



2D-NANOLATTICES

FP7-ICT-2009-C (FET Open)

*Highly anisotropic graphite-like semiconductor/dielectric
2D nanolattices*

Deliverable D2.2

Role of metals in graphene-like Si and Ge

Report Prepared by D. Tsoutsou, NCSR-D

Contributors: CNRS, NCSR-D

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A. Introduction

A growing interest in the formation of silicene on Ag(111) has been developed recently by several scientific groups [1-6]. Within the framework of the “2D Nanolattices” project, the formation of epitaxial silicene films on a Ag(111) substrate was recently demonstrated by both CNRS and CNR through the combination of experimental and theoretical techniques [1, 2]. In addition, silicene formation through surface segregation on zirconium diboride thin films (ZrB_2) grown on Si wafers has also been reported [7]. On the other hand, even though the existence of free standing germanene has been theoretically predicted [8, 9], the synthesis of 2D germanene layers has not been achieved so far. The primary aim of this deliverable is to study the role of various metal substrates besides Ag, on the deposition of Si and Ge and the possible formation of silicene and germanene layers. Furthermore, as an extension to our previous work performed on Ag(111), the deposition of a mixed SiGe layer with a composition of Ge: 55 at. %, Si: 45 at. % on Ag was also investigated.

In this work we present the growth and characterization of Si and Ge on metal substrates such as Au(111), Rh(111) and Pb(111). The selection of these particular metals was basically governed by their limited reactivity with Si and Ge. In particular, Rh and Au, just like Ag, are inert transition metals, and therefore they should not in principle react with Si and Ge (still, superconducting alloys Au-Ge are well-documented). In addition Au has a lattice constant (4.08 Å) nearly identical to the one of Ag (4.09 Å), and therefore similar surface superstructures might be expected for the two Si, Ge-deposited metals. Finally, Pb-Si and Pb-Ge phase diagrams [10, 11], indicate that Pb has a very low solubility in Si and Ge. The reverse process, i.e. deposition of Au, Rh and Pb metals on semiconducting Si and Ge substrates has been studied extensively [12-16] due to a variety of interesting properties which are significant both scientifically and technologically. Nevertheless, only very few data exist for Si/Ge deposition on metal substrates. In particular, the electrochemical deposition of germanium and silicon on Au(111) has been reported, and it turns out that elemental semiconducting Si and Ge can be formed, without intermixing with Au [17-20]. Moreover, the charge transfer for the interaction of Si atom on the Au (111) was also studied by first principles calculations [21] and it has been shown that the chemical bonding between Si and Au atoms is governed by covalent interactions. For our work, atom-thin 2D structures of silicon and germanium on metals were generated by molecular beam epitaxy (MBE). MBE was employed for the deposition of the SiGe alloy on Ag(111). A wide combination of experimental techniques such as LEED, STM, XPS, RHEED, ARPES and LEISS has been used in order to fully characterize the deposited samples.

In this work we screen a number of metal substrates (NCSRD) in order to identify the most suitable substrate for the growth of silicene and germanene. In parallel, we focus and deepen our investigation (CNRS) focusing on the most prospective system, that is Ge/Au(111) with the purpose to find optimum growth conditions (temperature and surface coverage).

B. Contribution of CNRS- CINaM (5 person months):

Brief Summary: CNRS-CINaM worked on Ge deposition on single crystal Ag (111) substrates; ordered structures of Ge on Au (111) have been achieved for the 150 °C to 300 °C deposition temperature range, whereas Ge diffusion in the bulk occurs for higher temperatures. Spectroscopic characterization of the deposited structures is currently under investigation.

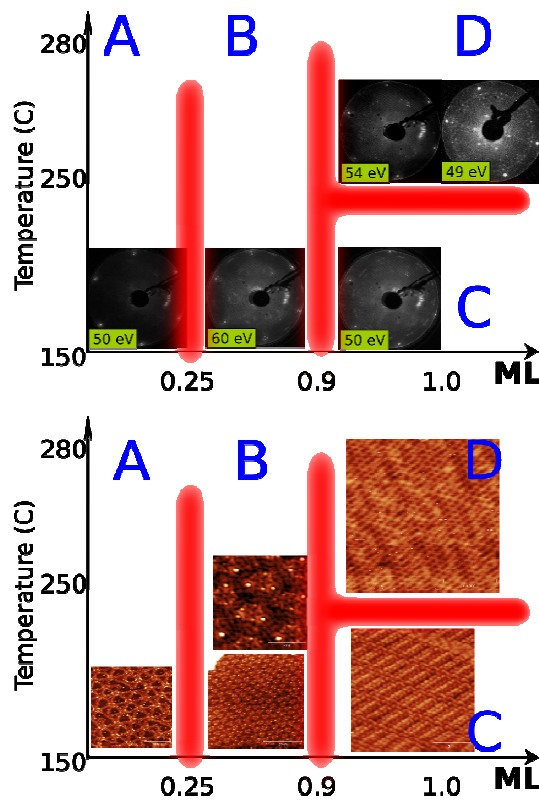


Figure 1: Phase diagram for Ge on Au(111). A) Low coverage phase LEED indicate a 15x15 reconstruction. B) Hexagons array displaced in a 15x15 periodicity. C) Complex structure with squared STM pattern. D) STM indicates an hexagonal structure, The LEED exhibit complex patterns.

The third experimental data set was recently collected at SLS and it concerns the spectroscopic characterization of the structures with promising symmetry to exclude the possibilities of alloys from our study. The latter data are currently under analysis.

Germanene: exploring Ge-Au Phase space

The literature for germanene is slimmer than for silicene. It has solid theoretical background as its sibling silicene but there are very little indications for germanium thin films on silver or gold. The few data available refer to electrochemical deposition of germanium on Au(111)[17-19]; first task is therefore close this gap in literature by studying the structures generated by germanium on gold. This task has been achieved thanks to mostly 3 set of experiments. The first set of experiments meant to scroll trough the phase space of sample temperature, deposition rate and deposited amount that lead to select a range of conditions where germanium form ordered structures on Au(111). Thanks to this experiment performed on the side laboratories of ID03 at ESRF we know that Ge ordered structures are presents on Au(111) from 150 C to 300C but over 270/280 °C Germanium starts to diffuse in the bulk. In the second set of experiments performed at CINaM laboratories we acquired more detailed information on the surface structures and define some preliminary boundary for the phase diagram.

The third experimental data set was recently

C. Contribution of NCSR-D (7 person months):

Brief Summary: In our work we have studied the role of several metal substrates (Au, Rh and Pb) on the growth of graphene-like Si and Ge. Even though, the formation of silicene/germanene layers on these metals cannot be claimed, some interesting results, requiring further investigation, have been obtained in the case of Au and Rh. Finally, we have extended our work on Ag metal by studying the deposition of a mixed SiGe layer. Our first results indicate that the mixed SiGe layer on Ag(111) still forms well ordered 2D lattices, which is remarkable.

(1) Si and Ge deposition on Au(111) metal:

(a) Experimental and growth details

Commercially purchased Au(111) high-purity crystals were used as the substrate material. Marking of the [1-10] crystallographic orientation was supplied by the vendor. For the cleaning process, repeated cycles of Ar⁺ sputtering (0.8 KeV, 30 mins, P=1x10⁻⁵ mbar) and annealing (500 °C, 15 mins) were deployed in order to ensure clean, well-ordered Au surfaces. Indeed, after cleaning the wide scan XPS spectrum (Figure 2) presents features solely related to Au with no traces of carbon or oxygen (insets).

Having ensured a clean metal surface, Si was evaporated from a BN effusion cell, while Ge from a Ta effusion cell, at estimated deposition rates of 4x10⁻⁴ Å/s and 0.04 Å/s, respectively. Deposition times of 70 mins for Si and 70s for Ge, were therefore used in order to achieve an estimated one monolayer coverage of the Au surface. Metal substrate temperatures were kept at 200°C and RT for Si and Ge, respectively. Deposited samples were analyzed *in-situ* by RHEED, XPS, LEISS and UPS.

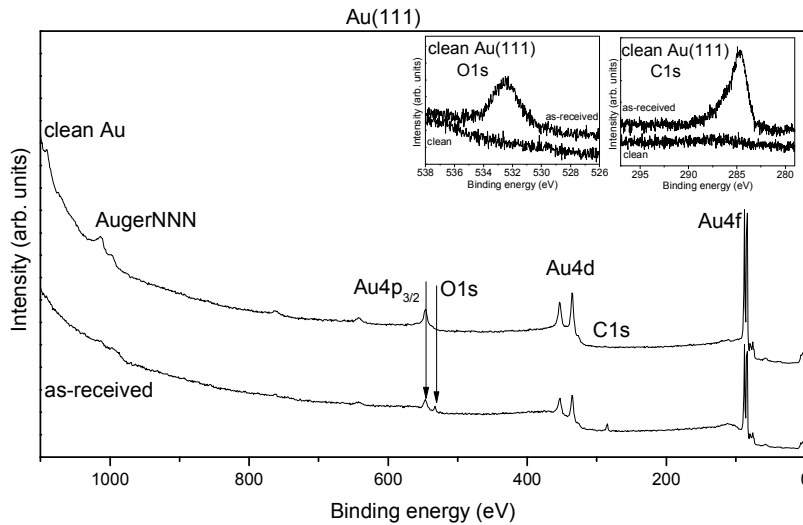


Figure 2: Wide scan XPS spectra of the as-received and clean Au(111) samples. The inset shows detailed O1s and C1s regions of the two samples.

Figure 3 presents detailed XPS spectra of the core level Au 4f (top), Si 2s (bottom-left), and Ge 3d (bottom-right) peaks for the Si, Ge-deposited Au(111) samples. It is clear that the Au 4f spectrum of the Si-deposited sample is broader and shifted to higher BE, as compared to the one recorded for the Ge-deposited sample. This finding accompanied by the presence of a small shoulder peak at ~152.5 eV in the Si 2s spectrum of the Si-deposited sample, point to the formation of a gold silicide surface alloy. The higher BE shift of the Si 2s peak in gold silicide as compared to elemental gold, is consistent with a charge transfer from Si to Au due to a higher electronegativity of Au than that of Si. Moreover, the higher BE shift of the Au 4f is known to be due to d-electron depletion to form an *sd* hybrid [22]. Finally the formation of a surface alloy in the Ge-deposited sample cannot be justified based on the XPS data, since Au 4f and Ge 3d peak positions in this case indicate the formation of elemental Ge.

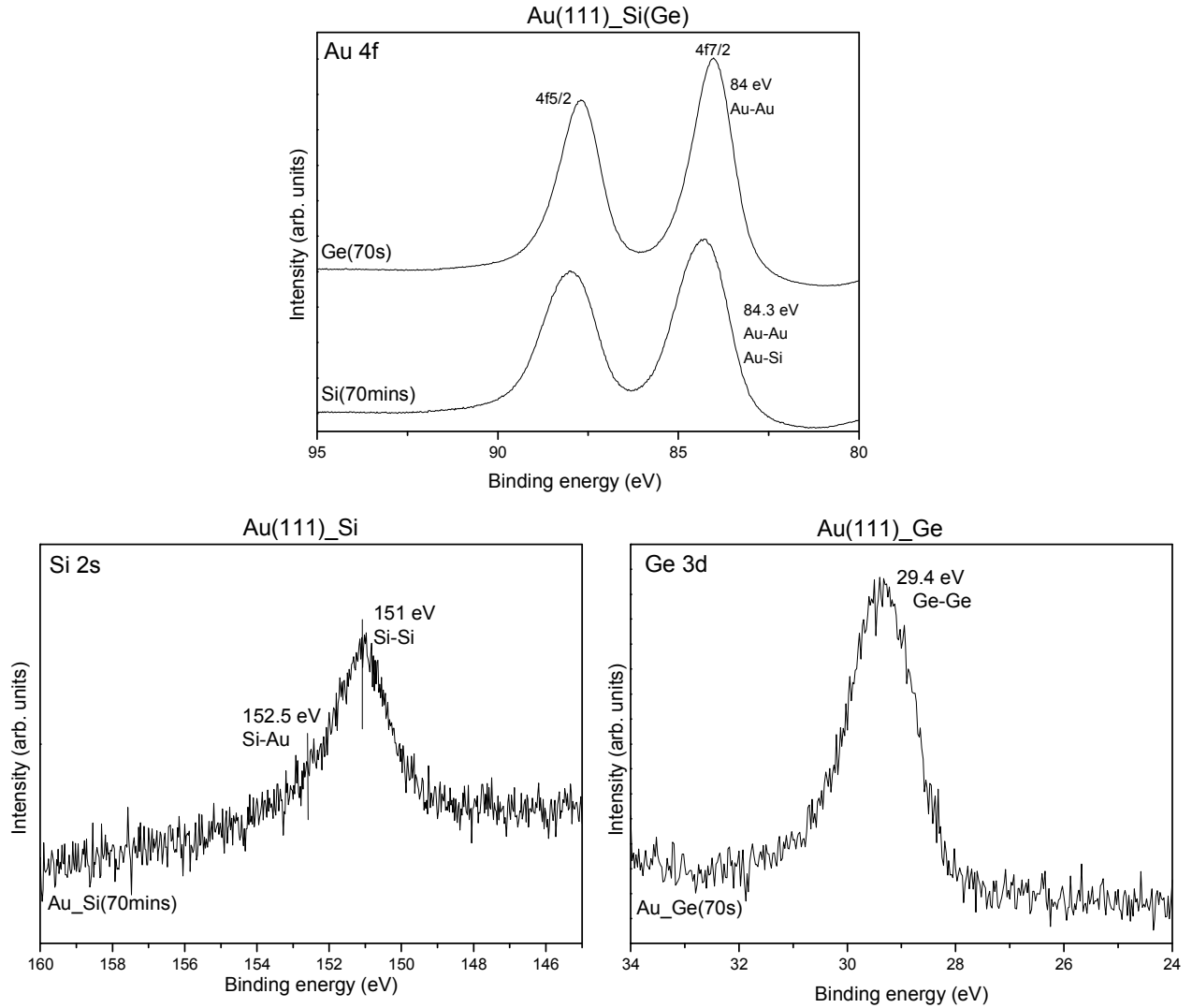


Figure 3: Detailed XPS spectra of the core level Au 4f (top), Si 2s (bottom-left) and Ge 3d (bottom-right) peaks for the Si, Ge-deposited Au(111) samples.

(b) RHEED investigation

The structure of the bare as well as the Si and Ge-deposited Au (111) surfaces, was *in-situ* monitored by RHEED (Figure 4). As expected, the RHEED pattern of the clean Au(111) surface shows a 1x1 reconstruction, qualified by relatively sharp diffraction streaks. Depositing Si (70mins) on the clean Au(111) surface, results in a x3 RHEED pattern recorded along the [1-10] azimuth as well as in the 60° rotated equivalent direction, indicating the formation of a 3x3 trigonal superstructure. It should be pointed out at this point, that even though the lattice constants of Au and Ag are nearly identical (i.e. 4.08 Å and 4.09 Å, respectively), the obtained RHEED pattern of the Ag(111)/Si (70mins) sample indicates a 4x4 trigonal structure. This could be explained by attributing the 3x3 trigonal structure to the formation of a surface alloy, as discussed in the previous (a) on the basis of XPS data. In the case of the Ge-deposited surface, a blurred x1 reconstruction is observed, with no additional streaks due to Ge deposition. This is in agreement with CNRS results, indicating that an ordered structure on Au(111) is obtained only above a growth temperature of 150 °C.

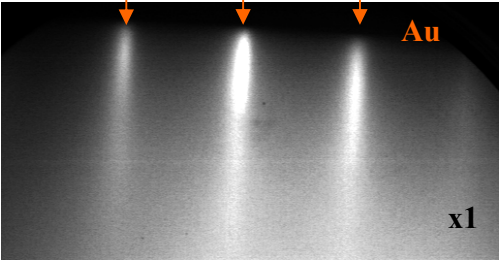
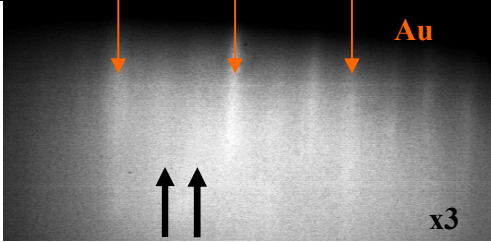
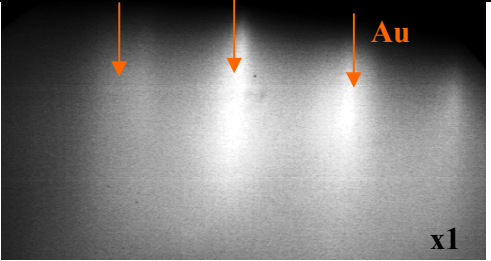
Sample	[1-10]
Au (111) clean	
Au_Si70mins	
Au_Ge70s	

Figure 4: RHEED patterns on clean Au (111) and Au/Si(70mins), Au/Ge(70s) samples. A x3 pattern along the Au [1-10] azimuth, as well as along the 60 rotated equivalent direction, appears in the case of the Si-deposited surface. A blurred x1 pattern appears after Ge deposition.

(c) VB structure investigation by angle-resolved UPS

Angle-dependent spectra ($\theta=0^\circ-48^\circ$) of the clean Au(111) surface along the ΓK (left) and ΓM (right) directions are presented in Figure 5. A HeI line at 21.22 eV photon energy was used for the photoexcitation. In agreement with the clean Ag(111) data at $\theta=0^\circ$ [23], a surface state peak appears at ~ 0.2 eV (Figure 3- inset), with its intensity rapidly decreasing with polar angle. In addition, for both directions the features in the 2-5 eV range arise from the Au d-band [24]. It can be seen however, that the relative intensity ratios of the features centered at ~ 4 eV is different for the ΓK (left) and ΓM (right) directions. Moreover, a non-dispersing shoulder is evident in the leading edge of the d-band (2.5 eV) [25]. The relative intensity of the latter peak increases with polar angle, resulting in a dominating DOS contribution at higher angles. This behavior is more clearly pronounced in the ARUPS data recorded along the ΓK direction. Finally it should be pointed out, that no evident structure is observed in the 1.5 eV- E_F range of the clean Au(111) ARUPS data, making the identification of possible silicene/germanene –related features easier.

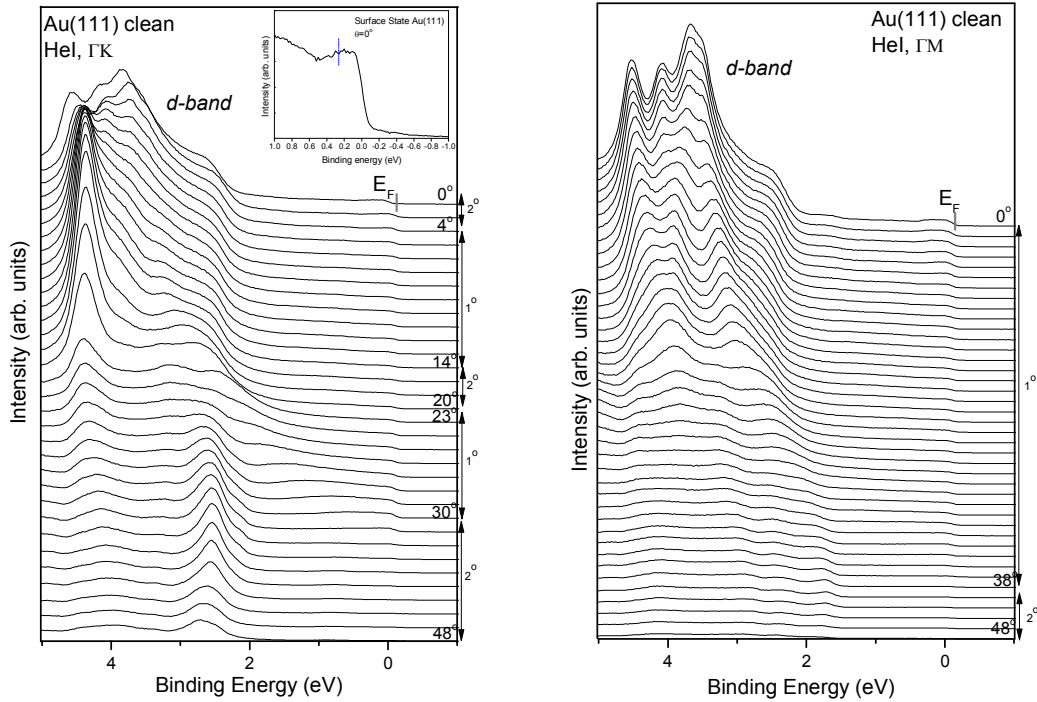


Figure 5: ARUPS spectra for the clean Au(111) surface at different polar angles θ , recorded along the ΓK (left) and ΓM (right) directions. The inset shows the surface state peak recorded at $\theta=0^\circ$ for the clean Au(111) surface.

Upon Si (70 mins) deposition, the overall d-band shape at ~ 4 eV has changed (Figure 6). Moreover, the shoulder peak is still visible at ~ 2.5 eV, however its intensity is not greatly enhanced with polar angle, as in the case of the bare Au(111) surface. Yet, the most interesting finding is a low intensity dispersive feature in the ARUPS data recorded along both the ΓK and the ΓM directions (circled area); this feature (better shown in the right column of Figure 6) is absent in the case of the bare Au(111) and Ag (111)/Si (70mins) surfaces [17]. As presented in Figure 7, the dispersion of this feature occurs at low angles ($\theta=0^\circ$ - 14°), or in other words close to the Γ point of the Brillouin zone. While such a feature is not predicted or expected in case of free-standing silicene, it is investigated at present with the help of DFT calculations whether it could be a signature of silicene valence band which is modified with respect to the free-standing silicene, due to the additional symmetry imposed by the substrate. Nevertheless, taking into account the XPS data presented in the previous section, the formation of gold silicide seems to be the most probable scenario for the growth of Si on Au(111), and such a feature could also be attributed to the formation of a surface alloy.

On the other hand, the ARUPS data of the Ge-modified surface (data not shown), show no significant differences with respect to the clean Au(111) surface. These results combined with the RHEED patterns discussed in the previous section, indicate that Ge does not form ordered structures on Au(111) substrates at RT, in agreement with CNRS results. Further structural and spectroscopic investigation on Au(111)/Ge samples grown at deposition temperatures in the $150^\circ\text{C} - 300^\circ\text{C}$ range is planned at NCSR-D.

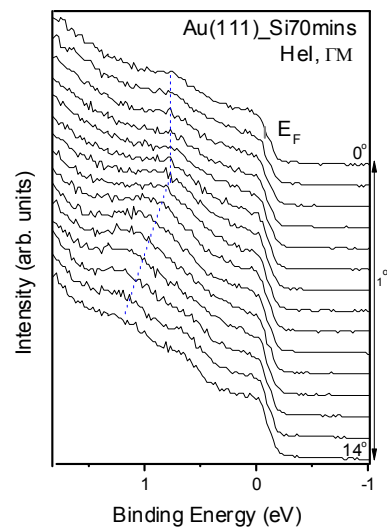
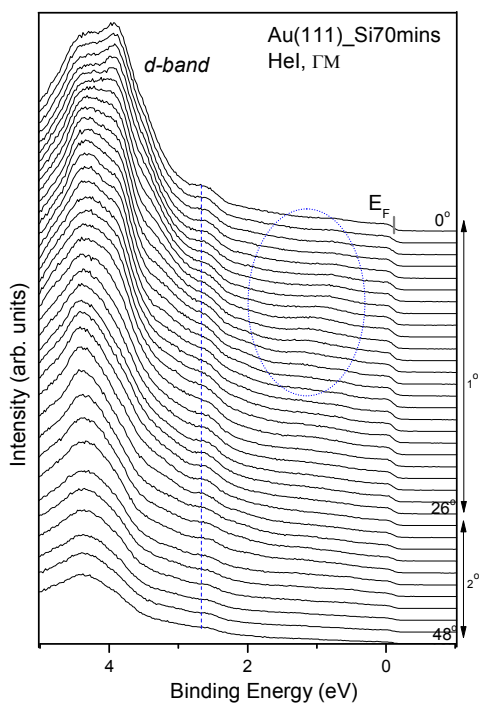
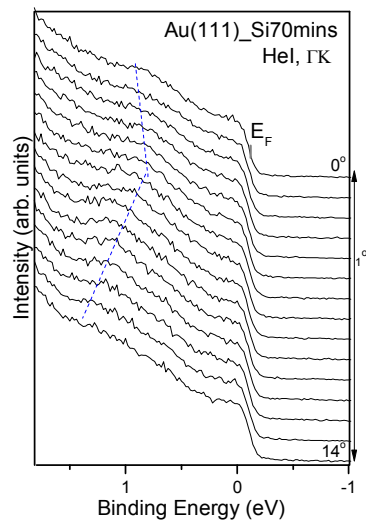
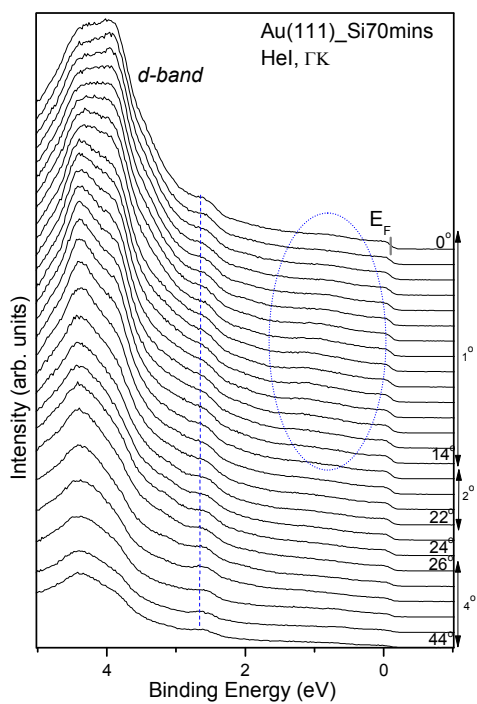


Figure 6: ARUPS spectra for clean and 70 min Si-deposited Au(111) samples at different polar angles θ , recorded along the ΓK (top) and ΓM (bottom) directions (left column). The detailed ARUPS data (1.8 to -1 eV energy range) marked as the circled area are also presented in the right column.

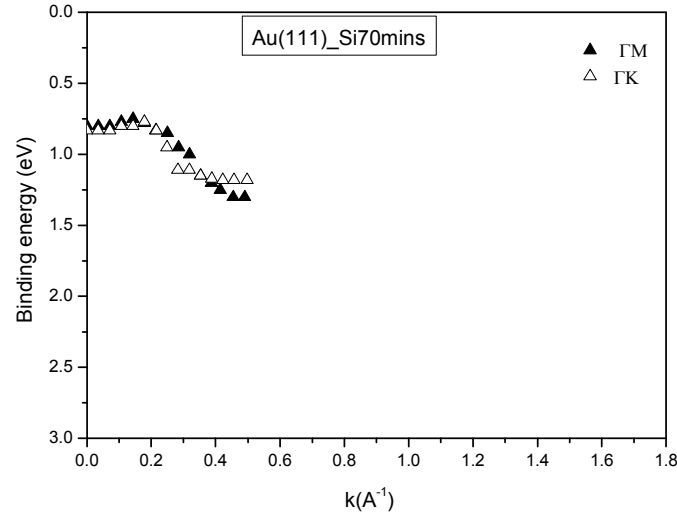


Figure 7: E vs k plot presenting the Brillouin zone mapping along the Au ΓK (closed symbols) and ΓM (open symbols) directions.

(2) Si and Ge deposition on Rh(111) metal:

(a) Experimental and growth details

High purity, one-side polished Rh(111) single crystals have been purchased by Mateck GmbH. Marking of the [1-10] crystallographic orientation was supplied by the vendor. In accordance with Musket *et al* [26], clean well-ordered Rh(111) surfaces were prepared by Ar⁺ bombardment (2.5 keV, 1×10^{-5} mbar, 30 mins), followed by molecular oxygen treatment at high temperature (650 °C, 10^{-7} Torr, 20 mins) and finally a flash annealing at 870 °C. After preparation XPS core level spectroscopy (Figure 8) revealed no traces of contaminants (carbon or oxygen) and RHEED patterns showed a clear 1×1 reconstruction.

Si and Ge were evaporated from a BN effusion cell and a Ta effusion cell, at estimated deposition rates of 4×10^{-4} Å/s and 0.04 Å/s, respectively. One monolayer (1 ML) coverage of the Rh(111) substrate was targeted, and therefore a deposition time of 70 mins for Si and was used. However, Si growth on Rh was unsuccessful. No RHEED pattern was observed indicating an amorphous Si-based overlayer. A possible cause is the unintentional Si oxidation as confirmed by XPS; however, the source of oxygen has not been identified. Regarding Ge growth, the Rh(111) substrate temperature was kept at RT, while two different deposition times were used (70s and 87s). Detailed Rh 3d and Ge 3d XPS spectra recorded for both clean Rh(111) and Ge-deposited Rh(111) samples, indicate deposition of elemental Ge, with no Rh-Ge intermixing.

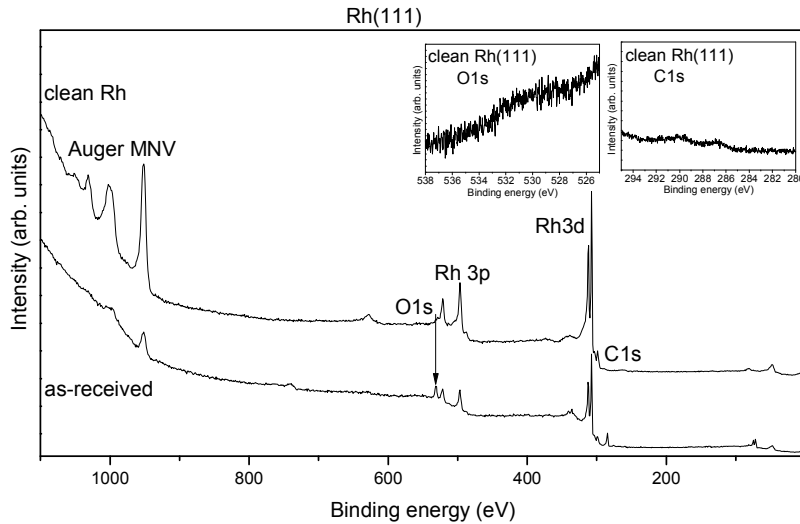


Figure 8: Wide scan XPS spectra of the as-received and clean Rh(111) samples. The inset shows detailed O1s and C1s regions of the two samples.

(b) RHEED investigation

The Ge deposition on clean Rh(111) is monitored by RHEED by observing the surface reconstructions at different deposition times (Figure 9). An 1x1 RHEED pattern, suggestive of a clean ordered surface was recorded for the bare Rh(111) surface. For the Ge-deposited surface, a x6 or x3 reconstruction is evident along the [11-2] azimuth, depending on coverage. The RHEED patterns observed along the [1-10] azimuth, not clear, and for this reason it is not possible to resolve the surface superstructure based on these data.

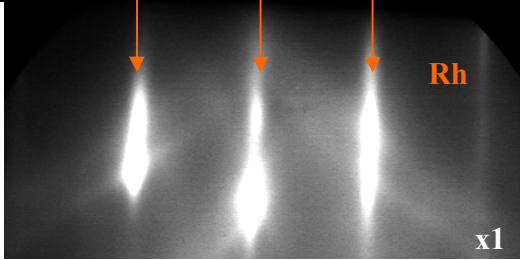
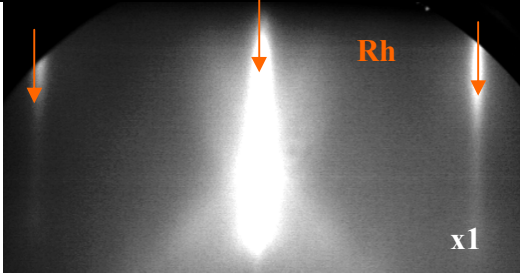
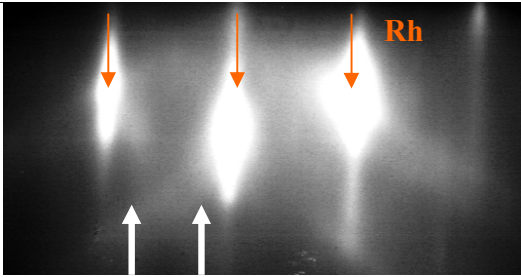
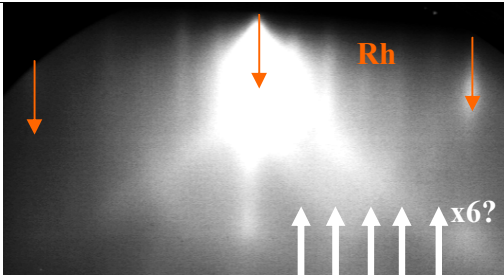
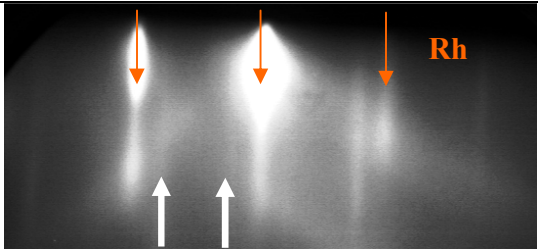
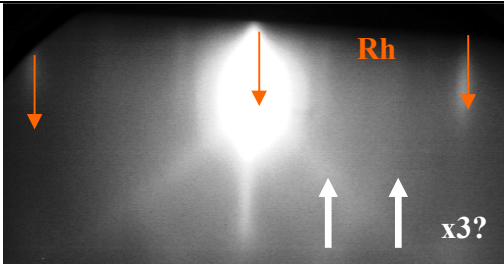
Sample	[1-10]	[11-2]
Rh (111) clean		
Rh_Ge70s		
Rh_Ge87s		

Figure 9: RHEED patterns on clean Rh (111) and Rh/Ge(70mins), Rh/Ge(87s) samples.

(c) VB structure investigation by angle-resolved UPS

Figure 10 presents the ARUPS data recorded for the clean and the 70s Ge-deposited Rh(111) surfaces, along the ΓK direction. The 87s Ge-deposited samples has shown similar behavior to the 70s one, and data are not presented here. For the bare Rh(111) surface features at 1 eV and 2.5 eV are attributed to Rh d-band [27]. It should be noted that contrary to the Ag and Au cases, here the proximity of the Rh d-band to E_F constitutes the identification of a possible germanene contribution more complicated. In the case of the Ge-deposited surface, a non-dispersive Ge-related feature at 1.8 eV has been observed in the ARUPS data (circled area in Figure 9-right), not evident in bare Rh(111) and Ag(111)/Ge (100mins) surfaces [17]. To a first approximation the aforementioned peak can be interpreted as the amplification of a pre-existing Rh(111) band. However, further investigation is needed, in order to be able to explain the nature of such a feature.

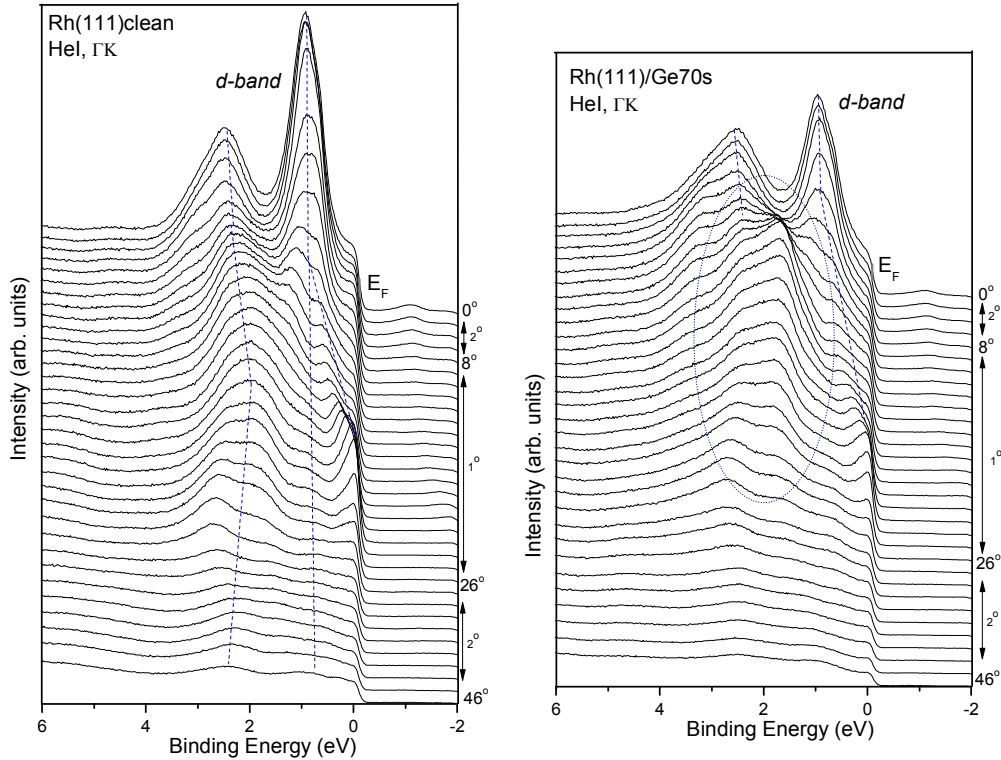


Figure 10: ARUPS spectra for clean (left) and 70 Ge-deposited Au(111) (right) samples at different polar angles θ , recorded along the ΓK direction.

(3) Si and Ge deposition on Pb(111) metal:

(a) Experimental and growth details

Growth on Pb was motivated by prediction that Pb does not mix thermodynamically with either Ge or Si. Single crystals of high purity Pb(111), marked with the [1-10] orientation were purchased. Due to the low melting point of Pb(327.46 °C), a mild cleaning procedure was used in ordered to produce clean (111) surfaces. Specifically as evident by the XPS data reported in Figure 11, repeated cycles of low energy Ar⁺ bombardment (1 keV, 1x10⁻⁵ mbar, 30 mins), followed by a low temperature annealing (150 °C for 15 mins) have shown to produce oxygen and carbon-free surfaces.

Si was evaporated from a BN effusion cell at 1225 °C, at an estimated deposition rate of 4x10⁻⁴ Å/s. Deposition times of 45 mins and 70 mins were used at two different substrate temperatures, 170 °C and RT, respectively. For Ge evaporation the Ta cell was heated at 1250 °C, resulting in a deposition rate of 0.04 Å/s. Deposition time and substrate temperature were in this case 70 s and RT, respectively.

Detailed XPS Si 2p (left) and Ge 3d (right) scans presented in Figure 12, confirm that indeed Si and Ge were deposited on the bare Pb(111) surface. Nevertheless, LEISS spectra of the deposited Pb(111) surfaces (Figure 13) have shown very weak intensity signals for Si and Ge. Taking into account that LEISS is a much more surface sensitive technique than XPS, one can conclude that Si and Ge are probably dissolved inside Pb with metal atoms coming on the top surface, and therefore the deposition of Si and Ge was unsuccessful in the case of the Pb (111).

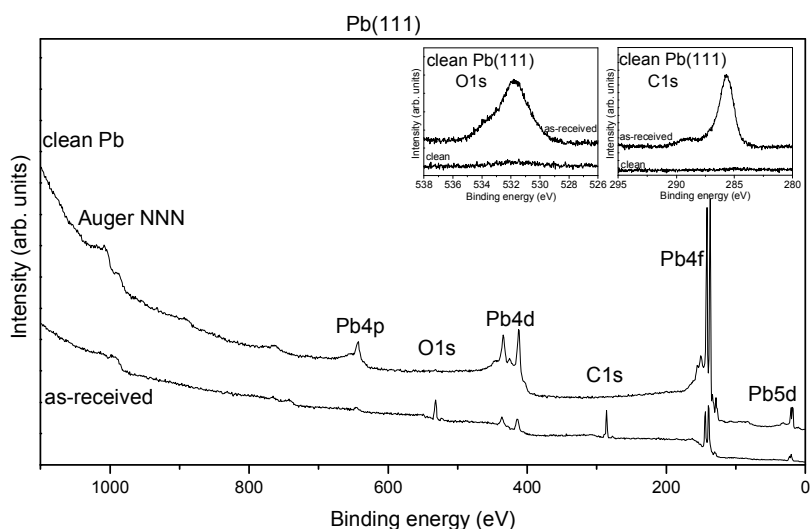


Figure 11: Wide scan XPS spectra of the as-received and clean Pb(111) samples. The inset shows detailed O1s and C1s regions of the two samples.

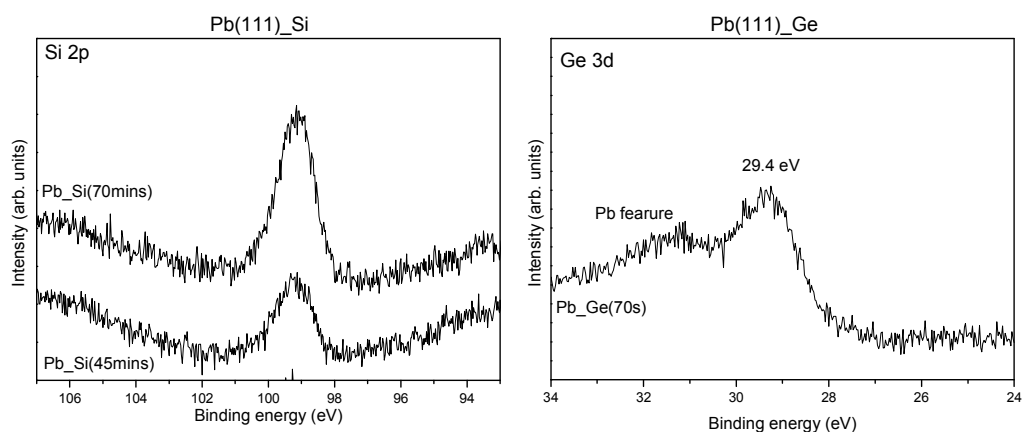


Figure 12: Detailed XPS spectra of the core level Si 2p (left) and Ge 3d (right) peaks for the Si and Ge-deposited Pb(111) surfaces.

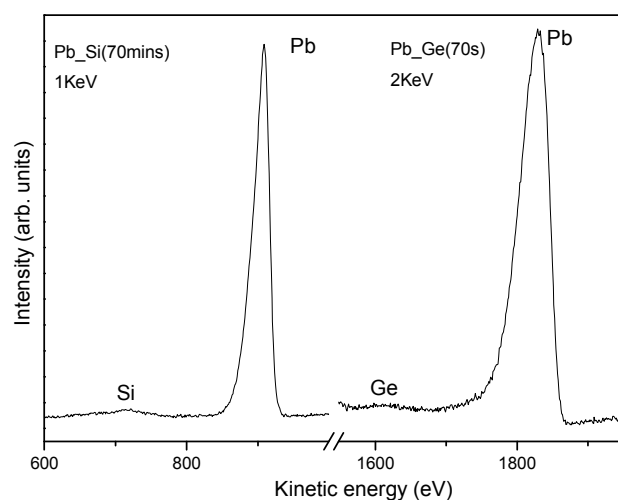


Figure 13: LEISS spectra of the Si and Ge-covered Pb(111) surfaces, showing the weak Si and Ge signals indicative of dissolution of Si and Ge atoms on the Rh(111) surface

(b) RHEED investigation

RHEED patterns recorded for the clean and Si, Ge-deposited Pb(111) surfaces are presented in Figure 14. An 1x1 reconstruction recorded even for the deposited Pb(111) surfaces, indicates that there is no ordered structure of Si and Ge on Pb.

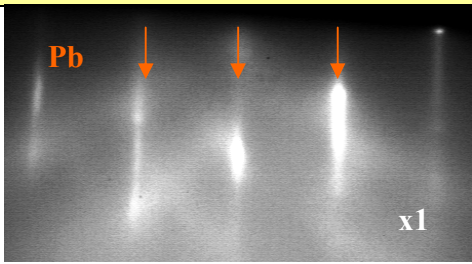
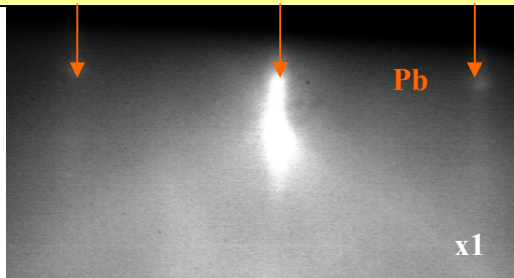
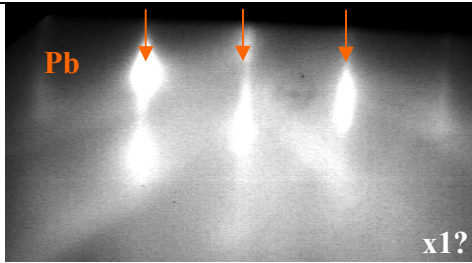
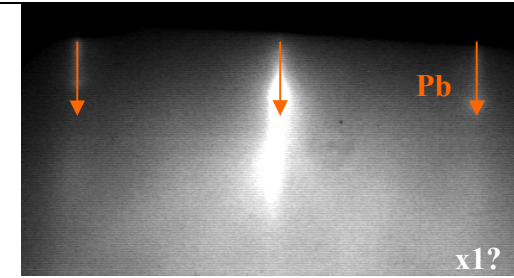
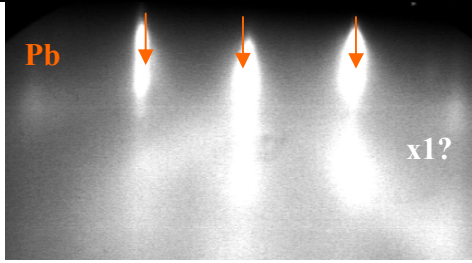
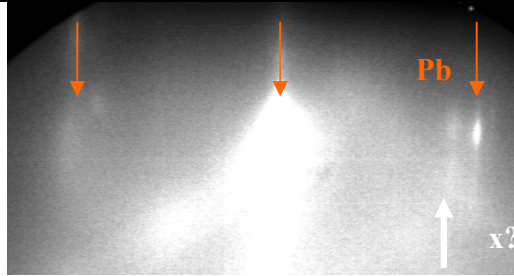
Sample	[1-10]	[11-2]
Pb (111) clean		
Pb_Si70mins		
Pb_Ge70s		

Figure 14: RHEED patterns on clean Pb (111) and Pb/Si(70mins), Pb/Ge(70s) samples. Blurred x1 reconstruction patterns are recorded after both Si and Ge deposition.

(4) SiGe alloy deposition on Ag(111) metal:

(b) Experimental and growth details

As an extension to our previous work on Ag(111), additional experiments (not reported in D2.1) are conducted here using 1 ML of mixed SiGe on Ag(111). A deposition rate of $\sim 4 \times 10^{-4}$ Å/s was used for both Si and Ge, aiming at a SiGe layer with a 50%-50% composition. The temperatures of the Si and Ge cells, were set at 1225 °C and 1080 °C, respectively, whereas the substrate temperature was held at 190 °C during deposition. A deposition time of 30 mins, is estimated to form ~ 1 ML of the SiGe alloy, whereas a higher coverage of 52.5 mins was also examined. The exact composition of the SiGe layer was found to be Ge: 55 at. %, Si: 45 at. %, using the detailed Si 2s (left) and Ge 3d (right) spectra presented in Figure 15.

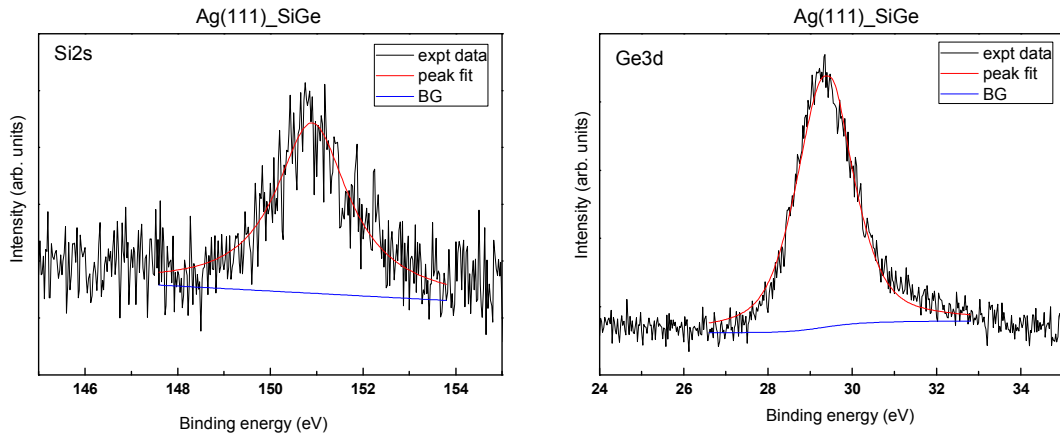


Figure 15: Detailed XPS spectra of the core level Si 2s (left) and Ge 3d (right) peaks for the SiGe-deposited Ag(111) surface.

(b) RHEED investigation

RHEED patterns recorded for the clean Ag(111) and SiGe-deposited Ag(111) surfaces are presented in Figure 16. As expected, a clean ordered 1x1 Ag(111) surface was obtained after the cleaning procedure. Upon SiGe-deposition a sharp RHEED pattern resembling a x4 strucure with a missing middle streak is observed along the [1-10] for both coverages. The RHEED patterns along [11-2] are more complex and they are probably a mixture (superposition of patterns). In particular, it can be inferred that in the case of the 52.5 mins-deposited SiGe layer, two of the overlayer streaks are enhanced in intensity as compared to the 30 mins-deposited sample. At present we are studying different SiGe compositions to observe the evolution from purely Ag/Si to pure Ag/Ge case. This may help us resolving the RHEED patterns and get a better idea of the possible superstructures formed. Nevertheless, the RHEED patterns presented in Figure 16, indicate that when Si and Ge are mixed on Ag, they still form ordered 2D structures, which is by itself very interesting. It should also be noted that similar RHEED patterns were recorded in the case of the Ag(111)/Ge(45mins)/Si(45mins), as reported in D3.1.

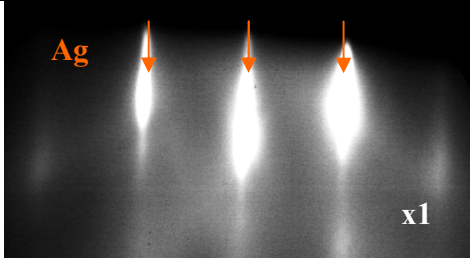
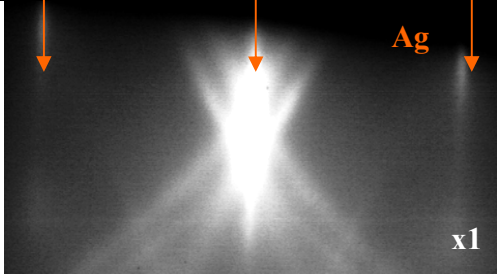
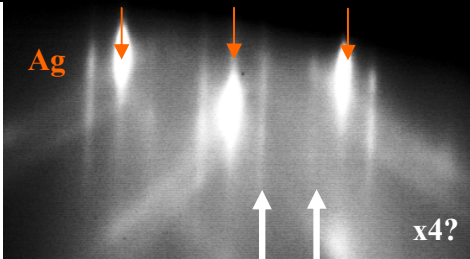
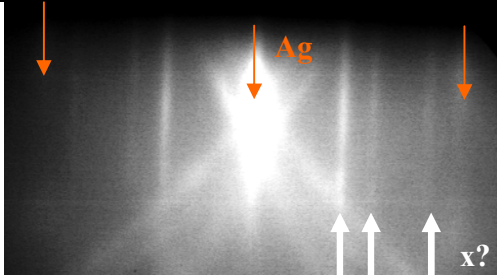
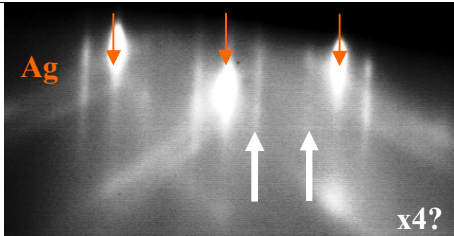
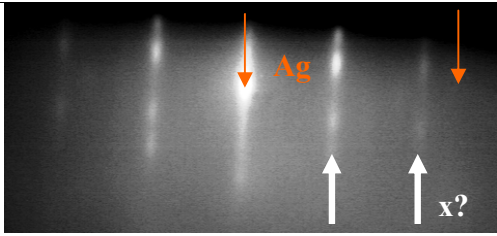
Sample	[1-10]	[11-2]
Ag (111) clean		
Ag_SiGe30mins		
Ag_SiGe52.5mins		

Figure 16: RHEED patterns on clean Ag (111) and SiGe-deposited (30 and 52.5mins) Ag(111) sample. The pattern along the [1-10] azimuth always shows a pattern which resembles a x4 with a missing middle steak.

(c) VB structure investigation by angle-resolved UPS

The ARUPS spectra along ΓK direction for the Ag(111)/SiGe structure (Figure 17) resemble those recorded for the Ag(111)/Ge(45mins)/Si(45mins) one, in agreement with the RHEED data presented in the previous section. In addition, it can also be said that no big differences are obtained with respect to the case of Si directly deposited on

Ag(111) with the 4x4 trigonal superstructure (D2.1), nevertheless silicene formation cannot be justified based on these results.

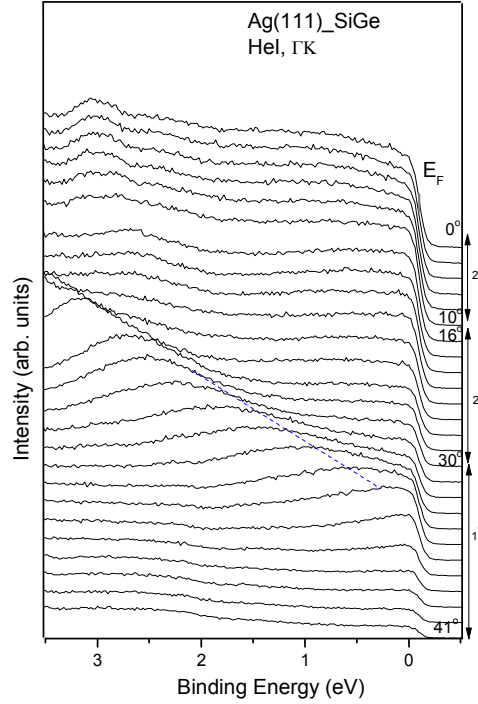


Figure 17: ARUPS spectra for the SiGe-deposited Ag(111) sample at different polar angles θ , recorded along the ΓK direction.

D. Summary

The aim of this deliverable was to study the role of various metals (Au, Rh, Pb), on the growth of graphene-like Si and Ge layers. Deposited samples were analyzed *in-situ* by LEED, RHEED, STM, XPS, LEISS and UPS. Some interesting structural and spectroscopic results have been obtained in the case of Au(111) and Rh(111) metals, without pointing however to the formation of silicene/germanene layers. Finally a mixed SiGe layer was also study, as an extension to the work already performed on Ag(111). The main results are briefly outlined as follows:

Growth on Au(111) substrate: Ordered structures of Si and Ge have been achieved on Au(111), as confirmed by both CNRS-CINaM and NCSR-D. Specifically, it turns out that in the case of Ge deposition, a substrate temperature of 150 °C, is critical in obtaining an ordered structure, whereas Ge diffusion into bulk Au(111) probably occurs at temperatures higher than 270 °C- 280 °C. Taking into account that elemental Ge is grown on Au(111) at RT, further investigation of the Au(111)/Ge system grown in the

150-300 °C range is planned at NCSR-D. Regarding Si deposition, a RHEED pattern indicating the formation of a 3x3 trigonal superstructure is being recorded, in contrast to the 4x4 trigonal structure obtained for the Ag(111)/Si system. Nevertheless, the formation of a gold silicide surface alloy seems to be the most probable scenario for the growth of Si on Au(111), as indicated by XPS data.

Growth on Rh(111) substrate: Ge deposition on clean Rh(111) results in x3 or x6 RHEED pattern for [11-2] azimuth, depending on coverage. However, the surface superstructure has not been resolved yet, since there is still an uncertainty in the patterns recorded along [1-10]. In addition, a non-dispersive Ge-related feature at 1.8 eV has been observed in the ARUPS data of the Rh(111)/Ge sample not evident in bare Rh(111) and Ag(111)/Ge (100mins) surfaces. Similarly to the case of the Au(111)/Si system, further theoretical investigation is needed, in order to be able to explain the nature of such a feature. Finally, Si growth on Rh was unsuccessful, probably due to the formation of an amorphous Si-based overlayer.

Growth on Pb(111) substrate: Growth of both Si and Ge on Pb(111) was unsuccessful as indicated by amorphous-like RHEED patterns. This finding has been explained in terms of XPS and LEISS data that have shown the possible dissolution of Si and Ge atoms on bulk Rh(111).

Growth of mixed SiGe on Ag(111) substrate: First results on a mixed SiGe (Ge: 55 at. %, Si: 45 at. %) layer grown on Ag(111), indicate an ordered 2D structure. Specifically, a x4 pattern is most probably observed along [1-10], whereas the surface superstructure remains unresolved due to the more complex pattern recorded along [11-2]. ARPES data of the mixed sample closely resemble those collected in the case of the Ag(111)/Si system.

E. Conclusive remarks about the role of metals

Although it is not possible at this stage to fully assess the role of metals in the formation of silicene, a few first hints could be given here. Perhaps the most important requirement/property is that metals should not mix with silicon or germanium to form alloys. So far, only for Ag we can say with certainty that it does not mix with Si and probably it does not mix extensively with Ge as well, except from a surface alloy formed at low coverage. Based on the evidence we have obtained so far, we can say that probably Au does not mix with Ge while the situation for the Au/Si system is not so clear (there may be a possibility that they mix). Si and Ge on Ag and Au respectively, exhibit a remarkable property: they wet the metal surface instead of forming 3D islands as one might expect. Yet they arrange themselves in an orderly manner forming well-defined superstructures (especially Si on Ag). In case of Ag, the special lattice coincidence $4d_{111}(\text{Ag}) = 3d(\text{silicene})$ may be a key point for the ordering of Si on Ag. Ag as a noble metal reacts weakly with Si giving it eventually the freedom to arrange itself with a variety of bond angles and buckling due to a mixture of sp² and sp³ hybridization. This may give Si the flexibility to form different silicene superstructures on Ag with different

degrees of buckling and, consequently, density or coverage. Yet, this still needs further exploration of both structural and electronic properties.

References

- [1] P. Vogt, P. De Padova, C. Quaresima, J. Avila, E. Frantzeskakis, M.C. Asensio, A. Resta, B. Ealet, and G. Le Lay, *Phys. Rev. Lett.* 108, 155501 (2012).
- [2] D. Chiappe, C. Grazianetti,, G. Tallarida, M. Fanciulli, and A. Molle
Advanced materials, in press
- [3] B. Lalmi, H. Oughaddou, H. Enriquez, A. Kara, S. Vizzini, B. Ealet, and B. Aufray, *Appl. Phys. Lett.* 97, 223109 (2010)
- [4] C.-L. Lin, R. Arafune, K. Kawahara, N. Tsukahara, E. Minamitani, Y. Kim, N. Takagi and M. Kawai, *M. Appl. Phys. Express* 5, 045802 (2012).
- [5] B. Feng, Z. Ding, S. Meng, Y. Yao, X. He, P. Cheng, L. Chen, and K. Wu, *Nano Lett*, in press
- [6] H Jamgotchian, Y Colignon, N Hamzaoui, B Ealet, J Y Hoarau, B Aufray and J P Biberian, *J. Phys.: Condens. Matter* 24, 172001 (2012)
- [7] A. Fleurence et al., *Phys. Rev. Lett.* 108, 245501 (2012).
- [8] M. Houssa, G. Pourtois, V. V. Afanas'ev, and A. Stesmans, *Appl. Phys. Lett.* 96, 082111 (2010)
- [9] S. Cahangirov, S., Topsakal, M., Aktörk, E., Sahin, H., Ciraci, S. *Phys. Rev. Lett.* 102, 236804 (2009).
- [10] R.W. Olesinki, G.J. Abbaschian, *Bull. Alloy Phase Diagr.* 5 (1984) 271.
- [11] ASM Metals HandBook Volume 03 - Alloy Phase Diagrams, 1992, ASM International
- [12] G. Le Lay, *Surf. Sci.* 132, 169 (1984)
- [13] D. Dornisch, W. Moritz, H. Schulz, R. Feidenhans'l, M. Nielsen, F. Grey and R. L. Johnson, *Phys. Rev. B* 44, 11221 (1991)
- [14] E.P. Burte and G. Newer, *Appl. Surf. Sci.* 53, 283 (1991)
- [15] A Petkova, J Wollschl"ager, H L G"unter and M Henzler, *J. Phys.: Condens. Matter* 11, 9925 (1999)
- [16] Y. Sato and S. Chiang, *Surf. Sci.* 603, 2300 (2009)
- [17] Frank Endres and Sherif Zein El Abedin *Phys. Chem. Chem. Phys.*, 2002,4, 1640-1648
- [18] Frank Endres and Sherif Zein El Abedin *Phys. Chem. Chem. Phys.*, 2002,4, 1649-1657
- [19] Xuehai Liang, Youn-Geun Kim, Daniel K. Gebergziabiher and John L. Stickney
Langmuir, 2010, 26 (4), pp 2877–2884
- [20] N. Birisenko, S. Zein, El Abedin and F. Endres, *J. Phys. Chem. B* 110, 6250 (2006)
- [21] Chiranjib Majumder, *Phys. Rev. B* 75, 235409 (2007)
- [22] B. Sundaravel, K. Sekar, G. Kuri, P.V. Satyam, B.N. Dev, Santanu Bera, S.V. Narasimhan, P. Chakraborty, F. Caccavale, *Appl. Surf. Sci.* 137, 103 (1999)
- [23] A. Dimoulas. D. Tsoutsou, E. Golias, D. Kaltsas, L. Tsetseris, B. Ealet and G. Le Lay, accepted to GraphEL Conference, 27-30 September 2012, Mykonos, Greece.
- [24] H. G. Zimmer and A. Goldmann, *Surf. Sci.* 7, 1 (1986)

- [25] K. A. Mills, R. F. Davis, S. D. Kevan, G. Thornton and D. A. Shirley *Phys. Rev. B* 22, 581 (1980)
- [26] R. G. Musket, W. McLean, C. A. Colmenares, D. M. Makowiecki and W. J. Siekhaus, *Appl. Surf. Sci.* 10, 143 (1982)
- [27] H. Hochst and M. K. Kelly, *Phys. Rev. B* 30, 1708 (1984)