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Ge deposition on Ag surfaces: Dependence of the adsorption characteristics on the surface orientation

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Using the *ab initio* full-potential linear muffin-tin orbital approach we have studied the characteristics of Ge adsorption on three different Ag surfaces. We have analyzed the surface-orientation-dependent characteristics of the Ge adsorption, focusing our attention on comparison between adatom and substitutional adsorption. We find that whereas on the (111) surface substitutional adsorption is preferential, on the (100) and (110) ones the two adsorption modes have similar energetics. Analysis of the adsorption-induced modifications of the electronic structure of both the substrate and the adsorbate supports the thesis that at small coverage, Ge deposition on the Ag surfaces is to a large extent determined by laws characteristic for metal on metal adsorption.

I. INTRODUCTION

Due to their direct technological applications and to a wide range of very fundamental questions that they evoke, the properties of metal-semiconductor interfaces are of significant interest, and studies have focused principally on the atomic-level description of the interfacial chemistry, and on a detailed characterization of the interfacial electronic structure.[1] Reflecting the historical evolution of metal/semiconductor devices, until recently, most of the studies have been performed by depositing metal films on semiconductor surfaces (M/S),[2–8] and it is only in recent years that a growing interest in semiconductors deposited on metal surfaces (S/M) has been noticed, and the first results concerning this situation have appeared.[9–11] In fact, in the early growth stage, the properties of the S/M and M/S systems are not necessarily symmetrical, and the evolution of respective metallic and semiconducting properties under the mutual influence of the two components becomes thus of particular interest. In this context, on a more applied level, the properties of the (potentially) self-assembling semiconductor nanoparticles on a metal support are likely to draw a significant industrial interest.

Experimentally, S/M systems can be obtained through two different procedures, either from growth at sufficiently low temperature (S/M), or by segregation of the semiconductor species at the surface of a dilute alloy M(S). Among the fundamental questions which are then raised, a main one concerns the evolution of the bonding character around the dilute (S) atoms as a function of coverage or concentration. Indeed, should there exist a critical value below which the adsorbed (segregated) film should no longer be semiconductor but instead metallic, or (more interestingly) something in between? In that case, the competition between the tendencies to form close-packed (metallic character) or orientational (covalent character) structures should lead to original geometrical and/or chemical rearrangements around the deposited (segregated) atoms, implying new trends for the evolution with substrate orientation of the adsorption characteristics and of the incorporation or, conversely, segregation tendencies. More generally, one can wonder to what extent the energetic forces which are known to drive the behavior of surfaces for dilute bimetallic systems [M/M deposit or M(M) alloys[12]] can still be used for surfaces of dilute metal/semiconductor ones [S/M deposit or M(S) dilute alloy]. Our aim here is to propose some possible answers to such questions, in the particular case of the Ge/Ag system for which very recent experiments have indeed shown a strong dependence of the adsorption characteristics on the surface orientation, and a relatively complex early atomic structure of the deposit which does not reflect directly either semiconductor or metal-like adsorption characteristics.[13,14] In this framework, the present *ab initio* study follows the former one,[15] in which we analyzed the modifications of a preferential adsorption site with the growing Ge coverage for a (100) Ag substrate, without considering either the possibility of incorporation of Ge adatoms into the Ag surface, or the possible dependence of the adsorption characteristics on the surface orientation. However, although the incorporation of Ge may seem contradictory with the instability of ordered AgGe alloys, it has been experimentally observed for Ge deposition on the Ag(111) surface and it may also reflect the aspects of particular surface controlled adsorption energetics, which has already been reported for several binary alloys.[16]

In the present paper, on the basis of the numerical results for Ge deposition on the Ag (111), (100), and (110) surfaces, we discuss the microscopic effects in terms of simple chemical concepts based on the atomic orbitals involved in the Ge-surface bonding, focusing our attention on the relation between the calculated electronic structure and the adsorption energetics. In particular, since when deposited on the surface, the Ge adatoms have the number of nearest neighbors close to their bulk Ge environment and when incorporated into an Ag surface they have the coordination typical for metallic close-packed systems, the analysis of the relative stability of these two adsorption modes helps us to propose a relatively general conclusion on the character of Ge superficial impurities, which can also furnish experimentalists with a guideline to the analysis of their findings.

The paper is organized as follows: In Sec. II we briefly describe the computational settings, in Secs. III and IV we

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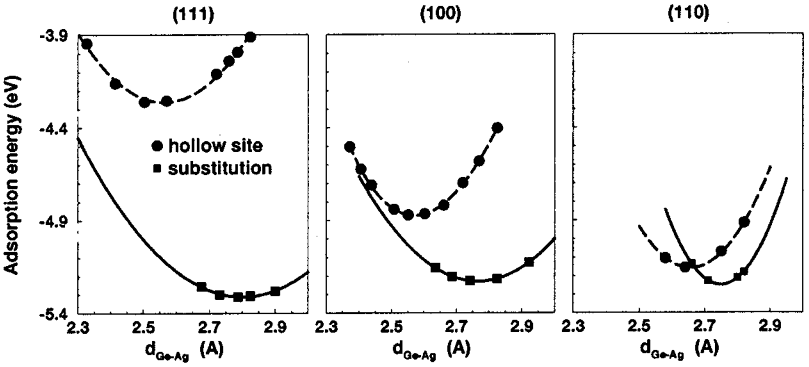

FIG. 1. Adsorption energy as a function of Ge-Ag nearest-neighbor distance for adsorption in the surface hollow site and for substitution in the first surface layer on the Ag (111), (100), and (110) surfaces.

resume the numerical results, respectively, on the adsorption energetics and on the adsorption-induced modifications of the electronic structure. We conclude in Sec. V.

II. COMPUTATIONAL DETAILS

The electronic band structure calculations were performed within the density-functional theory[17] framework, in the local-density approximation (LDA).[18,19] The Kohn-Sham equations were solved using the all-electron, full-potential linear muffin-tin orbitals (FP-LMTO) method.[20,21] Within the FP-LMTO approach the space is divided into nonoverlapping spheres centered on the atomic sites. The basis set consists of atom-centered Hankel envelope functions which are augmented inside the atomic spheres by means of numerical solutions of the scalar-relativistic Dirac equation. We have used three s, three p, and three d partial waves with kinetic energies of -0.7, -1.0, and -2.3 Ry, thus, 27 functions per sphere. Valence states are Ge($4s$ $4p$ $4d$) and Ag($5s$ $5p$ $4d$). The ''two-panel'' technique was used to include the $3p$ $3d$ electrons of germanium and the $4p$ semicore electrons of silver as full band states. In order to eliminate any possible errors due to changes of the basis set, atomic muffin-tin radii were fixed to 2.35 a.u. for Ag and 2.00 a.u. for Ge for all the calculations presented in this paper. We have verified that using a different set of muffin-tin radii leads to only small differences in the adsorption energies and in the equilibrium geometries. In any case, it does not modify the calculated trends. Details on the calculated bulk and surface equilibrium properties, together with the results of test calculations, are given in Ref. 15.

In order to obtain an accurate representation of the exponentially decaying density outside the surface, in slab calculations it is often necessary to cover the surface with one or several layers of empty spheres. In the present calculations the adsorbed Ge atoms were covered with a single layer of empty spheres. The empty-sphere angular-momentum cutoff for charge density and for the augmentation of the wave function was fixed to 6 and 4, respectively. The **k**-point summation was done on a uniform mesh in the irreducible wedge of the Brillouin zone and converged to within 10 meV/atom for 225 **k** points in the Brillouin zone, with a Gaussian broadening of 20 mRy.

For the three surfaces considered in the present study we have used the (2×2) surface unit cells. With this choice of the supercell the minimal distance between Ge adatoms is equal to 5.65 Å. In order to assure a satisfactory convergence of the clean surface properties we have used slabs of, respectively, 5, 5, and 7 layers for the (111), (100), and (110) faces.[22]

In all calculations only the vertical positions of adsorbed Ge atoms were optimized. On one hand, for a clean metal surface, it is known that the modification of the surface energy due to the surface relaxation is small and that the interatomic distances change by only a few percent.[23] On the other hand, in order to estimate the contribution to the adsorption energy due to the substrate relaxation we have tested the adsorption and substitution of an isolated Ge atom on the Ag (111) surface, optimizing simultaneously the vertical positions of both adsorbate and substrate atoms. This procedure resulted in an additional change of Ge-Ag distance by less then 2%, and induced only a 1% increase of the adsorption energy. In principle, the horizontal displacements of substrate atoms and the relaxation of deeper layers should be taken into account. One can also expect a change of magnitude of relaxations with the surface orientation. However, on the basis of performed tests we estimate that the relaxation of substrate will not modify the trends in adsorption characteristics discussed in the paper, and that its contribution is likely to be less important than the error introduced by the LDA.

III. ADSORPTION ENERGETICS

In this section we present the results on the adsorption energetics of Ge on the three Ag surfaces. Two adsorption modes are taken into account: adatom adsorption on the clean Ag surface, and substitutional adsorption in the surface layer. For the adatom adsorption, following the conclusion of Ref. 15, we have considered only the energetically most favorable, most coordinated, hollow surface site.

Adsorption energy of an adatom on a surface can be evaluated as $E_{ads}=E^{Ge/Ag}_{slab}-E^{Ag}_{slab}-E^{Ge}_{atom}$, $E^{Ge/Ag_{slab}}$, $E^{Ag_{slab}}$, and E^{Ge}_{atom} being the total energies of the adsorbate-covered Ag slab, of the clean Ag slab, and of the free Ge atom, respectively. In the case of substitutional adsorption, a somewhat different definition has to be used: $E_{ads}=E^{Ge/Ag_{slab}}-E^{Ag_{slab}}-E^{Ge}_{atom}+E^{Ag}_{bulk}$, $E^{Ge/Ag_{slab}}$, and E^{Ag}_{bulk} being the total energies of the Ag slab including the Ge substituted atom, and of the Ag atom in its own bulk, respectively. The microscopic process consists thus of a replacement of a surface Ag atom by a free Ge one, the Ag atom being reintegrated into bulk Ag.

In Fig. 1 we display the calculated dependence of the adsorption energy E_{ads} on the distance between deposited Ge and its nearest Ag neighbors. It can be seen that for the substitutional adsorption mode, the calculated adsorption energy changes little as a function of the surface orientation. We find -5.3, -5.2, and -5.2 eV, respectively, for the (111), (100), and (110) surfaces. On the other hand, adsorption energy calculated for the surface hollow sites shows an important increase along the series, passing from -4.3 eV for the (111) face to -4.9 eV for the (100), and to -5.2 eV for the (110) one.

This energetical tendency is consistent with the evolution of the Ge-Ag nearest-neighbor distances d_{Ge-Ag}. For the substitutional sites of the three surfaces d_{Ge-Ag} is equal to 2.8, 2.8, and 2.7 Å, whereas for the adatom adsorption it changes from 2.5 Å for the (111) surface to 2.6 Å for the (100), and to 2.7 Å for the (110) one. Both energetic and geometric trends can be directly related to changes of coordination (Z) of the adsorption site: 9, 8, and 7 for substitution, and 3, 4, and 5 for the adatom adsorption, respectively, on the (111), (100), and (110) surfaces, showing a clear preference of the Ge impurity to maximize the number of its neighbors.

Although one needs to keep in mind that the reference energetics for adatom adsorption and for substitution are not fully equivalent, so that any direct comparison of adsorption energies may be somewhat misleading (especially when taking into account the overestimation of Ag cohesion energy by the LDA), from the present results it is clear that the substitutional adsorption is largely favored on the (111) surface, whereas on the (100), and especially on the (110) one, the two adsorption modes are competitive. This remains in perfect agreement with the experimental findings.[13,14]

IV. ELECTRONIC STRUCTURE

In this section we present the results concerning the adsorption-induced modifications of the electronic structure of both substrate and adsorbate, relating them to the surface orientation and adsorption mode. In order to simplify the presentation we proceed in two steps. First, for the Ag (111) surface we compare the details of the electronic structure for the substitutional and the adatom adsorption modes. On this basis we then present schematically the evolution of the electronic structure characteristics as a function of the surface orientation.

In Fig. 2 we show the local (projected on the atomic spheres) densities of states (LDOS) obtained for the two different adsorption modes of Ge on the clean Ag (111) surface. Since the adsorption-induced modifications of the substrate are principally limited to the first neighbors of the adsorption site only surface Ag sites are shown in the figure. A bulk Ag site is plotted as a reference. The energy scales are aligned as to superpose the corresponding Fermi levels.

LDOS of bulk Ag is dominated by the $4d$ band centered at about 4.36 eV below the Fermi level. At a clean Ag (111) surface this band is shifted by 0.28 eV towards higher energies. The $5s$ and $5p$ bands hybridize with the $4d$ one and give, both in the bulk and at the clean surface, the dominant contribution around the Fermi level. A free Ge atom is characterized by the $4s$ and $4p$ Dirac-like peaks separated by about 7.7 eV. The Fermi level intersects the latter one, giving the nonmagnetic atomic ground state $4s^2 4p^2$.

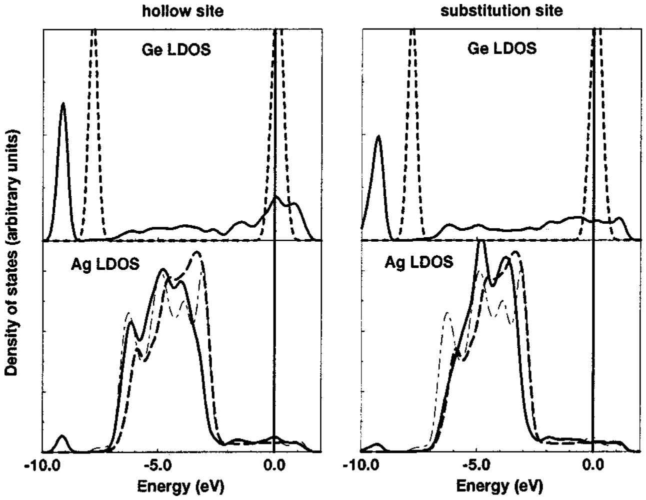

FIG. 2. Local DOS for a single Ge adatom deposited in the hollow (left column) and substitutional (right column) adsorption sites of the Ag (111) surface. Both Ge projected (upper panel) and surface Ag projected (lower panel) LDOS are plotted. Dashed lines represent the LDOS of a free Ge atom (upper panel), and of a clean surface Ag atom (lower panel). Dash-dotted lines (lower panel) correspond to LDOS of a bulk Ag atom. Systematically a Gaussian broadening of 20 mRy is used.

Upon adsorption, Ge p states hybridize with the substrate band, giving for both considered adsorption modes a clear contribution in the Ag $4d$ band energy region, and resulting in its downward shift with respect to the clean Ag surface. At the same time, due to the interaction with the substrate, the Ge s peak is significantly damped and shifted downwards on the energy scale. The amplitude of both these modifications strongly depends on the adsorption mode. As far as the modification of the Ge LDOS is concerned one can clearly see that the $3s$ peak undergoes a smaller downward shift and a smaller reduction of its intensity when Ge is adsorbed in the surface hollow site. Similarly, hybridization of the Ge $3p$ states with the metal band is weaker in this case. Both these effects can be directly related to the increase of the number of first neighbors of the adsorption site: 3 for the hollow site and 9 for the substitutional site. Conversely, when modifications of the Ag LDOS are concerned, it is for adsorption in the hollow site where the downward shift of the Ag $4d$ band (with respect to the clean Ag surface) is more pronounced. Two principal effects are at the origin of this difference. On the one hand, when Ge is adsorbed in the surface hollow site, the surface Ag atoms gain an additional neighbor, whereas there is no change in their coordination during the substitutional adsorption. On the other hand, as already noticed for adsorption of Ge on the Ag (100) surface,[15] the strength of the Ag-Ge bonds depends on their number. Since in the case of adsorption in the hollow site the number of created Ge-Ag bonds is smaller, the created bonds are stronger. Both these effects are consistent with a more pronounced downward shift of the Ag $4d$ for Ge adsorption in the surface hollow site.

The adsorption-induced modifications of the electronic structure can be thus related to the coordination of the

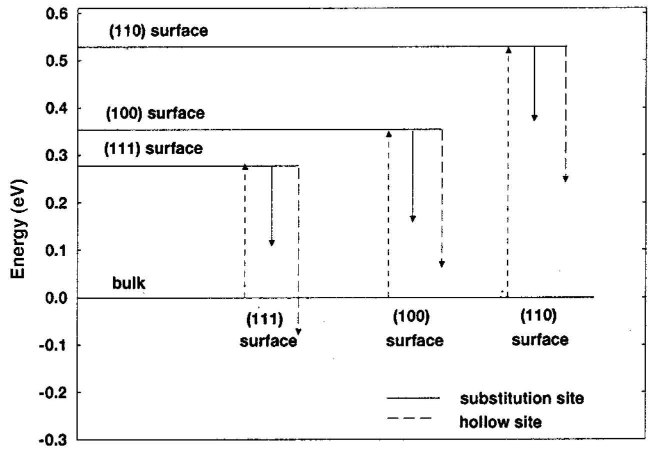

FIG. 3. Evolution of the first moment of the surface Ag 4d band calculated for different adsorption geometries of Ge on Ag (111), (100), and (110) surfaces.

adsorbed/substituted Ge atom and to the changes of coordination of the neighboring surface Ag site. Deduced weakening of the Ge-Ag bond strength as a function of the increasing number of created bonds is fully consistent with the energetic and structural tendencies reported in the preceding section.

Since we have shown that the adsorption-induced modification of the Ge and Ag LDOS are closely related and that they can be schematically described by changes of the position of the center of gravity of the Ag 4d band (μ_1), in the following we use the evolution of μ_1 to present schematically the effect of surface orientation on the characteristics of the surface electronic structure. Figure 3 displays the values of μ_1 calculated for both adsorption modes on the three surfaces considered. Values of μ_1 obtained for bulk Ag and for the three clean Ag surfaces are added as a reference.

As far as the μ_1 of the clean Ag surfaces is concerned, in all three cases we find a shift towards higher energies with respect to the bulk. Its enhancement for the more open surfaces [we find $\Delta\mu_1$ of 0.28, 0.36, and 0.53 eV, respectively, for (111), (100), and (110) surfaces], follows the well established general tendency reported both experimentally and theoretically for transition-metal surfaces.[24]

In all considered cases, adsorption of Ge induces a downward shift of μ_1 with respect to its value on the clean surface. For adsorption in the hollow site, this adsorption-induced downward shift is relatively well pronounced (we find $\Delta\mu_1$ of -0.35, -0.28, and -0.29 eV for the three orientations), and shows a progressive decrease on the more open surfaces. For adsorption in the substitutional site, the adsorption-induced downward shift of μ_1 is smaller (we find $\Delta\mu_1$ of -0.17, -0.20, and -0.15 eV), and its evolution along the series is less pronounced. Two principal factors can be related to the character of the calculated evolution of μ_1. As already pointed out, the strength of Ge-Ag bond (and thus the amplitude of $\Delta\mu_1$) decreases as a function of the number of created bonds. Since this many-body character of Ge-Ag interaction tends to saturate for higher coordinations, $\Delta\mu_1$ is similar for the three substitutional sites considered. Additionally, since the substitutional Ge atoms interact with both surface (S) and subsurface (SS) Ag atoms (of practically bulk μ) we expect a further attenuation of $\Delta\mu_1$ for the substitutional adsorption.

V. DISCUSSION

Results on both energetic and electronic characteristics reported in the previous sections suggest that the principal factor responsible for the properties of isolated Ge impurities on Ag substrate is the coordination of the adsorption site Z. In order to further explore this relation we reconsider the adsorption energetics of Ge and the Ag surfaces directly as a function of Z. Since the hollow sites of the three studied surfaces correspond to Z ranging from 3 for the (111) surface to 5 for the (110) one, and the substitutional sites correspond to Z ranging from 9 for the (111) surface to 7 for the (110) one, for the sake of the present discussion we consider also the results obtained for the two less favorable adsorption geometries of Ge on the Ag (100) surface, namely, the adsorption on top of a surface Ag ($Z=1$) and the on-bridge adsorption ($Z=2$).[15] On the other hand, we also take into account an incorporation of a Ge atom into the bulk Ag ($Z=12$) covering in this way, in a relatively uniform fashion, the coordination numbers ranging from 1 to 12.

In Fig. 4 we display the calculated dependence of the adsorption energy and of the Ge-Ag nearest-neighbor distance on the coordination of the adsorption site Z. In both cases we find a monotonous, nonlinear evolution, coherent with the weakening of the Ge-Ag interaction with the increasing Z. Resulting many-body character of the effective interaction energy is typical for transition metals, and can been explained on the basis of a simple tight-binding model.[25]

The incorporation energy calculated for $Z=12$, however, clearly does not follow the monotonous evolution. This shows that Z on its own is not an entirely sufficient parameter, and that the details of the local environment can influence the energetics. In the present case, the difference between the substitution energy in the surface layer and in the

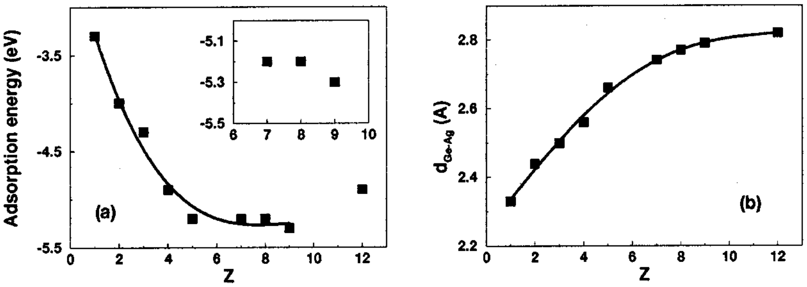

FIG. 4. Calculated evolution of the adsorption energy (a), and of the Ag-Ge nearest-neighbor distance (b), as a function of the coordination number of the adsorption site Z. The inset represents the adsorption energies for $Z=7$, 8, and 9, used for evaluation of the segregation energies for the three surfaces.

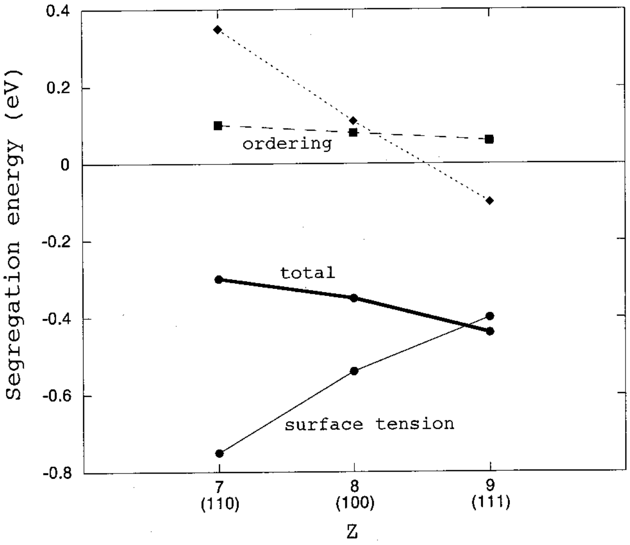

FIG. 5. Evolution of the segregation energy of Ge at Ag surfaces E_{seg} (eV) as a function of the coordination number Z: total energy (thick full line) and partial contributions due to the difference of surface tensions (thin full line), the ordering term (dashed line), and the *forgotten* ones (dotted line).

bulk, corresponds to the segregation energy of Ge in Ag. For the free surfaces considered our results indicate an energetical preference of Ge to segregate to the surface, in perfect agreement with the experimental findings for both Ag (111) and (100) surfaces,[13,14] reflecting a considerable difference of surface energies of Ge and Ag. Furthermore, the segregation energies calculated for the (111), (100), and (110) surfaces, and equal to -0.44, -0.35, and -0.30 eV, respectively, show a clear reinforcement of segregation on more compact surfaces (see Fig. 5). Note that these values have been obtained without taking into account surface relaxations since, as stated above, we have checked in simple cases that they only lead to weak modifications (1%) of the energies involved. Such an anisotropy can be considered as unusual, since for most of metallic binary alloys, segregation is stronger on more open surfaces. Actually it has been shown in that case that the total segregation energy could be decomposed into three contributions: the difference in surface energies between both components ($\Delta h_0^{\mathrm{eff}}$), the alloying term (V) which gives the tendency of the system to phase separate or order, and a term ($\Delta H_0^{\mathrm{size}}$) accounting for the size mismatch between the elements:[12]

$$E_{seg}=\Delta h_0^{\mathrm{eff}}+VZ'+\Delta H_0^{\mathrm{size}},$$

where Z′ is the number of broken bonds. In general, the first term ($\Delta h_0^{\mathrm{eff}}$) is the driving one, which leads to the usual anisotropy since the surface energy increases with the number of broken bonds. One could then suspect that the present reversal is linked to a possible peculiar behavior of surface energy for a Ge atom when constrained to the fcc lattice of Ag with the interatomic distance of the latter. This is not the case, as can be seen in Fig. 5, where the surface energy of fcc dilated Ge follows the usual trend [0.20, 0.24, and 0.37 eV, respectively, for the (111), (100), and (110) faces]. An alternative explanation for this singular anisotropy could then be the behavior of the alloying term $Z'V$. V can be calculated from bringing two isolated impurities into first neighbor positions, which leads to a positive value of 0.02 eV, i.e., a tendency to ordering. This is consistent with the experimental value of the mixing energy[26] which indicates that, despite the existence of a miscibility gap in the quasiwhole concentration range, a slight ordering tendency is found for low Ge concentration. This ordering term gives a tendency to segregation of the majority element (here Ag), which increases with the number of broken bonds, and therefore would compete with the surface energy term by decreasing Ge segregation, the most as the face is more open. Unfortunately, as can be seen in Fig. 5, this anisotropy is too weak to reverse the one due to surface energies. The last argument is then to invoke the size effect, which indeed should favor segregation of the biggest atom (here Ag) with the same trend as the alloying term. But this is in general true only when the largest atom is the minority one, which is not the case here. The question then remains open, and there still remains a ‘‘forgotten’’ contribution, drawn in Fig. 5 as the difference between the complete segregation energy and the two above-mentioned contributions. This could be related to the specificity of segregation of a covalent impurity at the surface of a metallic matrix, which could be out of the scope of usual segregation models.[12]

VI. CONCLUSIONS

In conclusion, we have compared the calculated characteristics of Ge adsorption on the Ag (111), (100), and (110) surfaces at low Ge coverage. We find a strong preference of Ge atoms to maximize the number of its Ag neighbors, which persists also for high coordination numbers. This reflects a well-known, many-body character of effective interaction proposed already for purely metallic systems and signaled for low coordinated Ge atoms deposited on Ag (100). As a consequence, Ge adatoms tend to occupy the substitutional sites rather than adsorb at the surface hollow sites on the (111) surface, whereas especially on the (100) surfaces the two sites become competitive, in perfect agreement with existing experimental evidence.

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