On the Use of Pb as Intermediate Adsorbate for the *In Situ* Preparation of Ideal Si(111)-(1x1):H Templates

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Abstract

A novel dry in situ passivation process is presented, based on the use of a group IV metal as intermediate adsorbate : a Pb-induced $(\sqrt{3}x\sqrt{3})R30^\circ$ - β phase with a saturation coverage of 1/3 ML is exposed to activated atomic hydrogen, resulting in the formation of a well-ordered flat unreconstructed Si(111)-(1x1): H surface. UHV STM observations reveal that the structural perfection of the hydrogenated (111) planes, far above the one of surfaces prepared by direct hydrogenation *in situ*, is comparable to the one of best surfaces chemically passivated *ex situ*. A Volmer-Weber growth mode is confirmed for the initial deposition of metal atoms onto a monohydride termination at room temperature. Non reversible phase transitions $((\sqrt{3}x\sqrt{3})$:Pb→(1x1): H→(7x7):Si) are clearly evidenced on the basis of LEED and AUGER data. The "prototypical" unreactive metal-silicon system Pb on unpinned Si(111)-(1x1):H is found to exhibit attractive properties for the fabrication of nanostructures with the group IV element.

1. Introduction

The characterization of the chemical nature, the structural arrangement, and the electronic properties related to Si(111)-(1x1): H monohydride templates is crucial for gaining a determinant understanding of numerous associated fundamental physical phenomena. As a matter of fact, the first measurement of the lifetime of an adsorbate-substrate vibration was realized on such an ideally terminated Si(111) surface prepared by wet chemical procedure [1]: a value $T_1 = 0.8$ ns ± 0.1 ns was attributed to a single Si-H stretch vibration purely polarized perpendicularly to the (111) plane. In addition, well-known intrinsic properties of ideal (1x1):H surfaces, i.e. a remarkable flatness of monohydride areas and a simple unit cell geometry, made the stable monohydride termination an excellent candidate to conclusive investigations on first principles calculations of the valence band surface electronic structure [2], and on substrate-adsorbate interactions contributing to an enhanced development of potential applications for the advanced patterning of nanometer-scale devices [3,4]. Such passivated surfaces, representing a simple ideal system tunable at the atomic scale by addition or removal of hydrogen atoms, motivated numerous theoretical and experimental relevant investigations for a better knowledge of the monohydride chemisorption phase on the various dimer adatom stacking-fault (DAS) structural units of a clean annealed and well-ordered Si(111) 7x7 reconstruction [5-14], leading to a more accurate theoretical approach of the initial chemisorption of hydrogen and to a detailed structural description of the surface rearrangements induced by different coverages of the ideal adsorbate.

So far, the influence of local order on the electronic structure of Si(111)-(1x1):H surfaces was studied once with high resolution core-level photoemission spectroscopy (CLPES) [2]. It was underlined in the above investigations that chemically prepared silicon surfaces exhibit the absence of any reconstruction, a case different from H-exposed silicon surfaces on which some reconstruction and/or local strain may drastically affect the electronic structure. The latter argument can be extended to the presence of In islands still remaining after *in situ* exposure of a $(\sqrt{3}x\sqrt{3})$:In reconstruction to atomic hydrogen. This is electronically speaking rather significative since it induces a large lateral variation of the Fermi level position, spectroscopically characterized by the observation of an asymmetric phonon broadening on the high energy side of a bulk-sensitive Si 2p spectrum ($h\nu = 108$ eV) [15].

A part of the work described in details here below, consisted in the development of a novel dry *in situ* passivation process based on the exposure of a Pb-induced $(\sqrt{3}x\sqrt{3})R30^\circ$- β phase to activated atomic hydrogen for the final formation of a well-ordered (1x1):H surface with remaining Pb islands.

This method is of particular interest since the lower desorption temperature value of the group IV metal (400℃) compared with the desorption temperature value of hydrogen (550℃) may permit to recover a pristine monohydride terminated surface with its original surface electronic structure characterized by flat band conditions. This is not the case with a scope of various intermediate adsorbates previously selected for the application of similar dry hydrogenation processes (In[15], Ag[16], Al[17]) : metal atoms were still present on an ideal (1x1):H surface for temperatures up to total desorption of the hydrogen monolayer.

The possibility to gently desorb Pb clusters by moderate heating while preserving an underlying (1x1): H reconstruction can be of a considerable impact when considering ideal conditions for probing the electronic structure of the (1x1): H surface, particularly by using surface sensitive spectroscopical methods such as CLPES [18]. The persistence of stacking faulted areas reported for direct hydrogen exposure of a Si(111) 7x7 reconstruction to atomic hydrogen is in our case eradicated since passivation occurs on an unreconstructed silicon topmost atomic layer with Pb adatoms in T_4 adsorption sites [19] : the application of a light 4000 L hydrogen dose and a precise setting of the substrate temperature at 400℃ favoures the replacement of Si-Pb bonds by saturated Si-H bonds.

Hence, the perfection of the final (1x1):H structure, far above the one of surfaces prepared by direct hydrogenation *in situ,* can be comparable to the one of best surfaces chemically etched *ex situ,* as evidenced by our atomically resolved STM images recorded in the constant current topographic mode (CCT).

We suggest this can be determinant for a straightforward and ideal interpretation of physical contributions in Si2p core-level spectra of clean *in situ* prepared Si(111)-(1x1):H surfaces.

2. Experimentals

Spectroscopical measurements and diffraction observations were carried out in a home-built ultra-high vacuum (UHV) system specially designed for molecular beam epitaxial (MBE) growth, with a base pressure remaining in the low 10^{-10} mbar range (P< 5.10^{-10} mbar). The analysis chamber was equipped with a double pass cylindrical mirror analyzer (CMA) for performing Auger electron spectroscopy (AES), a four grid low energy electron diffraction (LEED) optics, a Pb Knudsen cell, and a quartz crystal thickness monitor fixed on the reverse side of the sample stage in UHV. We used a commercial scanning tunneling microscope (OMICRON Vakuum physik GmbH) to study different samples surface topographies related to various experimental stages of the novel hydrogenation process.

Si(111) specimens were cut from a N-type mirror-polished wafer and degreased with organic solutions prior to their introduction into high vacuum. *In situ* cleaning by DC current heating consisted of a first degassing period of ~12 hours around 500℃ followed by several annealing steps up to a maximum temperature of ~1100℃ while maintaining the background pressure at values below 5.10^{-9} mbar. For final preparation in the low 10^{-10} mbar range, doped Si(111) samples were flashed up to 1200℃ (t<10s), maintained around 800℃ for 1 min. and slowly cooled down to room temperature (t = ~20 min.), giving rise to a very sharp 7x7 LEED pattern with no significant trace of contaminants detected on corresponding AES spectra.

In situ condensation of 0.8 ML of Pb (1 ML= 7.84 10^{14} atoms/cm^2) onto a clean well-ordered Si(111)7x7 reconstruction was monitored with an evaporation rate below 0.1 ML/min. . Further annealing lowered the coverage of metal, leading to the formation of the so-called $(\sqrt{3}x\sqrt{3})R30^\circ$ - β phase identified by its characteristic LEED pattern. Atomic hydrogen exposure of the well-known superstructure was consequently processed in stable conditions at a pressure of 4.10^{-6} Torr with the sample facing a hot (1700℃) Tungsten filament located at a distance of 10 cm. The surface of the silicon substrates was carefully maintained at 400℃ during the *in situ* application of a 4000 L hydrogen dose (1L = 1 Langmuir=10^{-6}Torr·s). After this treatment, LEED showed a 1x1 periodicity and no extra-spot attributed to the former $(\sqrt{3}x\sqrt{3})R30^\circ$- β phase was visible within a large range of primary energy values. Subsequent STM measurements confirmed the presence of the monohydride termination on wide passivated (111) terraces.

3. Results and discussion

3.1 Low Energy Electron Diffraction

The selection of a Pb induced $(\sqrt{3}x\sqrt{3})R30^{\circ}$ - β superstructure as good candidate for passivation was mainly motivated by its particular structural arrangement characterized by an underlying unreconstructed silicon topmost atomic layer [19]. The low saturation coverage ($\theta = 1/3$ ML) offered the opportunity to limit the possible interaction of Pb atoms with a UHV environment highly sensitive to contamination while processing at the atomic hydrogen exposure *in situ*.

The cleaning procedure of Si(111) specimens resulted in a very sharp 7x7 diffraction pattern with low background scattering, indicative of a clean well-ordered starting bare silicon surface. Deposition of 0.8 ML of metal onto the room temperature silicon substrate, followed by high temperature annealing at 430℃, rendered the $(\sqrt{3}x\sqrt{3})R30^{\circ}$ - β phase clearly visible at low primary energy value (40 eV), an observation consistent with the 2D phase diagram of the Pb/Si(111) system presented by Yaguchi et al. in a RHEED study of Pb submonolayer deposition onto a clean 7x7 reconstructed Si(111) surface [20] : it was reported that a $(\sqrt{3}x\sqrt{3})$ reconstruction could be formed at submonolayer coverage by thermal desorption from a 1x1 structure. We can clearly distinguish in Fig.1b) large bright spots corresponding to first order Si bulk lattice reflections together with medium-size faint spots representing the incommensurate Pb overlayer. No small dots related to Pb incommensurate spots by Si reciprocal lattice vectors are visible, traducing a non modulation of metal atom positions by the underlying Si substrate that is, Pb adatoms are all positioned in the same atomic plane.

After exposure of the unfaulted $(\sqrt{3}x\sqrt{3})R30^{\circ}$ - β superstructure to atomic hydrogen, the well-known pattern of a passivated Si(111) surface was clearly distinguishable at 40 eV (cf Fig.1c)). We believe Pb was still present on the ideal (1x1): H surface since, as a direct consequence, thermal desorption of metal monitored by AES permitted to significantly lower the background intensity without alteration of the previous 1x1 periodicity.

The presence of the group IV element just after passivation is also confirmed on the basis of our Auger data.

3.2 Auger Electron Spectroscopy

Auger spectra acquisition was performed for a primary energy value of 2500 eV in the derivative mode. Fig.2a) shows an AES spectrum measured on the freshly obtained Si(111)-(1x1):H surface. The intensity of the Pb Auger signal (NOO peak at 250 eV) confirms the presence of metal on the hydrogen terminated surface probably under the form of 3D clusters, assuming a mechanism similar to the one proposed by Landemark et al. for the H-exposure of a $(\sqrt{3}x\sqrt{3})$:In surface [15]: Si-Pb bonds are broken and replaced by saturated Si-H bonds while Pb atoms can be moved into islands.

Non reversible phase transitions ($(\sqrt{3}x\sqrt{3})$:Pb → (1x1):H → (7x7):Si) can be clearly evidenced with the overall set of AES data displayed in Fig.2. After thermal desorption of hydrogen at 550℃, the LEED pattern surprisingly exhibited a 7x7 periodicity, with a corresponding AES spectrum similar to the one obtained by *in situ* cleaning of our Si(111) substrates (cf Fig.2b)).

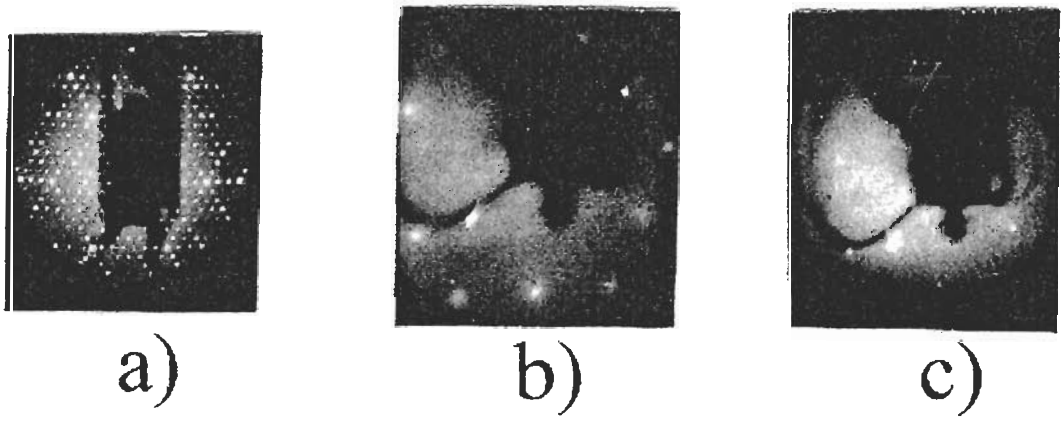

Fig.1 LEED patterns of the three fundamental phases implicated in our novel passivation process.
a) Si(111)-(7x7) - 78 eV
b) Si(111)-$(\sqrt{3}x\sqrt{3})$:Pb - 40 eV
c) Si(111)-(1x1):H - 40 eV

Fig.2a)

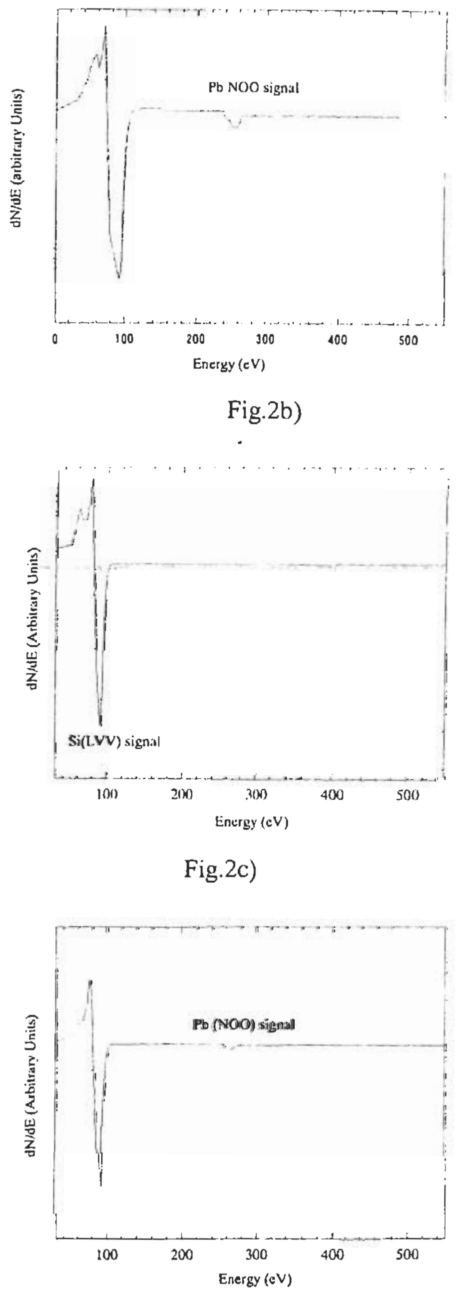

Fig.2 a) Auger spectrum of the ideal Si(111)-(1x1):H surface recorded just after dry *in situ* passivation. The Auger Pb signal (NOO at 250 eV) is present.
b) Auger spectrum of the Si(111) 7x7 reconstructed surface measured after thermal hydrogen desorption. No peak related to any previous adsorbate specie is still detectable.
c) Auger spectrum of the ($\sqrt{3}$x$\sqrt{3}$)R30° - β phase (identified by LEED) induced by submonolayer adsorption of Pb and moderate substrate heating. The presence of metal on the silicon substrate is deduced from the presence of the Pb NOO signal at ~250 eV.

No trace of peaks related to previous adsorbate species (Pb, H) was detectable. This is attributed to the higher desorption temperature value of hydrogen compared with the desorption temperature value of lead, in the case of silicon substrates. The lack of superficial metal atoms earlier desorbed at lower temperatures makes it impossible to recover the former ($\sqrt{3}$x$\sqrt{3}$)R30°-β phase induced by Pb adsorption and moderate substrate heating (cf Fig.2c)).

To our knowledge, this is the first time such an observation is reported, considering in situ passivation procedures with intermediate adsorbates arranged in a ($\sqrt{3}$x$\sqrt{3}$)R30° reconstruction.

3.3 Scanning Tunneling Microscopy

Fig.3 shows an atomically resolved STM image of the monohydride termination (U_{sample}= -1 V, I_{tunnel}= 0.5 nA, 60x60 Å^2) obtained without the use of statistical differencing. The corresponding grey scale, linked to the height of atomic protrusions is homogeneously distributed over 98.5% of the scanned area. The related corrugation is then expected to be very small (presumably less than 1Å) confirming the efficiency of our novel hydrogenation process at a local atomic scale, leading to a final flat unfaulted passivated surface with equidistant hydrogen atoms separated by approximately 4 Å distance.

Fig.4 shows a filled states STM image (U_{sample} = -2.2 V, I_{tunnel}= 1.0 nA, 1000x1000Å^2) recorded after MBE room temperature deposition of 0.6 ML of Pb onto a clean hydrogenated topmost silicon layer. Remaining metal atoms were

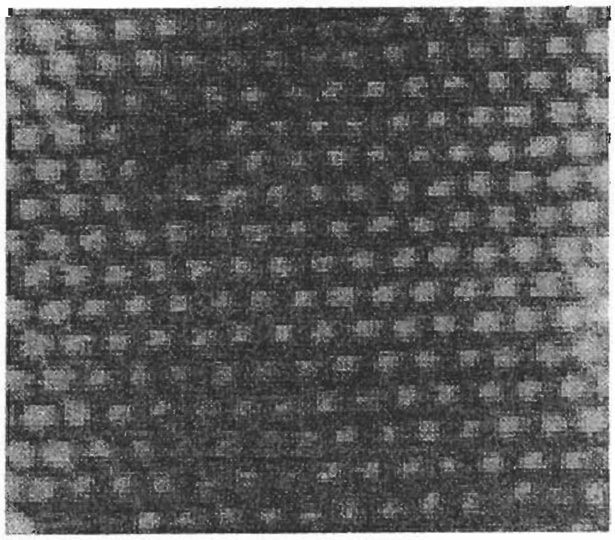

Fig.3 Local scale STM image of the monohydride termination obtained by application of our novel passivation process.

thermally desorbed prior to condensation *in situ* of the group IV element in order to clearly attribute the formation of 3D clusters to the evaporation of Pb by passing from flat topographical scanning conditions to tri-dimensional imaging. One can estimate the diameter of hemispherical islands to be equal to ~50Å . The corrugation measured for two of these islands revealed an average height of ~13Å. We noted a continuous decrease of corresponding diameters with increasing heights. Pb islands are essentially located near holes appearing as dark large areas in our filled states STM image. Few islands are also located at step edges, surprisingly forming a quasi-continuous line of ~250 Å length (right side of the image). The presence of bright tri-dimensional islands on flat wide hydrogenated terraces reveals a Volmer-Weber growth mode which is confirmed by the persistence of 3D growth at increasing coverages up to 10 ML in the same experimental conditions, as evidenced in Fig.5 (U_{sample}= -2.0 V, I_{tunnel}= 0.7 nA, 2200x2200 Å^2). Annealing such a surface at 300℃(t = 10 min.) changes not only the surface distribution but also the size with the shape of 3D clusters, now back to a more pronounced hemispherical geometry close to the Si(111)-(1x1):H surface (cf Fig.6) : islands have coalesced after thermally induced surface transport, now covering wide hydrogenated areas underneath.

The group IV element appears consequently to be quite suitable for advanced nanostructuring on ideal Si(111)-(1x1):H templates. It might be possible to rapidly fill depassivated areas of various extension scales by surface diffusion of Pb atoms at reasonable temperatures (T< 400℃). UHV VT STM is consequently promoted as an excellent tool for the patterning of metallic electrodes, together with extremely narrow lines (width< 10Å) of the group IV metal. The latter nanostructures could even be purely created by controlled diffusion of Pb atoms towards definite areas on passivated (1x1):H templates, opening the field to a variety of novel scientifical investigations related to a wealth of interesting phenomena.

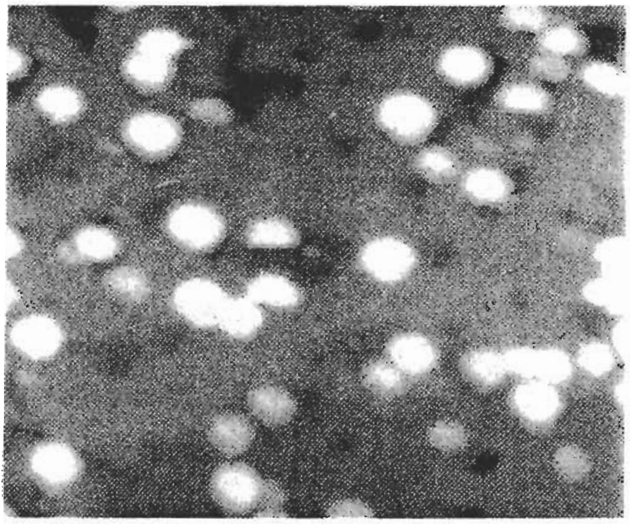

Fig.4 STM image of 0.6 ML of Pb deposited onto a clean Si(111)-(1x1):H surface at room temperature (evaporation rate below 0.1ML/min.). Large bright protrusions correspond to 3D Pb islands.

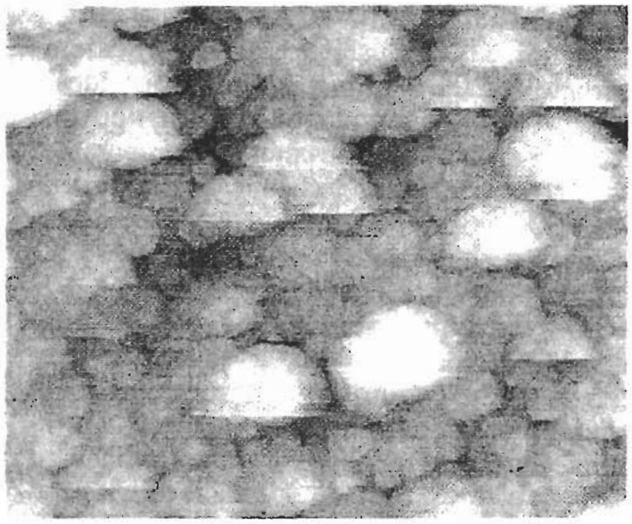

Fig.5 Filled states STM image of a 10 ML Pb deposit onto a Si(111)-(1x1):H surface at room temperature. The experimental conditions are similar to the ones briefly outlined Fig.4.

Our passivation process is therefore a promising candidate for the fabrication of Pb nanowires on ideal Si(111)-(1x1):H surfaces.

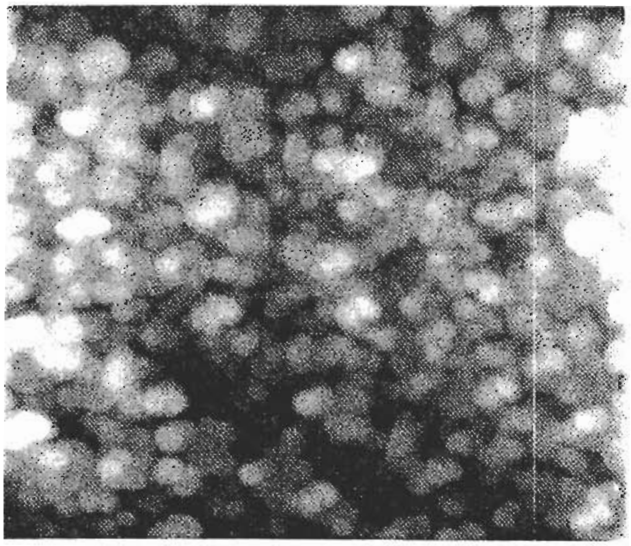

Fig.6 Coalesced Pb clusters imaged at negative sample bias after annealing a 10 ML Pb deposit at a temperature of 300℃ for 10 minutes.

4. Conclusion

In summary, we used Pb as intermediate adsorbate for the *in situ* preparation of ideal Si(111)-(1x1):H templates. The structural perfection of the 1x1:H structure is comparable to the one of best surfaces chemically passivated *ex situ*. A Volmer-Weber growth mode is evidenced for the initial condensation phase of Pb atoms on the passivated Si(111) surface.

The first experimental evidence of non reversible phase transitions gives a particular interest to the "prototypical" metal-silicon system Pb on unpinned Si(111)-(1x1):H which exhibits attractive properties for the fabrication of nanostructures. Surface diffusion might be a powerful method for an efficient formation of Pb nanowires on ideal Si(111)-(1x1):H templates. Related studies are currently under progress.

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