

DFT study of the effect in surface energy of metallic overlayers in semiconductors

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Abstract

The surface energy of various systems: semiconductors (Ge and Si), metals (Ag and Pb) and metallic overlayers on semiconductors Ag/Ge and Pb/Si) have been calculated using a DFT approximation. The Pb(111) and Ag(111) adlayers on Si and Ge(111) surfaces had been modeled using the periodic supercell approach. Self-consistent field energy periodic calculations for bulk and surfaces of Ge, Si, Pb and Ag, with 12, 11, 10, 9, 8, 7 and 6 layers and $SC_{12-n}M_n$ (where SC is Ge or Si; M is Ag and Pb, respectively and n is the number of layers) metallic adlayers on semiconductor super-system slab models were calculated using plane wave density functional theory, in particular employing the Perdew Wang (PW91) functional. The metallic adlayers on semiconductors modify its surface energy and *vice versa*. The values for $SC_{12-n}M_n$ systems follow a sinusoidal trend in similar way to for semiconductors, but softer. The surface energy values lay in between those corresponding to semiconductors and metals. These results indicate that if the number of metallic overlayers on a semiconductor can be controlled then the surface energy can be addressed.

Keywords. Metallic overlayers, Pb/Ge, Ag/Si, DFT.

Resumen

Se calculó teóricamente la energía superficial de Ag, Pb, Ge y Si de los sistemas formados por capas metálicas (Ag y Pb) en los semiconductores (Ge y Si), respectivamente para formar los sistemas Ag/Ge y Pb/Si. Para ello, se utilizó el funcional Perdew Wang (PW91) dentro de una aproximación DFT. Para modelar el *bulk* y las superficies (111) de Ag, Pb, Ge y Si se utilizó el modelo periódico de *slab*. Los modelos de los semiconductores se construyeron con 12, 11, 10, 9, 8, 7 y 6 capas, los de metales con 1, 2, 3, 4, 5 y 6 capas y para estudiar las monocapas metálicas en los semiconductores se empleó un modelo de 12 capas en total: $SC_{12-n}M_n$ (donde SC es Ge o Si; M es Ag y Pb, respectivamente y n es el número de capas). Conforme a los resultados obtenidos, se concluyó que el metal modifica la energía superficial de los semiconductores, y éstos a su vez modifican la energía superficial del metal. Los valores de los sistemas $SC_{12-n}M_n$ oscilan en forma similar a la de los semiconductores, aunque con valores intermedios entre el metal y el semiconductor. Estos resultados indican que si el número de monocapas metálicas en un semiconductor se puede controlar, también se puede controlar la energía de superficie del sistema.

Palabras Clave. Monocapas metálicas, metal-semiconductor, Pb/Ge, Ag/Si, DFT

Introducción

The study of metallic self-assembled monolayers on various substrates such as metals, semiconductors or oxides has attracted much attention due to novel chemical and electronic phenomena and the possibilities for innovative applications [1], for instance, bimetallic catalysts with enhanced activity and selectivity [2, 4]. The dif-

ferences between thin film systems and the bulk metals have been attributed to ligand and structural effects. The ligand effect is due to the different electronic environment of the atoms, in a monometallic or bimetallic system, caused by the hetero - atom bonds. The ensemble effects include geometric modifications caused by the interactions of the parent metals, with different metal-metal bond lengths to the original bonds [1, 5, 6]. On

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the other hand, metallic films on semiconductors have received attention by their particular electronic and optical properties [7, 8]. In addition, due to their particular structural properties, metal-semiconductor systems are attractive materials for electronic devices.

The metallic overlayers have shown novel morphologies when grown on semiconductors substrates which cannot be classified in the traditional growth modes. Bauer proposed the actual thermodynamic criterion for classify thin film growth on a support [9], which he called Frank-van der Merwe (layer-by-layer growth), Volmer-Weber (island growth) and Stranski-Krastanov growth (layer + island growth).

Thin film growth is a complex process and depends on the amount of material adsorbed on a substrate. For instance, an analysis of STM (Scanning Tunneling Microscopy) and AES (Auger Electron Spectroscopy) measurements of Sn grown on Mn(110), before to complete a monolayer is formed, show tin is nucleated randomly and forms islands on the Mn substrate suggesting island type of growth; however on continuous deposition the growth mode switch to layer-by-layer growth (Frank-van der Merwe mode) for the first two layers [10]. Moreover, impurities can modify the growth behavior, by changing the arrangement of substrate atoms, mobility of deposited atoms or growth energetics, this process has been named 'surfacing mediated' growth [7].

Pb adlayers on Ge and Si substrates are model systems to probe a metal-semiconductor interface due to the inert nature of Pb and its insolubility in these substrates which produces a sharp interface [11, 13]. Several experimental and theoretical studies have been carried out to measure, for example, the conductance of Pb wires grown by self-assembly on Si(557) as a function of coverage and calculate the surface diffusion of metallic atoms [11, 15, 16].

The adsorption of Ag on Si had been extensively studied by experimental techniques [15, 16]. Mathew et al. [11] employing TEM (transmission electron microscopy) and RBS (Rutherford backscattering spectrometry) studied Ag growth on a hydrogen-passivated Si (100) surface. They concluded that under controlled experimental settings nanoscale Ag islands of a desired size form via surfactant action of Pb. A study using RHEED-TRAXS (reflection high-energy electron diffraction-total reflection angle X-ray spectroscopy) showed that Stranski-Krastanov growth of Ag crystals ensues above 2.47 monolayers on a Si (110) substrate [16]. Deng et al. [17] analyzed structural and morphological changes of Ag grown on Si(111) as a function of temperature and coverage using SGH (Second-harmonic generation) and proposed the existence of a critical size of Ag islands for the nucleation on Si(111). Tong et al. [18] measuring coverage arrived to a similar conclusion, employing STM (Scanning Tunneling Microscopy). Zhang et al. [19] proposed a model for metallic thin films deposited

on semiconductor substrates, and showed the existence of critical/magic thicknesses above which smooth growth takes place. By contrast, Basile et al. [20] did not observe magic thickness in this system using x-ray measurements and RHEED (Reflection - High - Energy - Electron - Diffraction) system.

X-ray studies of Pb overlayers on a Si(111) surface revealed an unusual growth behavior. On initial deposition, Pb islands of uniform height formed. These islands grew laterally as additional material was deposited. Once the surface was completely covered by a the Pb film the growth switched to layer-by-layer growth; this particular behavior was attributed to quantum effects [21]. Theoretical calculations on the adsorption of Pb atoms on a clean Si(001) surface showed that the growth of chains from the most stable monomer configuration proceeds via the formation of inter- and intra-row ad-dimers, and ad-trimers [22]. The surface morphologies and stability of ultra-thin Pb films with thicknesses of 2, 4 and 6 monolayers on a substrate of Si(111)- α - $\sqrt{3} \times \sqrt{3}$, using STM and TDARPS (Temperature-Dependent Angle Resolved Photoemission Spectroscopy); the authors conclude that the diffusion barrier in Si(111)- α - $\sqrt{3} \times \sqrt{3}$ structure is lower than in Pb/Si(111) - 7×7 ; and different critical thickness interface and charge transfer are different, under same conditions [23].

The goals of this study is to model theoretically Ag and Pb overlayers on Si and Ge substrates and calculate modifications of the surface energy of Ge and Si, provoked by the presence of Ag and Pb, respectively; and analyze the results with respect to experimental data.

Computational model

The Pb(111) and Ag(111) adlayers on Si and Ge(111) surfaces had been modeled using the periodic supercell approach. Although, the studied metals and semiconductors have different structures (fcc for metals and diamond for semiconductors), we have chosen the (111) surface orientation for both fcc and diamond structures due to their similar atomic arrangement.

In all calculations, the computed lattice constants were used, for Ag, Pb, Ge and Si are 4.16 Å, 5.0301 Å, 5.7785 Å, and 5.4904 Å respectively, which compare well with the experimental value, 4.0853 Å, 4.9508 Å, 5.6575 and 5.4309 Å [24]. Therefore, the atom-atom distance bond for Ge-Ge is 2.50 Å, for Ag-Ag is 2.94 Å, for Si-Si 2.35 Å and for Pb-Pb is 3.55 Å.

The Ge model contains 16 atoms for layer with 2×4 structure, because this structure was found experimentally; the Ag model has 15 atoms for layer with a (3×5) structure, because its size is similar to (2×4) structure of Ge. Si and Pb models are (4×3) cell with 24 atoms for layer and 12 atoms, respectively.

All studied systems were modeled using periodic slab models containing 12 atomic layers. For analyze the

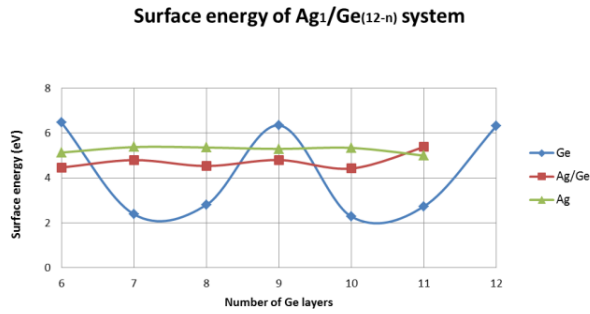


Figure 1: Surface energy of Ag/Ge surfaces, with respect to number of Ag adlayers. The energy is in eV.

effect of a metallic adlayer in the properties of the semiconductors, we started considering a supercell with 12 layers of Ge or Si, and the metal-semiconductor supercell was built substituting one-by-one layer for a metallic layer: $\text{Ge}_{12-n}\text{Ag}_n$ (where n is the number of metal layer) in example, 11 Ge layers and 1 Ag adlayer ($\text{Ge}_{11}\text{Ag}_1$), following until 6 Ge layers and 6 Ag layers (Ge_6Ag_6). The same procedure is followed to build the Pb/Si system. In this way, we will have models for study the effect of metal with 12 atoms per layer have been employed, this corresponds to a 4×3 supercell and is large enough to represent a variety of number of metallic layers on a enough amount of semiconductor layers. In all cases, the one upper layer of the semiconductor was allowed to relax completely during geometry optimization; and the metal atoms in the remaining layers were fixed at the bulk-like positions. Because of the use of a plane wave basis set, the slab model needs to be repeated in the direction perpendicular to the surface, the repeated slab models were separated by a vacuum width of 20 \AA guarantee no interaction between slabs consecutives in normal direction of the surface.

Computational details

Self - consistent field energy periodic calculations for bulk Ge, Si, Pb and Ag, with 12, 11, 10, 9, 8, 7 and 6 layers and $\text{SC}_{12-n}\text{M}_n$ (where SC is Ge or Si and M is Ag and Pb, respectively) metallic adlayer on semiconductor super-system slab models described in the previous sections were calculated using plane wave density functional theory [25, 26] as implemented in the VASP (Vienna Ab-initio Simulation Package) computational code [27]. The Perdew Wang (PW91) [28] functional was used within the Generalized Gradient Approximation (GGA) to describe non-local exchange and correlations effects. The Projected Augmented Wave (PAW) [29] method implemented by Kresse and Joubert [30] has been used to reproduce the effect of the core of the corresponding atoms in the electronic density of valence electrons. The Kohn-Sham one-electron wave functions were expanded in a basis of plane waves with kinetic energy below 240 eV. The Brillouin zone of the surface unit cell was described using a $3 \times 3 \times 1$ Monkhorst-Pack mesh [31]. The partial occupancies were set for each

| ML Ge | Ge | Ag/Ge | Ag | ML Ag |
|-------|------|-------------|------|-------|
| 11 | 6.31 | | | |
| 12 | 2.73 | 5.38 | 5.00 | 1 |
| 10 | 2.29 | 4.43 | 5.34 | 2 |
| 9 | 6.35 | 4.80 | 5.30 | 3 |
| 8 | 2.80 | 4.54 | 5.36 | 4 |
| 7 | 2.39 | 4.80 | 5.38 | 5 |
| 6 | 6.48 | 4.47 | 5.14 | 6 |

Table 1: Surface energy of Ge and Ag models with different number of layers and of Ag self-assembled monolayers on Ge models with respect to number of Ag monolayer

Bloch function obeying the order 2 Methfessel-Paxton scheme [32]. The calculations were carried out using a $k_{BT} = 0.2 \text{ eV}$ for metals and 0.05 for semiconductors, smearing of the electron density in the corresponding one electron wavefunctions, and upon convergence of the self-consistent field procedure the total energy was extrapolated to $k_{BT} = 0 \text{ eV}$. The RMM-DIIS (residual minimization method direct inversion in the iterative subspace) was employed as electronic minimization algorithm. The atomic positions were optimized using the quasi-Newton algorithm. All calculations carried out in this work are of the closed shell type.

Results

The surface energy of different systems: semiconductors (Ge and Si), metals (Ag and Pb) and metallic overlayers on semiconductors (Ag/Ge and Pb/Si) had been calculated using a DFT approximation for study effect of the metal in the properties of the semiconductor.

First, the work function was calculated for all pure materials, to validate the theoretical data with experimental ones. These values obtained by means of experiments for Si, Ag and Pb are 4.7, 4.72 and 4.25 eV, respectively and the calculated data in this work were: 5.21, 4.70, and 4.36 eV. The calculated value for Ge is very different to experimental one and we are re-calculating it. The difference between both data is not significant; consequently it is possible to consider the theoretical data as suitable.

The results of surface energy of Ge are shown in table 1 and figure 1, the graph with respect to the number of monolayers follows a sinusoidal trend each multiples of 3, it can be understood because both semiconductors, Ge and Si have a diamond structure and the (111) surface is formed periodically by blocks with two bilayers. The atoms of the upmost layer of each bilayer are the most stable, because the surface energy is the highest. On the other hand, the surface energy of Ag is very similar in the models with different number of monolayers; but when Ag monolayers are assembled to Ge, the trend follows a similar behavior of Ge but softer. The difference of surface energy in the block of bilayers is wide, from 6.3 to 2.3 eV. The surface energy of the models of Ag is around 5.3 eV, this value is inside the range of values for Ge. Comprehensibly, the range of surface energy of all adlayers-Ge systems is intermediate between

| ML Si | Si | Pb/Si | Pb | ML Pb |
|-------|-------|-------------|------|-------|
| 12 | 13.67 | | | |
| 11 | 10.52 | 4.33 | 2.71 | 1 |
| 10 | 5.25 | 4.14 | 3.50 | 2 |
| 9 | 13.67 | 3.27 | 3.37 | 3 |
| 8 | 6.53 | 3.99 | 3.54 | 4 |
| 7 | 5.25 | 4.27 | 3.53 | 5 |
| 6 | 13.65 | 3.59 | 3.20 | 6 |

Table 2: Surface energy of Si and Pb models with different number of layers and of Pb self-assembled monolayers on Si models with respect to number of Pb monolayer

Surface energy of $Pb_n/Si_{(12-n)}$ system

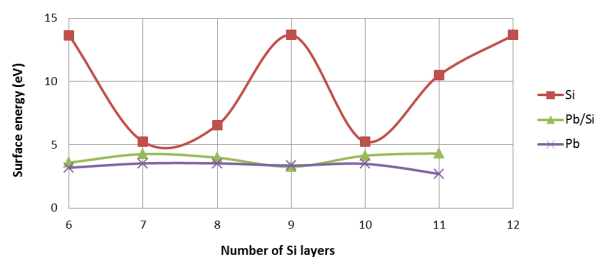


Figure 2: Surface energy of Pb/Si surfaces, with respect to number of Pb adlayers. The energy is in eV.

both materials, Ge and Ag; but the data are closer to Ag and the highest value for Ge.

The surface energy values of Si have an oscillant behavior in similar way to Ge, as is shown in table 2 and figure 2. However, the values are higher than of Ge, and the range is between 13.6 and 5.3 eV. While the values of surface energy for Pb models with 2 or 6 layers are almost 3.4 eV, out of range of values of Si. The trend of values of surface energy of $Pb_{12-n}-Si_n$ systems is sinusoidal, between 3.3 and 4.3 eV, this range is closer to corresponding to Pb and the lowest value of Si.

Conclusions

The surface energy of a diamond structure with (111) orientation follows a sinusoidal behavior, in multiples of 3, because the structure is on series of bilayers, and each 3 layers, the atoms are more stable. The metallic adlayers on semiconductors modifies surface energy of the semiconductors and vice versa. The values for the $SC_{12-n}M_n$ systems follow a trend similar to for semiconductors, but softer and the values are intermediate between both, the surface energy of the semiconductor and the metal. These results indicate that if the number of metallic overlayers on a semiconductor can be controlled then the surface energy can be addressed. So, if it is possible to control the surface energy, probably others properties can be controlled, this fact opens some interesting possibilities of manufacturing materials with special properties, modeled first with theoretical methods and after to probe the conclusions with experimental procedures.

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