

Ge/Ag(111) semiconductor-on-metal growth: Formation of an Ag_2Ge surface alloy

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We study a semiconductor on a close-packed surface of a metal for a system that tends to phase separation. At room temperature, deposition of $1/3$ monolayer of Ge on Ag(111) surprisingly induces a surface alloy forming a $p(\sqrt{3}\times\sqrt{3})R30^\circ$ superstructure observed in low energy electron diffraction patterns. Yet high-resolution scanning tunneling microscopy images do not exhibit any chemical contrast between Ge and Ag atoms. This is interpreted with *ab initio* total-energy calculations, which also show that the Ge atoms are located in substitutional sites forming an ordered two-dimensional surface alloy with almost identical local electronic densities for both elements.

The formation of alloys that exist only in a confined region near the surface of materials has important technological implications. They generally show new interesting physical and chemical properties. On metallic surfaces the formation of surface alloys are studied mainly in relation to either magnetism or chemical processes (as heterogeneous catalysis). Many metal on semiconductor interfaces have been investigated¹⁻³ in order to develop a more complete description of the Schottky barrier formation. Paradoxically there are only very few investigations on the reverse systems, i.e., semiconductors on metals,⁴⁻⁶ which opens up new fields of interest. These few studies concern systems that show a strong tendency towards ordering, i.e., formation of ordered compounds such as silicides or germanides. Conversely, up to now, there is no study of systems presenting a tendency to phase separation. For these systems, the balance between a metallic or a semiconducting character is delicate and may lead to frustrated behaviors. Indeed, in this case particular questions can be addressed concerning the evolution of the electronic properties of the deposited layer versus surface coverage resulting from the probable competition between the metallic tendency to maximize the number of neighbors and the covalent character with a reduced number of oriented bonds.^{7,8} From this point of view Ge-Ag can be considered as a model system with a tendency towards demixing as exhibited by the bulk binary phase diagram with a surface free energy of the semiconductor element lower than that of the metal. As a consequence one can expect *two-dimensional* cluster formation during the initial stages of deposition as it was indeed observed upon condensation onto the Ag(001) surface.^{9,10}

In this paper we report an unexpected ordered $p(\sqrt{3}\times\sqrt{3})R30^\circ$ superstructure of $1/3$ Ge monolayer (ML) deposited at room temperature on Ag(111). Moreover although a sharp $p(\sqrt{3}\times\sqrt{3})R30^\circ$ low energy electron diffraction (LEED) pattern is observed, the Ge atoms involved in the reconstruction appear indistinguishable from the silver atoms in the scanning tunneling microscopy (STM) images (Fig. 1) at any bias voltage. This ordered surface structure is very

surprising since the Ge-Ag system presents a phase separation tendency, i.e., a tendency to clustering; a size effect that is generally invoked for such types of unexpected behavior observed on some other systems^{11,12} cannot be invoked here since the Ge atoms are smaller than the Ag one (0.144 nm for Ag and 0.122 nm for Ge). Furthermore the lack of chemical contrast in the STM observations is also extremely surprising.

A concomitant photoemission spectroscopy (PES) study and theoretical *ab initio* calculations both show that Ge atoms form, at least during the first steps of the growth, a surface alloy with a high metallic character in agreement with the STM observations. These studies show a frustration of the phase separation tendency of this system at the surface.

Experiments were performed in two separate ultrahigh vacuum systems, comprising on one side LEED and STM and on the other side Auger electron spectroscopy (AES)-LEED and PES. The latter experimental setup uses the syn-

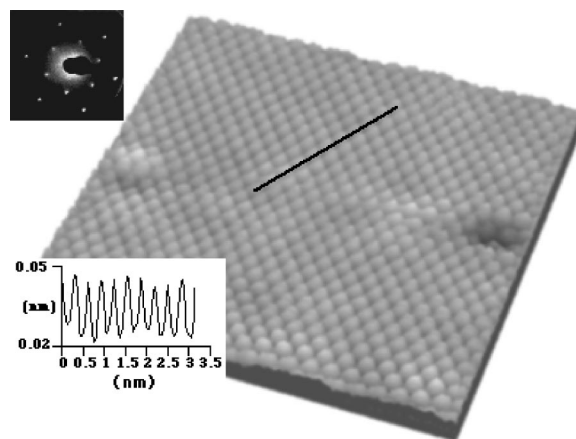


FIG. 1. $p(\sqrt{3}\times\sqrt{3})R30^\circ$ LEED pattern ($E_p=52$ eV) left-upper corner. Filled-state STM image (6.4 nm \times 6.4 nm, $V=-50$ mV, $I=2.0$ nA). A line scan along the $[110]$ direction gives the corrugation shown in the lower-left corner.

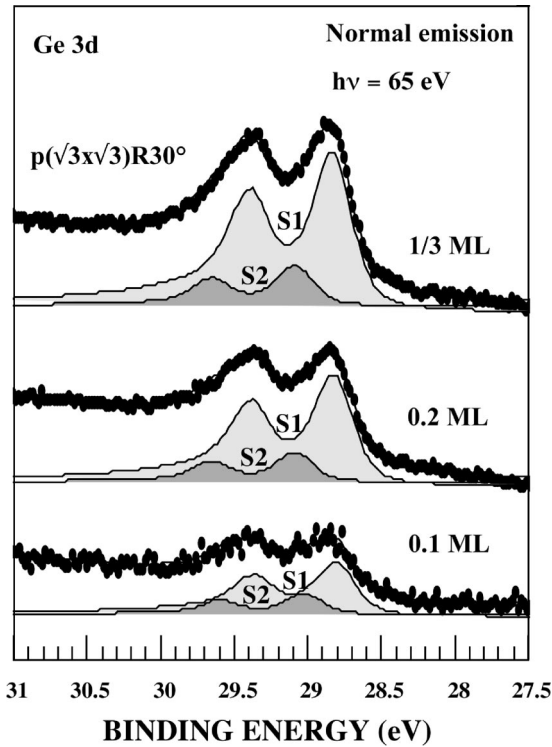


FIG. 2. Ge 3*d* core-level spectra recorded at normal emission at a photon energy of 65 eV during the growth.

chrotron radiation from Super-ACO in Orsay. A single crystal of silver oriented in the (111) direction ($\pm 0.1^\circ$) was cleaned by cycles of Ar⁺ ion sputtering, and annealed at 400 °C for a few minutes until a clean surface presenting a sharp $p(1 \times 1)$ LEED pattern was obtained. Ge is deposited in the low 10^{-10} Torr range from a Knudsen cell. The rate of evaporation is monitored using a quartz balance and the deposited amount checked by Auger spectroscopy.

At the beginning of the growth a $p(\sqrt{3} \times \sqrt{3})R30^\circ$ LEED pattern is observed, which becomes more and more intense and well defined as the deposition increases up to about 1/3 ML. Above this coverage the $p(\sqrt{3} \times \sqrt{3})R30^\circ$ starts to fade away while a new $p(7 \times 7)$ LEED pattern appears, which will be detailed precisely elsewhere.¹³ Figure 1 shows an atomically resolved STM image of the surface with 1/3 ML of Ge deposited at room temperature, which displays a sharp $p(\sqrt{3} \times \sqrt{3})R30^\circ$ LEED pattern. Surprisingly the surface observed by STM appears identical to a clean Ag(111) surface, exhibiting no chemical contrast, as checked at different places on the surface for both positive and negative biases between +0.5 and -0.5 V. The vertical corrugation is about 0.3 Å, whereas the lateral distance between two atoms is 3.1 ± 0.2 Å, which is close to the expected Ag-Ag distance in the (111) plane. This distance is definitely different from the parameter (5.0 Å) of the $p(\sqrt{3} \times \sqrt{3})R30^\circ$ superstructure. We emphasize again here that there is no effect of the sign of the bias voltage and that tunneling at 50 mV was possible as shown in Fig. 1, which reveals the metallic character of the surface.

The presence of Ge in the surface region can be ascertained both from the AES analysis and the Ge 3*d* core levels. Its metallic state is well corroborated by the set of spectra shown in Fig. 2 recorded during the first step of the growth

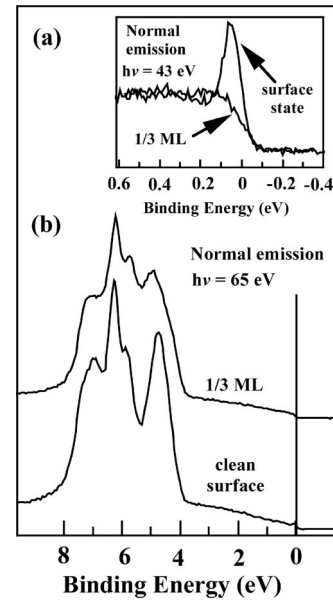


FIG. 3. (a) Two spectra around the Fermi level recorded in normal emission at 43 eV for the clean Ag(111) surface and after the deposition of 1/3 Ge ML. (b) Ag 4*d* valence-band spectra recorded in normal emission at 65 eV for the same Ge deposition.

up to 1/3 ML. For each spectrum the binding energy is referenced to the Fermi level. The following decomposition scheme was used to analyze them in more detail. A Shirley-type secondary electron background¹⁴ was used and the peak was fitted with a Doniach-Sunjić line shape¹⁵ involving the following parameters: a Gaussian full width at half-maximum (FWHM) around 0.19 eV (the experimental resolution), a Lorentzian FWHM of 0.15 eV (inverse lifetime of the core hole) and a large asymmetry parameter equal to 0.18, which is the signature of the metallic character of the Ge atoms. Indeed, if we define the metallic character by the existence of electronic states at the Fermi level [$n(E_F) \neq 0$] in the electronic density-of-states projected on the considered atom (here Ge), the asymmetry parameter of the Doniach-Sunjić core-level line is a direct signature since it is proportional to $n(E_F)$. The spin-orbit splitting was found to be 0.57 eV while the branching ratio was 0.62, close to the statistical value for *d* electrons (0.67). The Ge 3*d* spectra have been fitted with two components (*S1*) and (*S2*) at 28.80 eV and 29.07 eV, respectively, in the whole coverage range. The (*S1*) component is attributed to the $p(\sqrt{3} \times \sqrt{3})R30^\circ$ superstructure. The (*S2*) component, which is weak at low coverage, increases markedly beyond 1/3 ML. We assign it to the second superstructure [$p(7 \times 7)$], which grows, whereas the $p(\sqrt{3} \times \sqrt{3})R30^\circ$ begins to disappear. The [$p(7 \times 7)$] superstructure will be studied in more detail in a forthcoming paper.¹³ The binding energy 29.07 eV is close to the bulk Ge value 29.19.¹⁶ At this point it is worth emphasizing that the $p(7 \times 7)$ superstructure is clearly observed by STM whereas the $p(\sqrt{3} \times \sqrt{3})R30^\circ$ is not.

Figure 3(a) shows two spectra around the Fermi level recorded for the clean Ag(111) surface and after the deposition of 1/3 Ge ML. The clean Ag(111) surface shows a very sharp peak just below the Fermi level derived from a Shockley surface state.¹⁷ This intense peak is totally quenched already after 0.1 Ge ML deposition, while instead a clear Fermi step

persists up to completion of $p(\sqrt{3}\times\sqrt{3})R30^\circ$ phase at $1/3$ Ge ML. Figure 3(b) shows Ag $4d$ valence-band spectra recorded in very surface sensitive conditions for the same Ge deposition. The Ge deposition alters significantly the density-of-states in the $4d$ region. The disappearance of the surface state together with the modification noticed in the $4d$ region are signatures of significantly modified electronic properties of the surface by the $p(\sqrt{3}\times\sqrt{3})R30^\circ$ superstructure, which could be explained by the formation of a 2D surface alloy characterized by the hybridization of the Ag d states with the Ge sp states.

To summarize, this PES study reveals the metallic character of the Ge atoms in the $p(\sqrt{3}\times\sqrt{3})R30^\circ$ superstructure, which have only one type of chemical environment. This environment could correspond to Ge atoms either in adatom or substitutional position. The STM study observations, which show that Ge and Ag atoms are absolutely indistinguishable, would indicate that the later case is more plausible. In order to analyze and discuss these surprising experimental findings, we have performed an *ab initio* study of the deposition of Ge on the Ag(111) surface. All calculations were done within the local-density approximation framework,^{18,19} using the all-electron, full-potential linear muffin-tin orbital method.^{20,21} The detailed description of the computational settings for the Ge/Ag system, together with the results of convergence tests on bulk materials and the (001) surface are given in Ref. 22. Both clean and Ge-covered Ag(111) surfaces were modeled by slabs consisting of five (111) layers of Ag, separated by seven layers of vacuum (about 16 Å). A unique $(\sqrt{3}\times\sqrt{3})R30^\circ$ surface unit cell was used in all the calculations. Since we have verified that substrate relaxation modifies only slightly the adsorption characteristics,²² in the present paper only the positions of the adsorbate atoms were optimized.

In order to determine the preferential Ge site we have calculated the energies of adsorption and substitution of an ordered $1/3$ ML of Ge on the Ag(111) surface. The adsorption energy per germanium adatom is given by $E_{\text{ads}} = E_{\text{Ge/Ag(111)}} - E_{\text{Ag(111)}} - E_{\text{atom}}^{\text{Ge}}$, with $E_{\text{Ge/Ag(111)}}$, $E_{\text{Ag(111)}}$, and $E_{\text{atom}}^{\text{Ge}}$ being the total energies of the Ge-covered slab, of the clean slab, and of the free Ge atom, respectively. In the case of substitution, the corresponding expression is $E_{\text{sub}} = E_{\text{Ge/Ag(111)}} - E_{\text{Ag(111)}} - E_{\text{atom}}^{\text{Ge}} + E_{\text{bulk}}^{\text{Ag}}$, $E_{\text{Ge/Ag(111)}}$, and $E_{\text{bulk}}^{\text{Ag}}$ being the total energies of the Ag slab including the substitutional Ge atoms, and of one Ag atom in the bulk, respectively. In this case the microscopic process consists in the replacement of a surface Ag atom by a free Ge one, the Ag atom being reintegrated into the Ag bulk.

We have considered three alternative positions of the Ge atom: adsorbed in the surface hollow site, substituted in the surface layer, and substituted in the subsurface layer. The calculated adsorption energies are -4.26 , -5.31 , and -4.87 eV per Ge atom respectively, showing a clear preference for the substitutional site in the surface layer. The nonmonotonous evolution of the adsorption energy reflects the competition between two effects. On the one hand, the low surface energy of Ge favors its segregation to the surface and makes the subsurface substitution energetically unfavorable. On the other hand, the important difference of coordination between the surface hollow site (three nearest neighbors) and the substitution site within the surface layer (nine nearest neigh-

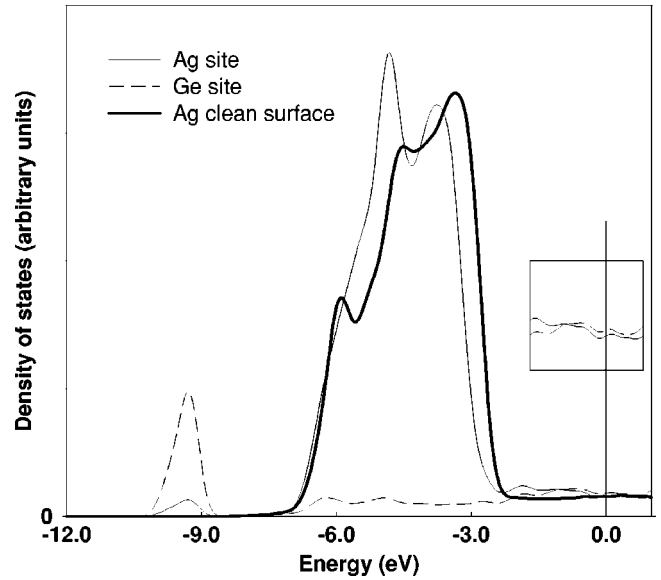


FIG. 4. Density-of-states projected on a Ge atom substituted in the surface Ag (111) layer and on its first surface Ag neighbor. As a reference, the DOS of an Ag atom at a clean Ag (111) surface is also plotted. The insert shows a zoom of the Fermi level region.

hors), and the metalliclike tendency of Ge to maximize the number of its first neighbors,²³ make substitution in the surface layer more favorable than adsorption on the surface. Furthermore, by considering a series of different configurations and coverage rates for Ge, we were able to estimate the effective interaction²³ between the Ge atoms substituted in the surface layer of the Ag (111) surface. Its repulsive character for low Ge coverage confirms the experimental tendency for formation of an ordered surface alloy and is consistent with the experimental mixing energy that reveals a weak tendency to ordering in the dilute Ag (Ge) limit.²⁵ Note however that our calculations do not take into account atomic relaxations which, as it was shown recently, can reverse in some cases the tendency to order.²⁴ Complete results concerning the characteristics of Ge adsorption on different silver surfaces are presented and discussed in Ref. 23.

In order to analyze the puzzling absence of detectable chemical contrast in the STM measurements, we have analyzed the details of the electronic structure of an ordered $1/3$ ML of Ge substituted in the surface layer of Ag (111). In Fig. 4 we present the calculated densities-of-states (DOS) projected on the substitutional Ge atom and on its nearest surface Ag neighbor. As a reference, the DOS of an Ag atom on a clean Ag(111) surface is also plotted. One notices that the germanium s and p states hybridize with the substrate bands, giving a clear contribution in the whole region of the Ag $4d$ band. Due to this interaction a non-negligible part of the Ge states is pushed towards higher energies and clearly, in the region of the Fermi level, the shapes of the Ag and the Ge projected DOS are extremely similar, reflecting the metallic-like character of the substitutional Ge atoms. With respect to the clean surface, the Ag $4d$ band is shifted towards higher binding energies. If estimated from the position of the first moment of the DOS, this shift amounts to about -0.25 eV. An additional peak due to the interaction with the sp shell of Ge appears below the main $4d$ structure.

In order to evaluate the experimentally observed corruga-

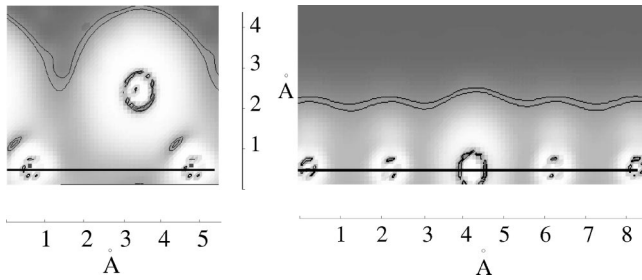


FIG. 5. Electron densities at the Fermi level for a Ge adatom (left panel) and for a Ge atom integrated (right panel) into the first layer of the Ag (111) surface.

tion and to estimate the difference between an adsorbed and a substitutional Ge atom, we have simulated the STM images using the most basic approximation taking into account the electronic effects, in which the tunneling current is proportional to the density of electrons in the region of the Fermi level.

Figure 5 presents the cross sections of the electronic densities evaluated in an energy window of ± 0.5 eV around the Fermi level, as obtained for adsorption and substitution of an ordered $1/3$ ML of Ge on the Ag (111) surface. Using an arbitrary $\rho = 1 \times 10^{-3}$ e/a.u.³ contour for the two systems we find the corrugation equal to 2.0 and 0.3 Å, respectively showing, as it could have been expected, an important dif-

ference between the two alternative adsorption geometries. As for adsorption on the Ag(100) surface,²² this difference is mainly related to the local packing of atoms, electronic effects giving only a small contribution. On the other hand, the calculated small corrugation of substitutional Ge and its metallic character induced by interactions with Ag neighbors are reflected in the small chemical contrast between the surface Ag and the substitutional Ge and explain the lack of appearance of $p(\sqrt{3} \times \sqrt{3})R30^\circ$ reconstruction cell in the STM images.

In conclusion, we have used STM, PES, and LEED to investigate the Ag(111)-Ge surface at Ge coverage ranging from 0.1 to 0.4 ML. For $1/3$ ML Ge, a surface alloy giving a $p(\sqrt{3} \times \sqrt{3})R30^\circ$ LEED pattern was observed. STM images show that the Ge atoms are absolutely indistinguishable from the silver ones at any bias voltages when the $p(\sqrt{3} \times \sqrt{3})R30^\circ$ superstructure forms. *Ab initio* total-energy calculations confirm that the Ge atoms are in substitutional sites and present only a very small corrugation.

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- ¹C. Collazo-Davila, D. Grozea, L. D. Marks, R. Feidenhans'l, M. Nielsen, L. Seehofer, L. Lottermoser, G. Falkenberg, R. L. Johnson, M. Göthelid, and U. Karlsson, *Surf. Sci.* **418**, 395 (1998).
- ²M. Hammar, M. Göthelid, U. O. Karlsson, and S. A. Flodström, *Phys. Rev. B* **47**, 15 669 (1993).
- ³D. Grozea, E. Landree, L. D. Marks, R. Feidenhans'l, M. Nielsen, and R. L. Johnson, *Surf. Sci.* **32**, 418 (1998).
- ⁴J. A. Martín-Gago, R. Fasel, J. Hayoz, R. G. Agostino, D. Naimović, P. Aebi, and L. Schlapbach, *Phys. Rev. B* **55**, 12 896 (1997).
- ⁵R. Dudde, H. Bernhoff, and B. Reil, *Phys. Rev. B* **51**, 12 029 (1990).
- ⁶C. Polop, J. L. Sacedon, and J. A. Martín-Gago, *Surf. Sci.* **402**, 245 (1998).
- ⁷Y. Chang, Y. Hwu, J. Hanson, F. Zanini, and G. Margaritondo, *Phys. Rev. Lett.* **63**, 1845 (1989).
- ⁸D. W. Niles, Nacira Tache, D. G. Kilday, M. K. Kelly, and G. Margaritondo, *Phys. Rev. Lett.* **34**, 967 (1986).
- ⁹H. Oughaddou, B. Aufray, J. P. Bibérian, and J. Y. Hoarau, *Surf. Sci.* **429**, 320 (1999).
- ¹⁰H. Oughaddou, J. M. Gay, B. Aufray, L. Lapena, G. Le Lay, O. Bunk, G. Falkenberg, J. H. Zeysing, and R. L. Johnson, *Phys. Rev. B* **61**, 5692 (2000).
- ¹¹C. Nagl, E. Platzgummer, O. Haller, M. Schmid, and P. Varga, *Surf. Sci.* **333**, 831 (1998).
- ¹²J. Tersoff, *Phys. Rev. Lett.* **74**, 434 (1995).
- ¹³H. Oughaddou, B. Aufray, G. Le Lay, J. M. Gay, A. Mayne, and G. Dujardin (unpublished).
- ¹⁴D. A. Shirley, *Phys. Rev. B* **5**, 4709 (1972).
- ¹⁵S. Doniach and M. Sunjic, *J. Phys. C* **3**, 185 (1970).
- ¹⁶M. Göthelid, T. M. Grehk, M. Hammar, U. O. Karlsson, and S. A. Flodström *Phys. Rev. B* **48**, 2012 (1993).
- ¹⁷T. Miller, W. E. McMahon, and T. C. Chiang, *Phys. Rev. Lett.* **77**, 1167 (1996).
- ¹⁸W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).
- ¹⁹D. M. Ceperley and B. J. Alder, *Phys. Rev. Lett.* **45**, 566 (1980).
- ²⁰M. Methfessel, *Phys. Rev. B* **38**, 1537 (1988).
- ²¹M. Methfessel, C. O. Rodriguez, and O. K. Andersen, *Phys. Rev. B* **40**, 2009 (1989).
- ²²S. Sawaya, J. Goniakowski, and G. Tréglia, *Phys. Rev. B* **59**, 15 337 (1999).
- ²³S. Sawaya, J. Goniakowski, and G. Tréglia, *Phys. Rev. B* **61**, 8469 (2000).
- ²⁴I. Meunier, G. Tréglia, and B. Legrand, *Surf. Sci.* **441**, 225 (1999).
- ²⁵R. W. Olesinski and G. J. Abbaschian, *Bull. Alloy Phase Diagrams* **9**, 59 (1988).