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Generation of one-dimensional metal-atom nano-rods in insulating SAM films: first-principles study

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Abstract

SAM (self assembled monolayer) films are useful as ideal insulating layers in various organic devices. In this work, we show that new one-dimensional metal systems can be produced spontaneously in SAM films by inserting metal atoms into SAM, by the first-principles calculation. This occurs because inserted metal atoms have little interaction with SAM molecules and prefer to produce metal-atom nano-rod clusters. These systems are expected to work as electrical wires and metal-nano-wire memories embedded in insulators.

1. Introduction

Self assembled monolayer (SAM) films made of alkane molecules are ideal insulators owing to their large band gaps and good quality of crystal structures, thus being often employed as insulating layers in both organic and inorganic devices. When metal atoms are supplied on the SAM films, however, metal atoms easily penetrate into SAM films. In addition, such penetration is controlled by terminating the SAM-film surface by functional-group units [1,2].

In previous work, we showed that, once the metal atom is inserted in a SAM films, the metal atom easily diffuses between SAM molecules along the molecule-skeleton direction and collides with other metal atoms to produce metal-atom clusters [3]. This result indicates that supplied metal atoms gradually increase the size of clusters by the collision and eventually produce one-dimensional and long metal-atom nano-rods in SAM films as displayed in Fig. 1. Since the SAM films around such nano-rods are electrically insulating, such nano-rods might become the ideal one-dimensional metals. The generation of one-dimensional metallic systems provides not only the fundamental stage to examine the carrier transport in low-dimensional systems in scientific research but also the systems to produce electronic wirings and charge-storage memory devices in bottom-up nano-technology [4].

In this work, by using the first-principles calculations, we study how supplied metal atoms produce one-dimensional meta-atom nano-rods in SAM films and what electronic structure is realized by such nano-rods.

2. Calculation Model and Method

To study the formation of one-dimensional metal-atom rods, we adopt a (2×2) repeated unit cell including four $(CH_2)_{24}$ SAM molecules, as shown by solid squares in Fig. 1. Metal atoms are inserted in this cell to study the stable forms of metal atoms in SAM films and the generation processes of metal-atom rods. Au and Al atoms, which have large and small electro-negativities, respectively, are employed for metal atoms.

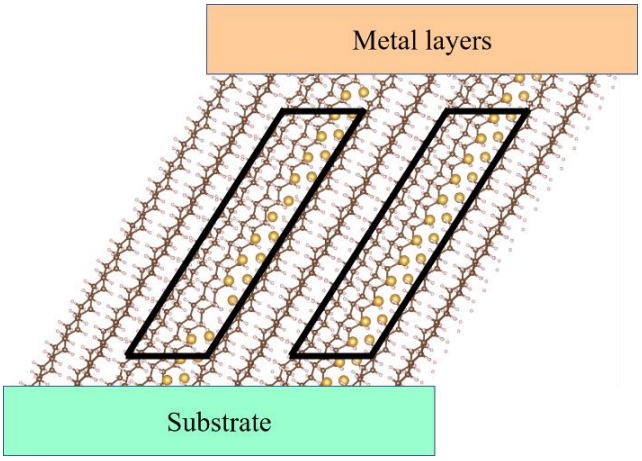

Fig.1 Schematic picture of metal-atom nano- rods in SAM film. Solid squares are unit cells adopted in the present calculations.

Atom positions and electronic structures of metal atoms in SAM films are calculated by the standard first-principles method in the density functional theory, using the VASP code. We adopt the PW91 exchange-correlation functional, the 400eV energy cutoff for the plane-wave expansion of wave functions, and $1 \times 1 \times 1$ k-point for the Brillouin-zone integration. Other calculation details are described in our previous publications [3,5].

3. Results and Discussions

Generation of metal-atom nano-rods in SAM

We first examine stable forms of metal nano-rods in SAM. Figures 2(a) and (b) show optimized structures of finite-length Au_6 and infinite-length Au rods in SAM. In both figures, Au rods have belt-like truss structures with the width made of two atom arrays. Moreover, we note that the SAM molecules receive the stress from the rods and are deformed around the dots.

Next, we consider how these nano-rods are generated. Left of Fig. 3(a) shows such processes, where a single metal atom (upper panel) or a pair of metal atoms (lower panel) diffuses to approach and combine with a metal cluster. Both these processes increase the length of metal-atom nano-rod

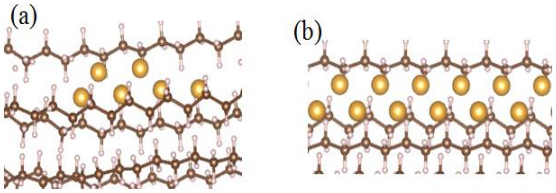

Fig.2 Atomic structures of (a) Au_6 and (b) infinite-length Au nano-rods in SAM films. Gold balls display Au atoms, while white and brown balls are H and C atoms, respectively.

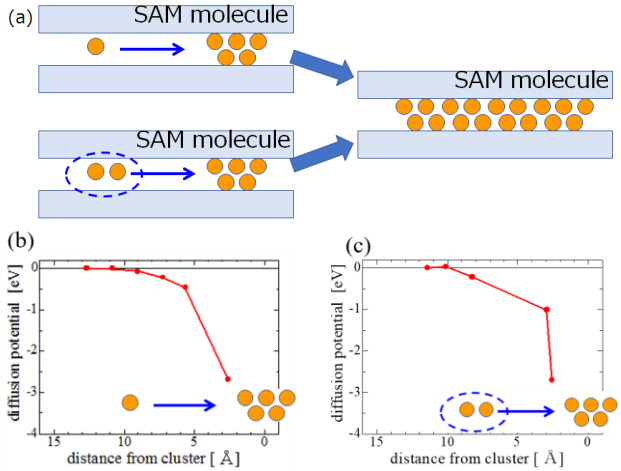

Fig.3 (a) Representative processes to generate metal-atom nano-rods in SAM films. Orange circles represent metal atoms. (b) and (c): Adiabatic potentials for Au atoms to combine with Au-atom clusters, as a function of Au-atom position near the clusters. (b) and (c) correspond to the processes shown in upper and lower left panels in (a).

and eventually generate long nano-rods as shown in the light of Fig. 3(a). Figures 3(b) and 3(c) show the adiabatic diffusion potentials of metal atoms corresponding to these approaching processes, respectively. Both figures clearly demonstrate that metal atoms prefer to combine with the adsorption energies around 3eV and proceed to generate long nano-rods. These figures also indicate that such nano-rods are stable against the desorption of metal atoms from the rods. By analyzing electronic structures, we found that such large adsorption energy originates from the metallic bonding between metal atoms.

The similar results are obtained for the case of Al. In this way, once sufficient amount of metal atoms are supplied, metal atoms easily combine with each other and simultaneously produce one-dimensional metal nano-rods in SAM films.

Electronic structures of metal-atom nano-rods in SAM

Then, we consider electronic structures of metal-atom nano-rods in SAM films. Figures 4(a) and 4(b) show band structures of SAM films with infinite-length Au and Al rods, respectively. Band structure of SAM film without rods is also shown in Fig. 4(c), for reference. In both Figs. 4(a) and

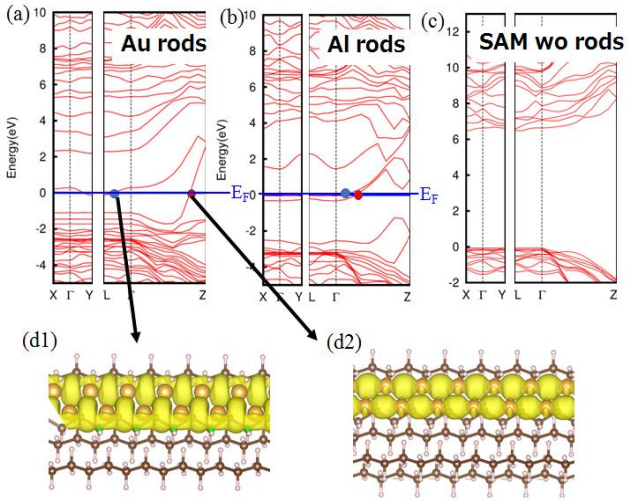

Fig.4 Band structures of (a) Au and (b) Al rods in SAM, and (c) SAM without rods. (d1) and (d2) show wave functions of Au rod located in the band gap of SAM. Gold ball indicate Au atoms, while white and brown balls are H and C atoms. Wave function is represented by a cloud.

4(b), there appear two metallic bands in the band gap of SAM film. These band have large dispersion along the rod direction, ΓZ, while have less dispersion perpendicular to such direction, which indicates one-dimensional metallic bands. The wave functions of these bands are shown in Figs. 4(d1) and 4(d2) in the case of Au rod, which indicates that these bands are made of Au-atom states.

Finally, we shortly comment on characters of metallic bands. By changing the period of metal-atom rods along the rod direction, we found that the Peiels transition does not occur in the present metal-atom-rod systems. This is because the position of metal atoms is restricted to follow the structure of SAM molecules having no skeletons with the super-periods. In addition, even when metal-atom vacancies are produced in metal-atom rods, metallic bands still exist, which indicates the insensibility of metallic bands to some disorders.

4. Conclusions

By the first-principles calculation, we showed that metal atoms in SAM films spontaneously produce metal-atom rods and generate ideal one-dimensional metallic bands. These rod systems are expected to work as electrical wires and metal-nano-wire memories in future nano-technology.

Acknowledgements

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