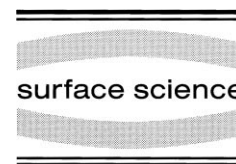




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Surface Science 429 (1999) 320–326



www.elsevier.nl/locate/susc

Growth mode and dissolution kinetics of germanium thin films on Ag(001) surface: an AES–LEED investigation

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Received 19 December 1998; accepted for publication 5 March 1999

Abstract

This paper presents an experimental study by Auger electron spectroscopy (AES) and low energy electron diffraction (LEED) of the growth and thermal behavior (dissolution kinetics isotherms) of a semiconductor (germanium) deposited on an oriented metallic surface [Ag(001)]. The growth mode of germanium on Ag(001) is studied at 100°C and reveals a nearly layer-by-layer type growth mode, up to six monolayers. In the initial stages of growth, a surface superstructure $p(4\sqrt{2} \times 2\sqrt{2})R45^\circ$ appears which remains up to about half a monolayer. Above this coverage the superstructure rapidly disappears and the surface becomes more and more disordered, as deduced from the fuzziness of the LEED diffraction spots. The dissolution kinetics isotherms of one monolayer of germanium are studied in the temperature range 250–320°C. Only the dissolutions at the highest temperature studied are total, the others stop at some surface concentration. At the lowest temperature it corresponds to the formation of the same $p(4\sqrt{2} \times 2\sqrt{2})R45^\circ$ superstructure. These unusual behaviors are interpreted in terms of local equilibrium in the surface selvage and incoherent lattice relaxation at the semiconductor/metal interface. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Auger electron spectroscopy; Germanium; Growth; Low energy electron diffraction; Low index single crystal surfaces; Silver; Surface structure

1. Introduction

The temperature dependence of metallic thin films deposited on metallic substrates has been the subject of many investigations in relation to possible technological applications. Indeed, the formation of surface alloys which appear during the dissolution process of a thin film can present new chemical and physical properties with respect to their small thickness (typically a few atomic layers). The composition of these surface alloys is closely related to both chemical interactions

between elements (deposit and substrate) and a surface segregation tendency [1]; for a review, see for instance Refs. [2–4]. Most modern theories [5–7] describe the surface segregation phenomenon in metallic alloys as resulting from three main driving forces: (i) the relative surface stress of pure elements; (ii) their chemical interactions; and (iii) their size mismatch. From these models, the segregation phenomenon can in some cases appear as a precursor of the bulk phase transformations. Thus, surface segregation can lead to the formation at the surface of a pure plane of solute for systems showing a tendency to demix, and a two-dimensional ordered surface alloy for systems presenting a tendency to order. This has been experimentally

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observed for two model systems: Ag/Cu(111) (phase separating system) [8,9] and Sb/Cu(111) (ordering system) [10]. This segregation behavior induces different dissolution kinetics in both cases in order to preserve a local equilibrium in the surface selvage. Indeed, the dissolution kinetics (450°C) of one monolayer of silver deposited on Cu(111) are slower than those expected (due to the tendency of silver to segregate) while obeying a square root of time dependence law which is the signature of a surface transition from a quasi-pure silver layer to a quasi-pure copper layer [8,9]. On the contrary, at the same temperature the dissolution kinetics of one monolayer of antimony deposited on Cu(111) are not slowed down at the beginning but are later blocked when the surface concentration corresponds to a surface alloy Cu_2Sb forming a $p(\sqrt{3} \times \sqrt{3})R30^\circ$ surface superstructure [11]. Both kinetic behaviors on Cu(111) have been theoretically simulated using the kinetics tight binding Ising model (KTbIM) [12,13] either in a mean field approximation or/and within Monte Carlo simulations [14], in order to take into account only the three main driving forces for segregation previously mentioned. Metal/metal systems show little crystallographic structural differences, therefore chemical interactions are sufficient to account for the previous trends. This should not be the case for semiconductor/metal systems because deposits and substrates present drastically different crystallographic structures, also related to their drastic difference in chemical bonding (covalent versus metallic). In that situation one can expect a stronger structural effect. This is the reason why we have studied the thermal behavior of germanium thin films on silver, which present a strong tendency to demix — as shown by the bulk phase diagram [15,16] — and a large germanium surface segregation.

This paper is divided into five sections. Section 2 is devoted to the description of the experimental set-up. In Sections 3 and 4 we present and discuss a set of experimental results obtained by Auger electron spectroscopy (AES) and low energy electron diffraction (LEED) during the first stages of the growth of germanium on Ag(001) [up to six monolayers (ML)] and during dissolution

kinetics of germanium at different temperatures. The final Section 5 gives our conclusions.

2. Experimental set-up

The experimental procedure is briefly described here. A high purity (5 N) single crystal of silver oriented in the (001) direction (at $\pm 0.1^\circ$ checked by X-ray diffraction) is mechanically and chemically polished. All experiments were performed in a standard ultra-high vacuum (UHV) chamber with a cylindrical mirror analyzer (CMA) for AES measurements and a rear view four grids optics for LEED observations. Auger spectra were acquired in the derivative mode, and the data were collected with a computer system allowing an easy measurement of the peak-to-peak height of the Auger signal of the two elements versus annealing time or deposition time. The sample is heated with a heater located under the sample and cleaned by argon ion sputtering. Germanium deposition is carried out in the main chamber by thermal evaporation from a crucible heated by the Joule effect.

3. Growth of germanium on Ag(001)

The sample is alternately maintained in front of the germanium evaporation cell for a constant time (a few minutes depending on the temperature of the evaporation cell), then in front of the Auger spectrometer to record the surface concentration, and then in front of the LEED optics to observe the surface structure. Note that during an evaporation run, the surface sample temperature increases quickly up to about 100°C then stays constant. This increase of the sample temperature is due to the short distance between the surface sample and the crucible (about 4 cm). We have no cooling device on the sample holder, therefore we are limited to experiments above 100°C. However, we have checked elsewhere [17] that the growth mode is not affected by temperature in the 20–150°C range. A typical curve of the evolution of the peak-to-peak Auger intensities of the substrate Ag₃₅₆ (eV) and of the adsorbate Ge₁₁₄₇ (eV) versus deposition time is given in Fig. 1. On this

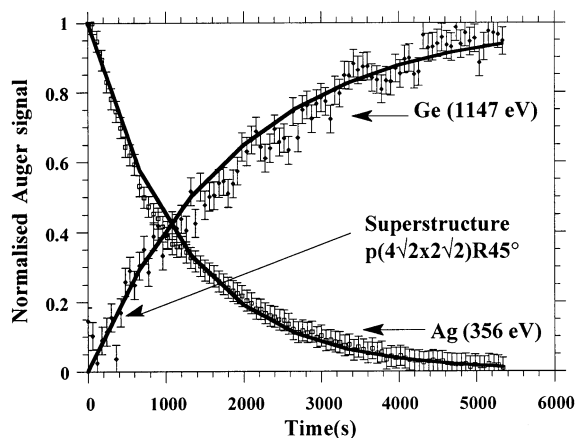


Fig. 1. Auger signal normalized to maximum intensity as a function of time during the deposition of germanium on Ag(001) at about 100°C. Continuous line is the best fit for a layer-by-layer growth mode.

normalized curve (the value 1 corresponds to Auger signals of the clean silver surface and to the thick germanium deposit), a continuous variation appears for both silver and germanium Auger signals until constant values (close to 0 for silver and to 1 for germanium) are reached. The LEED observations performed during deposition can be summarized as follows: during the first stages of growth ($0 < t < 100$ s) one observes at the beginning of the deposition a weak LEED pattern corresponding to a $p(2\sqrt{2} \times \sqrt{2})R45^\circ$ superstructure which becomes more and more intense as the germanium coverage increases. At a precise coverage, corresponding on the curve to a deposition time $t = 200$ s, a set of weak additional spots appears, changing the $p(2\sqrt{2} \times \sqrt{2})R45^\circ$ into a $p(4\sqrt{2} \times 2\sqrt{2})R45^\circ$ superstructure. A typical LEED pattern of this superstructure is shown in Fig. 2a [at this special point the normalized Auger intensities of silver (I_{Ag}) and germanium (I_{Ge}) are respectively equal to 0.58 and 0.15]. It is noticeable that spots corresponding to the $p(2\sqrt{2} \times \sqrt{2})R45^\circ$ are still more intense and sharper than the extra spots producing the $p(4\sqrt{2} \times 2\sqrt{2})R45^\circ$. Above this coverage, the superstructure quickly disappears (after two cycles of deposition) leading to a fuzzy $p(1 \times 1)$ pattern characteristic of the substrate, but which also

rapidly disappears as the background increases after a deposition time larger than 1000 s.

3.1. Discussion

From the shape of the curves of both substrate and adsorbate Auger line intensities versus deposition time (AS- t curves) it is generally possible to deduce the growth mode mechanism. A logarithmic representation of the Auger silver signal versus deposition time shows a nearly linear decay corresponding to an exponential attenuation indicating a layer-by-layer growth mode. Nevertheless, one does not observe any obvious breaks on the curves (as expected for a layer-by-layer growth mode). Therefore, we have fitted the experimental deposition curves with theoretical curves characteristic of a pure layer-by-layer growth mode. The best fit is obtained with electron escape depth respectively equal to 6 Å and 10 Å for Ag_(356 eV) and Ge_(1147 eV) Auger lines. Assuming that one monolayer of germanium corresponds to the first break on the curve which corresponds to the formation of a close-packed pure germanium layer [i.e. 1.4×10^{15} at/cm² which is close to one monolayer of Ag(001) 1.3×10^{15} at/cm²] the superstructure would correspond roughly to about 7×10^{14} at/cm².

A schematic representation of the LEED pattern of the $p(4\sqrt{2} \times 2\sqrt{2})R45^\circ$ superstructure is shown in Fig. 2b. It shows a systematic extinction of spots with indices $(0, 2n+1)$ indicating the presence of a glide plane. Therefore the two-dimensional group symmetry of the surface structure ought to be 'pg'. One of the consequences of this symmetry group is that the number of atoms in the unit cell of the superstructure must be even. Therefore, if we assume eight or 10 germanium atoms in the unit cell this implies respectively a density of 6.0×10^{14} at/cm² and of 7.5×10^{14} at/cm², which are close to the previous value deduced from the Auger estimation (7×10^{14} at/cm²). Very recently, scanning tunneling microscopy (STM) and surface X-ray diffraction (SXRD) studies of the superstructure confirm the value of 6.03×10^{14} at/cm² [17]. This calibration has been used for the study of the dissolution

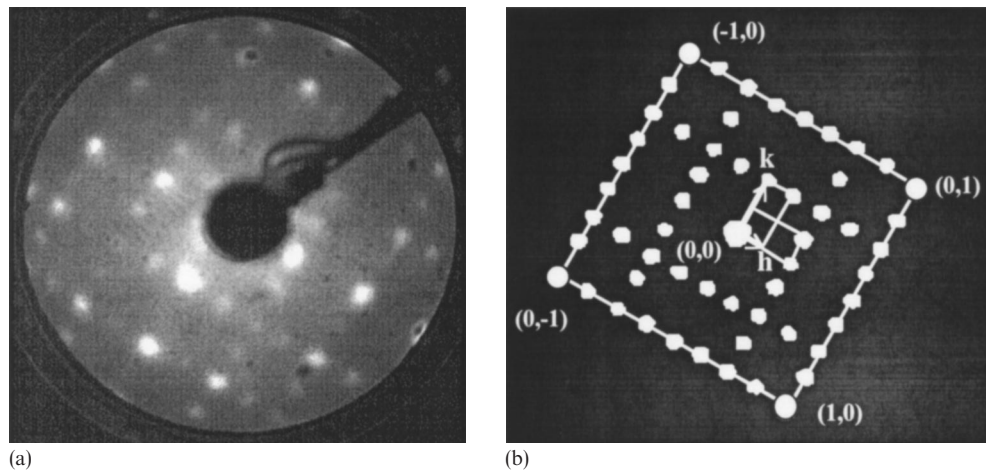


Fig. 2. (a) Typical LEED pattern of the $p(4\sqrt{2} \times 2\sqrt{2})R45^\circ$ superstructure of Ge/Ag(001) observed during germanium growth and at the end of the dissolution kinetics at 250°C ($E_p=45\text{ eV}$). (b) A schematic representation of the diffraction LEED pattern showing the unit cell of the superstructure and the 'pg' group symmetry.

kinetics. Let us add that from a general viewpoint the AES technique is not sensitive enough to the surface to give information about the first step of the growth. Indeed, there is no significant difference in Auger signal intensity between adatoms on the surface and atoms inserted in the first substrate layer {notably in this system for which the relative Auger sensitivity factor of Ge is very low (0.1) in comparison to silver which is large (1) [18]}. Similarly, AES cannot distinguish between isolated atoms on the surface and two-dimensional clusters. Interfacial mixing between the germanium deposit and the silver substrate localized in one monolayer cannot be completely ruled out. However, we think that it is highly unlikely since there is a strong tendency to demix between silver and germanium and a strong tendency to surface segregation of germanium. Furthermore, it is known [19] that the interface metal on semiconductor is diffuse whereas the opposite interface is abrupt.

4. Dissolution kinetics

All the dissolution kinetics are recorded after deposition of about one monolayer of germanium on Ag(001) using the calibration curve given in Fig. 1. Between two dissolution runs, the sample

is annealed at 550°C for 1 h in order to dissolve deep inside the bulk of the silver sample the germanium monolayer previously deposited. It is therefore possible to consider after each experiment the sample as pure silver. The variations of $\text{Ag}_{(356\text{ eV})}$ and $\text{Ge}_{(1147\text{ eV})}$ Auger peak-to-peak intensity ratio ($I_{\text{Ge}}/I_{\text{Ag}}$) versus time are displayed in Fig. 3. Part I illustrates an example of the deposition of about one monolayer of germanium (at 100°C but in this example with an evaporation rate different from the one in Fig. 1) and Part II the dissolution kinetics in the bulk recorded for different temperatures just after deposition. Both kinetics, recorded at 250°C and 264°C , show at the beginning of annealing a rapid dissolution followed by a blocking of this dissolution on a plateau whose level depends on temperature. At 320°C one observes also the rapid dissolution at the beginning of the kinetics followed by a slower one up to a quasi-complete dissolution. The LEED observations carried out at room temperature at the end of each run exhibit: (i) a sharp and well-defined $p(4\sqrt{2} \times 2\sqrt{2})R45^\circ$ LEED pattern after dissolution at 250°C ; (ii) a fuzzy (1×1) LEED pattern after dissolution at 264°C ; and (iii) a sharp (1×1) LEED pattern after dissolution at 320°C in good agreement with the quasi-complete dissolution observed on the kinetics. We have recorded a

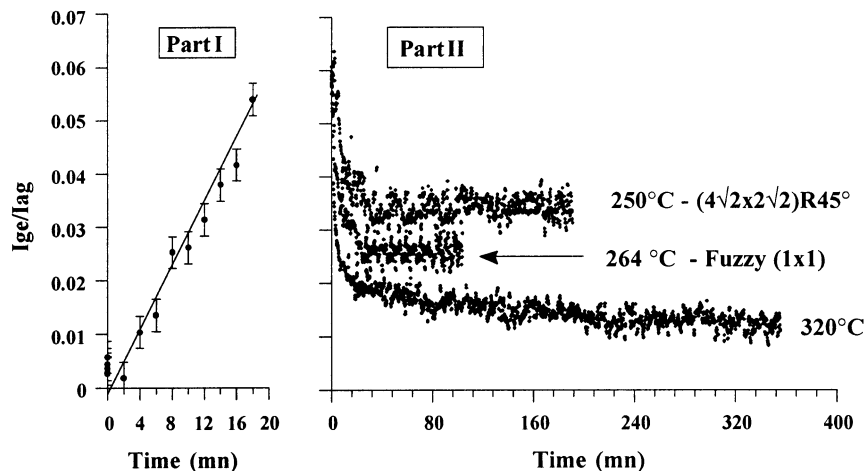


Fig. 3. Time dependence of the Auger peak-to-peak intensity ratio (I_{Ge}/I_{Ag}). Part I: deposition at 100°C of one monolayer of germanium on Ag(001). Part II: dissolution kinetics of this deposit recorded at 250°C, 264°C and 320°C.

set of dissolution kinetics from 210°C to 350°C and only these two plateaus have been observed. From our calibration the first plateau ($I_{Ge}/I_{Ag}=0.035$) corresponds to 0.6×10^{15} at/cm² (using the deposition curve as a calibration) and corresponds to the superstructure $p(4\sqrt{2} \times 2\sqrt{2})R45^\circ$. The second plateau ($I_{Ge}/I_{Ag}=0.025$) corresponds to about 0.4×10^{15} at/cm² and does not seem to be linked to a special surface superstructure (no extra spot on the LEED pattern). The latter kinetics being difficult to interpret only based on AES and LEED data, we have started an STM study of the surface structures after the dissolution process. The first STM images seem to show different large structures presenting a large unit cell that could explain the absence of LEED observations. A complete study of these large structures is still in progress. An alternative explanation of the decrease in Auger signal of germanium and subsequent increase of the silver Auger signal could be explained by the formation of three-dimensional germanium crystallites at the surface of silver. The STM images ruled out this possibility.

4.1. Discussion

From a general point of view it has been shown that the shape of dissolution kinetics recorded at

a constant temperature is closely related to the segregation phenomenon, i.e. to the shape of the equilibrium segregation isotherm at this temperature [20–22]. Then a tendency to segregate of the deposit usually gives rise to a slowing down of its dissolution kinetics [8,9,11–13]. We can analyze the kinetics process of germanium dissolution within the usual Fick formalism. A rough evaluation of the bulk diffusion coefficient (D) can be derived from the first part of the dissolution kinetics using the relation:

$$C_s(t=0) - C_s(t) = 2C_v(x=0, t)(Dt/\pi)^{1/2} \quad (1)$$

where $C_v(x=0, t)$ is the bulk concentration at the surface seldge ($x=0$) at time t and $C_s(t=0) - C_s(t)$ is the surface concentration variation at time t .

As shown in Fig. 4, the surface concentration plot versus the square root of time exhibits a linear part which means that $C_v(x=0, t)$ is constant with time at least in this region. If one assumes now that $C_v(x=0, t)$ is equal to the limit of the solubility of germanium in silver [15,16], one can derive from the slope of the curve a bulk diffusion coefficient. As shown in Table 1, from Eq. (1) we deduce the bulk diffusion coefficient which is systematically higher by one order of magnitude than those extrapolated from high temperature experi-

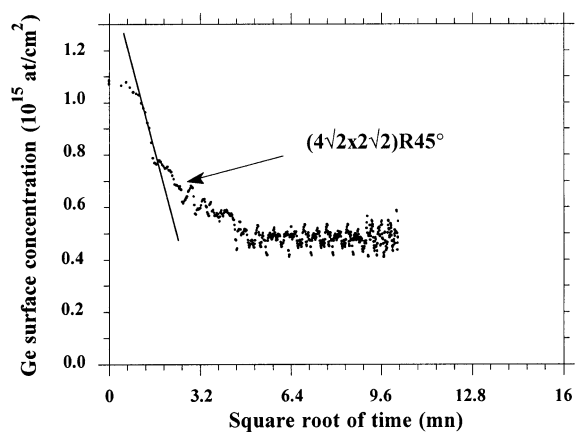


Fig. 4. Surface concentration of germanium versus the square root of time during the dissolution kinetics at 264°C. The bulk diffusion coefficient is derived from the slope of the first part.

Table 1
Bulk diffusion coefficients

Temperature (°C)	D (cm ² /s) extrapolated from high temperatures	D (cm ² /s) deduced from first part of the kinetics
250	4.68×10^{-17}	1.22×10^{-15}
264	1.17×10^{-16}	1.76×10^{-15}
320	2.95×10^{-15}	1.06×10^{-14}

ments [23] using the relation:

$$D \text{ (cm}^2 \text{ s}^{-1}\text{)} = 0.084 \exp\left[-\frac{36500 \text{ (cal/mol)}}{RT}\right]. \quad (2)$$

The comparison of these values shows an unexpected fast dissolution process during the first stages of the dissolution kinetics. If one considers that the dissolution is driven by a *local equilibrium* at the surface selvedge, as was demonstrated to explain most kinetics behavior [20–22], then the acceleration of the dissolution process appears as a signature of a surface energetic instability. This means that a complete monolayer of germanium deposited on Ag(001) is not a stable state in the temperature range studied here. However, the second part of the dissolution kinetics exhibits a

slowing down of the dissolution process followed by a blocking at 250°C and 264°C corresponding to specific surface compounds. The same arguments imply that these blockings are the kinetic signature of an excess of stability of those surface compounds.

Such kinetic behavior for Ge/Ag(001) is quite surprising since it appears that the kinetic shapes are closer to those obtained for systems with a tendency to order (Sb/Cu) than to those obtained for systems with a tendency to demix (Ag/Cu). More precisely, it is quite surprising that one complete monolayer of germanium seems to increase the silver surface free energy since the effect is reversed when comparing surface energies of both pure elements ($\tau_{\text{Ge}} = 0.88 \text{ J m}^{-2}$ and $\tau_{\text{Ag}} = 1.25 \text{ J m}^{-2}$ [24]). This special behavior must therefore be correlated to the covalent nature of germanium for which a (001) fcc type two-dimensional layer is probably highly unstable. The germanium film would prefer an atomic structure closer to its diamond-like character. This could generate a strong surface stress (due to the structural incoherence between silver and germanium) which would increase the total surface free energy leading to the fast dissolution of the (001) fcc germanium layer. From this point of view, this special behavior which had never been observed before shows that it is possible to get a new class of surface alloys driven by structural coherence effects when substrate deposited elements present very different types of chemical bonding. This is the case for semiconductors-on-metals but not for metals-on-metals.

5. Conclusions

The growth mode of germanium on Ag(001) studied at 100°C by AES and LEED is nearly a perfect layer-by-layer type at least up to six monolayers. Up to about half a monolayer, a surface superstructure $p(4\sqrt{2} \times 2\sqrt{2})R45^\circ$ is observed, which then rapidly disappears while the surface becomes more and more disordered as deduced from the fuzziness of the LEED diffraction spots. Dissolution kinetics of one monolayer of germa-

nium have been recorded in the temperature range 250–320°C. The kinetics always show a first part corresponding to an unexpected rapid dissolution of germanium. After this rapid dissolution, kinetics slow down up to a plateau whose concentration depends on temperature: at low temperature (250°C) the plateau corresponds to the superstructure $p(4\sqrt{2} \times 2\sqrt{2})R45^\circ$, while at higher temperature (264°C) the kinetics stop on a second plateau which (probably) corresponds to another ordered surface superstructure, although no special LEED pattern was observed. A quasi-complete dissolution is observed at 320°C. We have interpreted these kinetics in the general frame of local equilibrium in the surface selvedge: the first rapid dissolution reveals a surface instability probably linked to the incoherence between covalent structure of germanium and the metallic nature of silver. On the contrary, the slowing down which leads to blocking of the dissolution reveals an enhanced stability of surface compounds of composition Ge_nAg_m type. A comparison of these kinetics with those obtained on bimetallic model systems reveals the existence of a new class of surface alloys obtained by annealing a semiconductor-on-metal thin film, due to a synergetic effect of surface segregation and bulk crystallography stress.

Acknowledgements

The authors gratefully acknowledge G. Tréglia for a critical reading of the manuscript. They also thank J. Goniakowsky, A. Saül, S. Sawaya, J.M. Gay and G. Le Lay for fruitful discussions.

References

- [1] U. Bardi, Rep. Progr. Phys. 57 (1994) 939.
- [2] F. Ducastelle, B. Legrand, G. Tréglia, Progr. Theor. Phys. 101 (Suppl.) (1990) 159.
- [3] J. du Plessis, Solid State Phenom. 11 (1990) 1.
- [4] P. Wynblatt (Ed.), Modeling of Segregation Phenomena at Alloy Surface Computational Materials Science (1999), in press.
- [5] P. Wynblatt, R.C. Ku, Surf. Sci. 65 (1977) 511.
- [6] G. Tréglia, B. Legrand, F. Ducastelle, Europhys. Lett. 7 (1988) 575.
- [7] F. Ducastelle, Progr. Theor. Phys. 101 (Suppl.) (1990) 159.
- [8] J. Eugène, B. Aufray, F. Cabané, Surf. Sci. 241 (1991) 1.
- [9] Y. Liu, P. Wynblatt, Surf. Sci. 240 (1990) 245.
- [10] H. Giordano, O. Alem, B. Aufray, Scr. Metall. 28 (1993) 257.
- [11] H. Giordano, B. Aufray, Surf. Sci. 307–309 (1994) 816.
- [12] G. Tréglia, B. Legrand, J. Eugène, B. Aufray, F. Cabané, Phys. Rev. B 44 (1991) 5842.
- [13] H. Giordano, B. Aufray, Surf. Sci. 352–354 (1996) 280.
- [14] A. Saül, B. Legrand, G. Tréglia, Phys. Rev. B 50 (1994) 1912.
- [15] T.B. Massalski, Binary Alloy Phase Diagrams, 2nd edn., Materials Society, 1992.
- [16] R.W. Olesinski, G.J. Abbaschian, Bull. Alloy Phase Diagr. 9 (1988) 59.
- [17] H. Oughaddou, J.M. Gay, B. Aufray, L. Lapena, G. Le Lay, O. Bunk, J.H. Zeysing, R.L. Johnson, in preparation.
- [18] L.E. Davis, N.C. MacDonald, P.W. Palmberg, G.E. Riach, R.E. Weber, Handbook of Auger Electron Spectroscopy, 2nd edn. Physical Electronics Industries, 1976.
- [19] J.A. Martín-Gago, R. Fasel, J. Hayoz, R.G. Agostino, D. Naumovic, P. Aebi, L. Schlapbach, Phys. Rev. B 55 (1997) 12896.
- [20] M. Laguës, J.L. Domange, Surf. Sci. 47 (1975) 77.
- [21] A. Senhaji, G. Tréglia, J. Eugène, A. Khoutami, B. Legrand, Surf. Sci. 287/288 (1993) 371.
- [22] G. Tréglia, A. Saül, B. Legrand, Il Vuoto, Scienza e Tecnologia 25 (1996) 32.
- [23] R.E. Hoffman, Acta Metall. 6 (1958) 95.
- [24] W.R. Tyson, W.A. Miller, Surf. Sci. 62 (1977) 267.