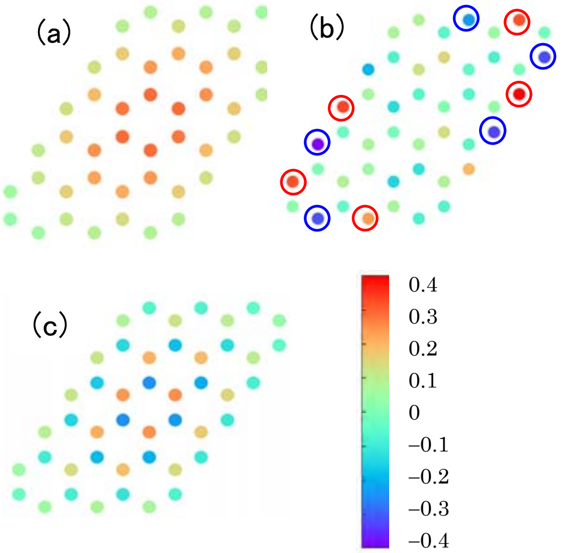

Fig. 3 p_z-orbital coefficients in color scale for a parallelogram graphene. (a) Lowest- energy state, (b) Highest-occupied state, (c) Highest-energy state.

References

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