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First principles studies of adsorption of Pd, Ag, Pt, and Au on yttrium disilicide nanowires

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Abstract

Stability and electronic properties of pristine and metal covered cylindrical yttrium disilicide, YSi_2, nanowires were investigated through first principles calculations. The YSi_2 nanowire prefers Y-rich surface morphology and is attractive toward metal adsorbates such as silver, gold, palladium, and platinum. Strong charge polarization is found from adsorbate to wires, which reduces the work function and alters the chemical activity of the core-shell structures.

1. Introduction

Nanowires have attracted tremendous interest due to their peculiar one dimensional (1D) properties and potential applications in numerous modern technologies such as high-frequency nanomechanical resonators, spintronics, single nanowire logic devices, and bio-chemical sensor [1–3]. Uniform nanowires of hexagonal rare earth disilicides ($RESi_2$) can be fabricated on flat [4] or vicinal [5] Si(1 0 0) surfaces through self assembly [6–8]. $RESi_2$ are of special importance since they have low Schottky barriers with the Si substrates [9,10], and hence can be used as low resistance electrodes in nanodevices [11]. Furthermore, they may serve as templates for large scale fabrication of metal/$RESi_2$ core/shell nanocatalysts with high thermal stability against coalescence. When depositing Pt onto $ErSi_2$/Si(0 0 1) surfaces, selective aggregation of Pt atoms onto $ErSi_2$ nanowires versus the silicon substrate occurs after an annealing step at 550 °C [12]. Combined with reactive ion etching (RIE), this process produces uniform core-shell nanostructures with particle diameter (width) of less than 10 nm, a narrow size distribution $< \pm 1$ nm, and inter-particle spacing of ~10 nm [13]. The strong near field coupling between closely spaced metal nanostructures may also benefit optics and field enhanced sensing technologies. To further develop these promising nanostructures for practical applications, it is crucial to understand the surface morphology and electronic properties of pristine and metal-adsorbed $RESi_2$ nanowires. As demonstrated in many cases, density functional approaches are very powerful for such explorations. As far as we know, very few studies have been conducted for the atomic and electronic structures of $RESi_2$. To circumvent the technical difficulty in dealing with the strongly localized 4f states of rare earth elements, it is common to first study disilicide of yttrium, a trivalent element that resembles rare earths in most environments. For instance, Rogero et al. [14,15] identified that the atomic and electronic structures of YSi_2 monolayer on Si(1 1 1) are similar to those of rare-earth disilicide films, using low energy electron diffraction (LEED) and density functional calculations.

In this Letter, we investigate the structural and electronic properties of pristine and adsorbed YSi_2 nanowires in two possible geometries. It is found that the Y-rich geometry is energetically more stable and also more attractive toward metal adatoms such as Ag, Au, Pd, and Pt. Analyses in charge redistribution and density of states shed some light for the chemical properties of these nanowires,

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which may find important applications in various areas such as nanocatalysis.

2. Methodology and computational details

The calculations were performed in the framework of density functional theory using the Vienna *ab initio* simulation package (VASP) [16]. The exchange-correlation interaction among electrons was described by using the generalized-gradient approximation with the PW91 functional [17]. We used an energy cutoff of 245 eV for the plane wave basis expansion and the projector augmented wave (PAW) potentials for the ionic cores [18]. To mimic the single wire environment, the square supercell in the lateral plane is 22 Å in each dimension, with a separation of 10 Å from surface to surface between adjacent wires. The periodicity along the z-direction is 7.68 Å, two times of the length of the c-axis of the bulk YSi_2. We sampled the quasi one dimensional Brillouin zone with 9 k-points. The nanowires were relaxed with a criterion that force on each atom is smaller than 0.01 eV/Å.

3. Results and discussion

The pristine YSi_2 nanowires were created from its hexagonal AlB_2-type bulk along the (0001) axis with a cylindrical shape. We explored two types of cylindrical nanowires, terminated with either Si (denoted as zigzag wire) or Y (denoted as round wire), as shown in Fig. 1a and b. To characterize the stability, we define the formation energy as

$$E_{\text{form}} = [E_t - \sum_i N_i\mu_i]/\sum_i N_i \quad (1)$$

here E_t is the total energy of the YSi_2 nanowire, N_i are the numbers of Y or Si atoms the wire encompasses. The chemical potentials, μ_i, are determined from total energies of the bulk Y and Si. It was found that E_{form} of the round YSi_2 nanowire is 0.88 eV lower than that of the zigzag nanowire, primarily because of the saturation of Si dangling bonds. The large energy difference indicates high abundance of the round YSi_2 nanowires in fabrications. However, the zigzag YSi_2 might be stabilized by metal adsorbates and it is thus useful to discuss both geometries. Unlike pure Si nanowires [19], no complex surface reconstruction was found on the zigzag and round YSi_2 nanowires after the relaxation procedures. The Y–Si distances (d_{Y-Si}) in the interior region of the zigzag YSi_2 nanowire are very close to that in the bulk YSi_2 ($d_{Y-Si} = 3.057$ Å), whereas, they expand to 3.136 Å in the surface region. The Si–Si distances at the surface ($d_1 = 2.333$ Å and $d_2 = 2.377$ Å) are reduced by 2% compared to that in the core region. The $\angle\theta_{Si-Si-Si}$ also changes from 120° to 122.4° because of the dimerization of the surface Si atoms.

We next study the adsorption of Pd, Ag, Pt, and Au single atoms on YSi_2 nanowires. For the description of their site preference and stability, we defined the binding energy E_b,

$$E_b = [E_t(YSi_2) + NE_t(\text{adatom}) - E_t(\text{adsorbed } YSi_2)]/N \quad (2)$$

here E_t(adsorbed YSi_2) is the total energy of YSi_2 nanowire adsorbed by N adatoms, $E_t(YSi_2)$ and E_t(adatom) are the total energies of the pure YSi_2 nanowire and an isolated metal atom, respectively. As sketched in Fig. 2, we first determined the preferential adsorption site of a single adatom. For the zigzag YSi_2 nanowire, adatoms take the valley-bridge site, in the middle of Si furrow, as shown in Fig. 2a. By contrast, adatoms prefer the fourfold hollow site on the round YSi_2 nanowire and form a geometry as presented in Fig. 2f. Overall, E_b increases in the order of Ag, Au, Pd, and Pt, as listed in Tables 1 and 2. The large magnitude of E_b clearly indicates the activity of YSi_2 nanowires toward metallic atoms, in good accordance with results of our experimental observations. The other important finding is that binding energies of Pd and Pt on the round YSi_2 nanowire are much larger than their counterparts on the zigzag one. The same trend can be found for Ag and Au but the energy changes are less dramatic.

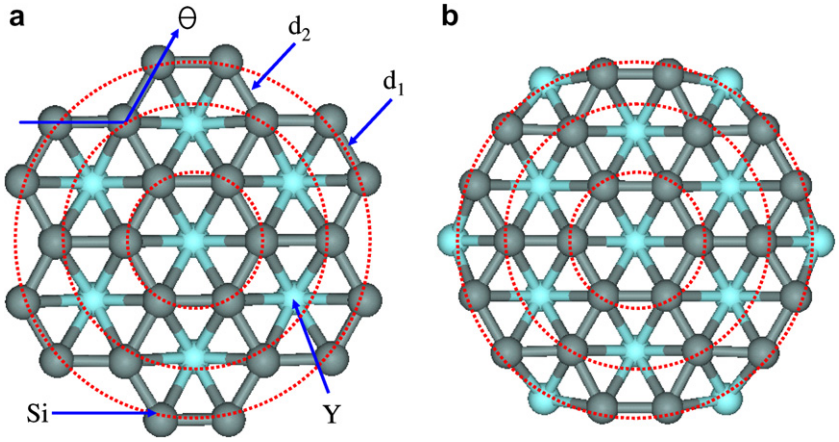

Fig. 1. Models of (a) zigzag and (b) round cylindrical YSi_2 nanowires for the present calculations. Concentric circles indicate the shell of Y and Si atoms.

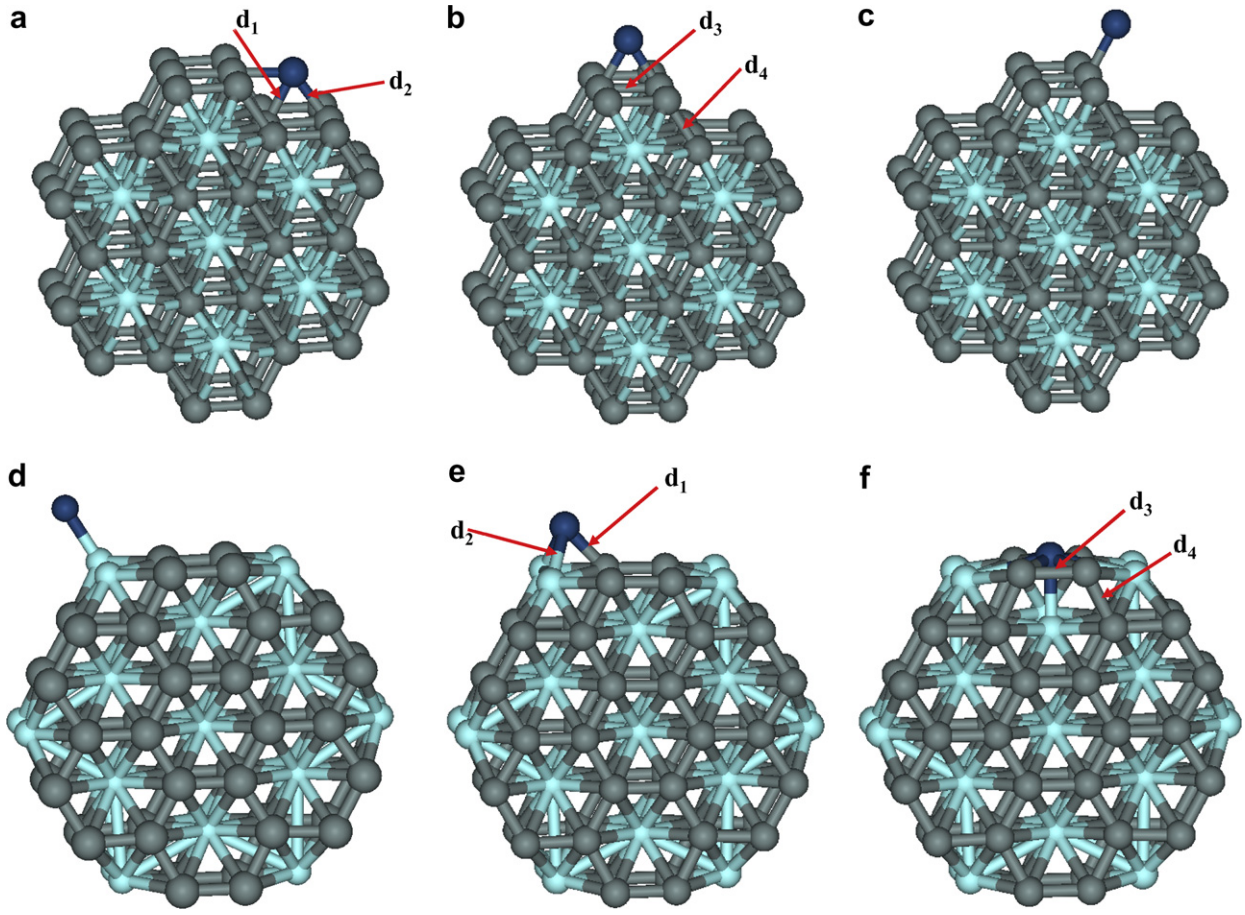

Fig. 2. Adsorption sites for a single metal adsorbate such as (a) valley-bridge, (b) bridge, and (c) top on the zigzag YSi_2 nanowire, and (d) Y-top, (e) threefold hollow, and (f) fourfold hollow on the round YSi_2 nanowire. The blue spheres are adatoms, the gray spheres are Si atoms, and the cyan spheres are Y atoms. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Bond lengths, bond angles, and binding energies for metal on the zigzag YSi_2 nanowire

Adsorbate	Adsorption site	d_1, d_2 (Å)	d_3, d_4 (Å)	$\angle\theta_{Si-m-Si}$ (°)	E_b (eV)
Pd	Top	2.28	2.40, 2.42	–	3.28
	Bridge	2.29	2.34, 2.38	59.2	3.68
	Valley-bridge	2.34, 2.38	2.33, 2.43	123.7	4.29
Ag	Top	2.38	2.30, 2.37	–	2.23
	Bridge	2.54	2.31, 2.37	54.2	2.21
	Valley-bridge	2.72, 2.55	2.33, 2.37	106.9	2.75
Pt	Top	2.36	2.34, 2.49	–	5.02
	Bridge	2.26	2.36, 2.38	58.6	4.65
	Valley-bridge	2.32, 2.35	2.33, 2.44	125.6	5.52
Au	Top	2.26	2.30, 2.38	–	3.08
	Bridge	2.66	2.34, 2.37	52.2	2.86
	Valley-bridge	2.56, 2.46	2.33, 2.38	113.2	3.48

Table 2
Bond lengths and binding energies for metal adsorbates on the round YSi_2 nanowire

Adsorbate	Adsorption site	d_1, d_2 (Å)	d_3, d_4 (Å)	E_b (eV)
Pd	Threefold	2.34, 2.85	2.40, 2.40	4.37
	Fourfold	2.45	2.48, 2.48	5.75
Ag	Threefold	2.53, 3.01	2.40, 2.42	2.02
	Y-top	3.40	2.39, 2.39	1.70
	Fourfold	2.48	2.47, 2.44	2.61
Pt	Threefold	2.33, 2.79	2.40, 2.40	6.44
	Fourfold	2.44	2.51, 2.46	7.50
Au	Threefold	2.45, 2.86	2.42, 2.41	3.09
	Y- top	2.94	2.40, 2.40	3.50
	Fourfold	2.46	2.48, 2.46	3.76

It is interesting to note that the nearest adsorbate-Si distances, d_1, are almost the same for the four adsorbates, despite the fact that their covalent radii are rather different. Also the adsorbates are almost coplanar with the surface Si atoms after the structural relaxation. This may have important consequence on the physical properties of metal/YSi2 nanowires toward catalysis, a subject of our further investigations for these systems. In order to appreciate the adsorbate/wire interaction, it is instructive to analyze the charge density redistribution, $\Delta\rho = \rho(\text{adatom}/YSi_2) -$

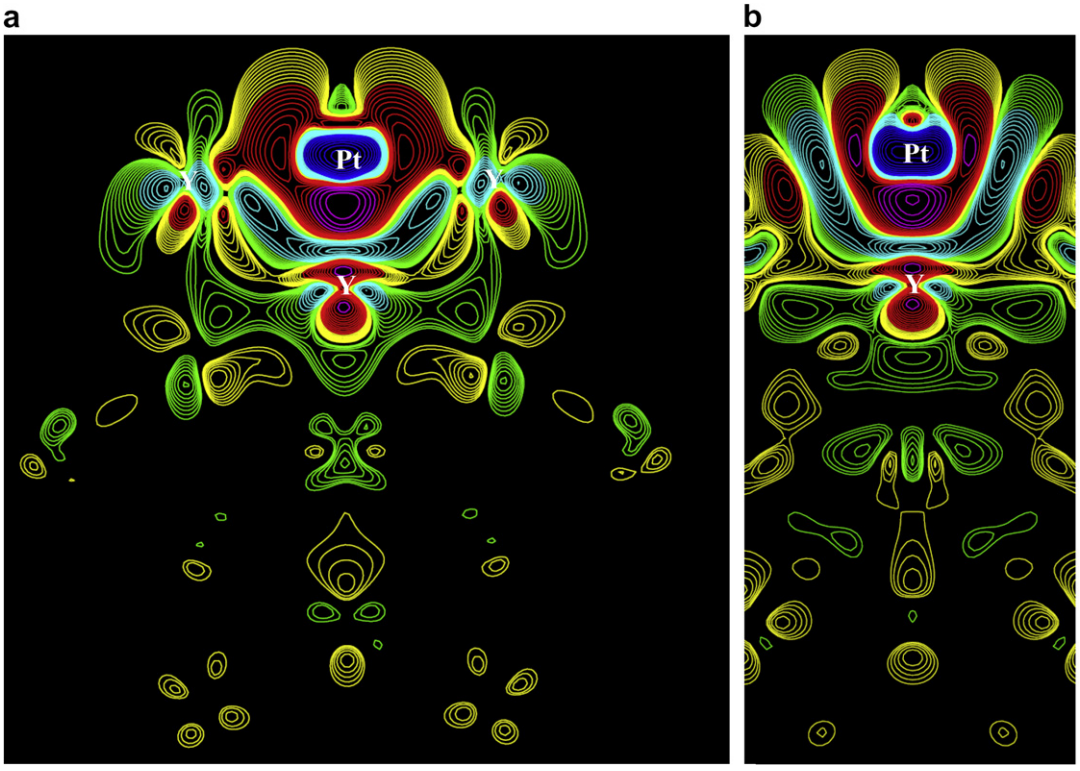

Fig. 3. The charge density difference of Pt on the fourfold hollow site of the round YSi_2 nanowire in (a) the (0001) plane and (b) the (11–20) plane. Yellow, red and pink (dark grey) lines are for charge accumulation whereas green, cyan and blue (light grey) lines are for charge depletion. Contours start from $\pm$ 0.005 e/au^3 and change successively by a factor of $10^{1/4}$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

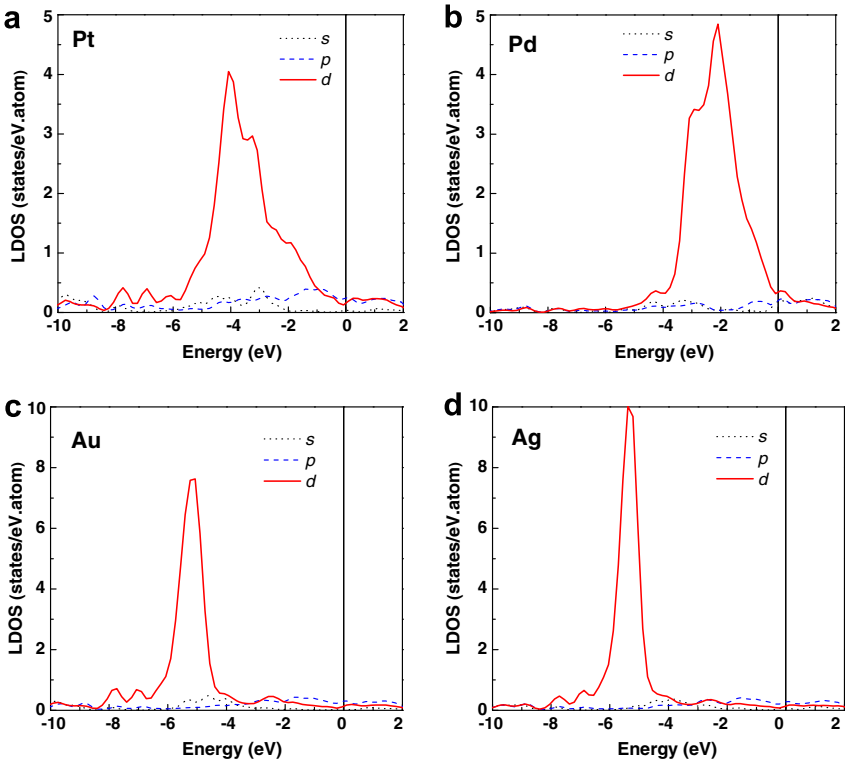

Fig. 4. Local density of states on (a) Pt, (b) Pd, (c) Au, and (d) Ag atoms adsorbed on the fourfold hollow site of the round YSi_2 nanowire. The Fermi level is set to zero energy.

$\rho(YSi_2) - \rho(\text{adatom})$; here we used charge densities of Ag ($4d^{10}5s^1$), Pt ($5d^96s^1$), Au ($5d^{10}6s^1$), and Pd ($4d^{10}$) atoms as the references. Corresponding to the largest adsorption energy, the charge redistribution induced by Pt is the most significant one among systems investigated. As shown in Fig. 3 for Pt on the round YSi_2 nanowire, the disturbance of adsorbate is limited within the upper half of the wire. Electrons deplete from both the adatom and substrate Y atoms and accumulate in the region between them. The charge polarization from adsorbates toward the substrate reduces the local work function on the nanowire [20,21]. It can be seen that Pt/substrate bonds have more covalent nature in Fig. 3.

Fig. 4 provides the local density of states (LDOS) of different adsorbates on the round YSi_2 nanowire. It is interesting to see that Pt and Pd d-band is rather broad for single adsorbates. This manifests the strong hybridization between the sp-states of Si and the d-states of Pt and Pd, in accordance to the charge density in Fig. 3. The d-bands of Pd and Pt extend to the unoccupied region and have meaningful amount of holes. Meanwhile, their d-band centers are close to the Fermi level. These results indicate that Pd and Pt atoms are chemically active on YSi_2 or $RESi_2$ nanowires, suitable for catalysis applications. In contrast, the d-bands of Au and Ag are far below the Fermi level and they are expected to be inert toward other molecules.

4. Conclusions

In summary, we have investigated stability and electronic properties of pristine and metal covered YSi_2 nanowires. The round YSi_2 nanowire is more preferential than the zigzag one. Results of adsorption energies also indicate that this geometry is also more attractive toward metal adsorbates such as Ag, Au, Pd, and Pt. Significant charge polarization is found from adsorbate to substrate, which alters the local chemical activity. In particular, the Pd and Pt adatoms are found to be active on YSi_2 nanowire, whereas, Ag and Au are apparently inert. More synergistic experimental and theoretical studies in the future may establish clear physics insights to guide the further development of these materials for practical exploitations.

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