

Interstitial chemisorption and interface formation of Pt on Si(111) observed by surface extended x-ray-absorption fine-structure and $L_{2,3}$ -edge x-ray-absorption resonance spectroscopies

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The first structural description of the Pt/Si(111)7×7 interface formation at room temperature is derived from Pt L_3 -edge surface extended x-ray-absorption fine-structure spectroscopy and x-ray-absorption resonance spectroscopy. Pt chemisorbs in the top Si double-layer sixfold interstitial sites, introducing stress in the surface and subsurface. Above monolayer thicknesses Pt diffuses within the silicon substrate and, upon Pt enrichment of the intermixed phase, clusters with Pt₂Si local coordination nucleate.

One of the most fundamental goals of interface science is to understand the nucleation and growth phenomenology of metal-semiconductor interfaces. A well-established approach is that of studying the metastable early stages of interface formation that are obtained by limiting the supply of metal atoms on atomically clean semiconductor surfaces. The reaction kinetics is turned on and off by allowing subsequent exposures of the substrate to metal vapors and/or by annealing the interface. The complexity of native interfaces (not annealed) forces the crystallographic analysis to be local since long-range order is lacking and interface heterogeneity is possible.¹

The Pt/Si(111) interface is a prototype of the reactive transition-metal-semiconductor systems,²⁻⁷ as well as a Schottky junction of great technological importance.⁸ Yet a direct structural description of the early stages of the Pt/Si(111) interface formation is unavailable. Surface extended x-ray-absorption fine-structure spectroscopy (SEXAFS) has already been employed for the study of two typical metal silicon interfaces: Ag/Si(111)7×7 (Ref. 9) and Ni/Si(111)7×7.¹⁰ The Ag/Si(111)7×7 system is weakly reactive: At submonolayer coverages and room temperature (RT) Ag chemisorbs in the threefold hollow sites, but upon annealing and reconstruction, it penetrates into the intralayer sixfold hollow sites. The Ni/Si(111) reactive interface is characterized by chemisorption directly into the sixfold interstitial sites at submonolayer coverage. The chemisorbed layer was interpreted as forming the template structure for the epitaxial growth of cubic NiSi₂ via Ni substitution in Si lattice positions.¹⁰

The Pt/Si(111) system is a more complex case. Both stable compounds [Pt₂Si (tetragonal), PtSi (orthorhombic)] and metastable phases (Pt₃Si, monoclinic) have anisotropic crystal structures.¹¹

Epitaxy is possible for PtSi(010) parallel to Si(111),¹² but PtSi is the end product of the interface reaction obtained after annealing at above 600 °C, and is not expected at RT.⁷

The energy distribution of the density of states (DOS) measured at the Pt/Si interface by photoemission³ is silicidlike. We present here SEXAFS and x-ray-absorption

resonance spectroscopy (XARS) results that give a clear picture of the interface evolution and which nicely explain and complement the published spectroscopic data.

The local environment of the Pt atoms adsorbed onto atomically clean Si(111)7×7 was derived for some Pt coverages from the Pt L_3 -edge extended x-ray-absorption fine-structure (EXAFS) oscillations that were measured with the total-electron-yield technique.¹³ The excitation source was synchrotron radiation from the DCI storage ring (operated at 1.72 GeV, 200 mA) at Laboratoire pour l'Utilisation du Rayonnement Electromagnetique (LURE). Monochromatization was assured by a double-crystal Si(311) device operated in the range 11 450–12 250 eV and at around 13 275 eV for Pt L_3 and L_2 edges, respectively. Si(111)7×7 surfaces were prepared by direct Ohmic heating of the wafer up to 1200 °C and subsequent slow cooling down to RT, and checked *in situ* (by low-energy electron diffraction and Auger electron spectroscopy). The Pt deposits were made by heating Pt-wrapped W filaments and were monitored by a quartz microbalance that could be put in the sample position (at 10 cm from the Pt source) and by Auger peak amplitude ratios. We estimate the absolute coverage accuracy to be ±30%. Slow evaporation rates were used in order to minimize the spurious effects of substrate heating. Epitaxial PtSi was grown *in situ* by exposing a resistively heated Si(111) substrate held at 600 °C to the flux from two Pt evaporators, for 2 h (deposition rate 2 Å/min).

The data were taken with the light polarization vector nearly parallel to the sample surface, adding spectra taken at slightly different angles for filtering the substrate Bragg diffractions. Standard L_3 EXAFS analysis¹⁴ was done on the experimental curves of Fig. 1, and on the PtSi standard. First, interatomic distances were derived by transferring the experimental phase shift from PtSi (Ref. 15) to the interface data, while information on the higher coordination shells was obtained by comparing the data with simulated EXAFS spectra that were constructed using the experimental phase and amplitudes. For the submonolayer data (Figs. 1 and 2) the analysis of the first coordination peak indicates a Pt-Si nearest-neighbor dis-

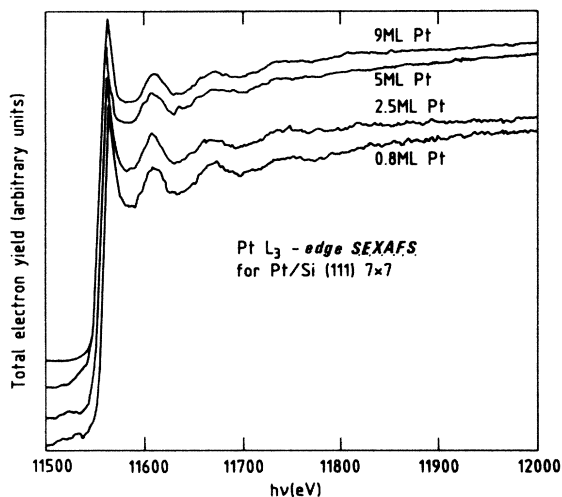


FIG. 1. Total-electron-yield measure of the x-ray-absorption coefficient of Pt above the L_3 edge for Pt atoms adsorbed onto Si(111) at room temperature. The sharp white lines are due to dipole transitions from Pt $2p_{3/2}$ to the empty part of the Pt $5d$ -Si $3p$ antibonding hybrid states.

tance of $2.48 \pm 0.03 \text{ \AA}$ (to be compared with 2.46 \AA in Pt_2Si , and average 2.5 \AA in PtSi), and a coordination number of 6 ± 1 . These results unambiguously determine the Pt chemisorption site as the sixfold surface interstitial site between the top and second Si(111) planes. The measured Pt-Si distance implies displacements within the Si lattice due to the interstitial Pt. The expansion of the sixfold Si cage containing the metal interstitial atom is a point of crucial importance in understanding the energetics of the chemisorption and the onset of the interdiffusion. In the case of Ni/Si(111) (Ni-Si first distance = $2.37 \pm 0.03 \text{ \AA}$) a large vertical expansion of the top Si layer (0.8 \AA) was suggested,¹⁰ while in the case of $(\sqrt{3} \times \sqrt{3})\text{Ag/Si(111)}$ (Ag-Si first distance of $2.48 \pm 0.03 \text{ \AA}$), the requirement of lateral expansion of the Si cage was mentioned.⁹ If only vertical expansion of the top Si layer was considered in the present case it would have to be $1.44 \pm 0.05 \text{ \AA}$, corresponding to a Si(111) top double-layer spacing of 2.22 \AA , with the Pt ideal plane in between ($1.11 \pm 0.05 \text{ \AA}$ below the Si surface). These displacements seem too large, and should cause a lateral Si lattice relaxation around the Pt interstitial sites.

A combination of vertical and lateral expansions of the sixfold Si cage is an alternative hypothesis. The Pt-Si second- and higher-neighbor distances calculated for the unperturbed Si lattice positions from the geometrical sixfold interstitial point were added in a SEXAFS simulation of the chemisorption site to the experimentally determined first-neighbor distance. The correspondence of the simulated peaks to the experimental peaks, in the Fourier transforms (FT's) up to the fifth Pt-Si simulated distance give strength to the hypothesis that information related to the Si next neighbors is contained in the peaks between 3 and 6 \AA . All other possible surface chemisorption sites, and the adamantane interstitial site were ruled out by this method, both for incompatible width, position, and/or amplitude of the first neighbor peak, and for disagreement

with the higher shell peaks. Beyond the confirmation of the site assignment, the comparison of the second- and fourth-nearest-neighbor simulated distances to the experiment allows us to discuss the distortion of the Si-Si bonds which are due to the Pt interstitial atoms. Higher than first-nearest-neighbor shell distances are seldom observed with SEXAFS; the corresponding FT peaks are less reliable than the first-neighbor peak due to the higher sensitivity to background subtraction procedures and noise. The best simulated data indicate the existence of both a moderate vertical expansion and of some lateral expansion of the Si(111) double-layer sixfold cages. Figure 2 shows the Fourier transform of the submonolayer data of Fig. 1, and the FT of an EXAFS simulation for the sixfold interstitial site of the top Si(111) double layer, as shown in the inset.

The correspondence of the simulated Pt-Si second-neighbor distance ($3.81 \pm 0.05 \text{ \AA}$) to the FT second peak implies a vertical outward displacement of the top-layer Si atoms of $0.58 \pm 0.05 \text{ \AA}$, and a lateral outward displacement (expansion) of all six first neighbors of $0.16 \pm 0.05 \text{ \AA}$, leaving the second-to-third-Si-layer distance unperturbed ($2.35 \pm 0.05 \text{ \AA}$). The influence of the data treatment on the position of the second experimental FT peak is of the order of $\pm 0.05 \text{ \AA}$. A further source of error follows from the use of first-shell phase and amplitudes for higher-shell analysis. The single-Si-third-nearest neighbor lies vertically underneath the Pt atom and contributes negligible scattering intensity in our measurement geometry. The fourth-nearest-neighbor peak fits with a distance of $4.54 \pm 0.05 \text{ \AA}$ which is 0.09 \AA larger than expected for an unperturbed top double layer. This would indicate a compression of the second-to-third-Si-neighbor

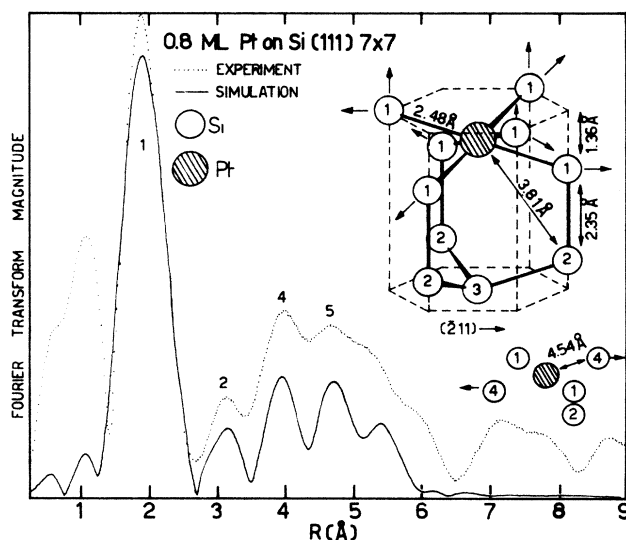


FIG. 2. Fourier transform of the background subtracted data for 0.8-ML Pt/Si(111) (bottom curve of Fig. 1), dotted line, and simulated SEXAFS results (solid line) for Pt in the sixfold surface interstitial (inset). The matching of the experimental peaks has been obtained by setting first nearest neighbors (NN) at 2.48 \AA , second NN at 3.81 \AA , fourth NN at 4.54 \AA , fifth NN at 5.21 \AA , and sixth NN at 5.87 \AA .

distance parallel to the surface. These results suggest medium-range perturbation parallel to the surface. According to the proposed higher-shell analysis the Pt environment is represented in the inset of Fig. 1. The observed medium-range perturbation of the Si top double layer induced by the chemisorption of Pt explains the changes in the Si DOS observed with Cooper minimum photoemission for submonolayers of Pt on cleaved Si(111) that were attributed to "Si surface disruption upon Pt chemisorption."²

Saturation of the Pt interstitial chemisorption in the top Si double layer, allowing for the lateral Si displacements, would be reached for a fraction of a monolayer (ML). At higher coverages the elastic energy stored in the Si double layer should increase and determine the onset of interdiffusion. The apparent homogeneity of the local coordination for the coverage of 0.8 ± 0.2 ML and the lack of Pt-Pt neighbors could possibly be explained by some occupancy of the identical sixfold sites between the third and fourth Si layers, as it was found for Ni/Si(111).¹⁰ Also in strict analogy to the (1 ML)Ag/Si(111) annealed system⁹ the metal sixfold interstitial position explains the $(\sqrt{3} \times \sqrt{3})$ Pt/Si(111) surface reconstruction obtained after mild annealing.¹⁶ Pt $L_{2,3}$ x-ray-absorption resonance spectroscopy (XARS) provides a measure of the redistribution and relative population changes of the empty d vs p local DOS.^{17,18} The Pt $L_{2,3}$ absorption edges for the submonolayer Pt/Si(111) interface show edge resonances much more pronounced than those of pure Pt. This implies a molecular-orbital bonding scheme with a very high density of unoccupied Pt $5d$ -Si $3p$ antibonding hybrid states. Due to the lack, at this stage, of Pt-Pt second-neighbor coordination the chemisorption phase cannot be considered silicelike.

FT's of the 2.5-ML Pt/Si(111) SEXAFS data are shown in Fig. 3. At 2.5 ML a reduction of the first-neighbor peak amplitude and the absence of higher-shell peaks out of the noise are observed.

Although the first-neighbor distance is unchanged (2.49 ± 0.03 Å) the peak amplitude indicates an average decrease of the Pt-Si coordination number (4.5 ± 1). No changes are seen in the XARS. This can be understood as the diffusion of Pt inside the Si substrate, with occupation of nonequivalent sites with average nearest-neighbor distance of 2.49 ± 0.03 Å and lack of longer-range order. At 5 ML the first-shell peak is further reduced in amplitude (peak A, Fig. 3) and a second coordination shell (peak B) appears out of the noise. The best simulation attributes this configuration to a local Pt₂Si-like coordination, i.e., four Si nearest neighbors at 2.46 Å, and four Pt second neighbors at 2.78 Å. The Pt-Si and Pt-Pt EXAFS oscillations are almost in phase opposition; this causes cancellation of EXAFS amplitude creating a deep valley between the peaks A and B. Consequently, peak B (and to a lesser extent peak A) are artificially narrow and cannot be isolated and back Fourier transformed, but only compared to two-shell SEXAFS simulations. The best simulation is shown in Fig. 3: It fits well the peak positions and widths, but not the relative intensities.

The L_3 resonance to continuum absorption ratio is reduced to a value intermediate between that of the diluted

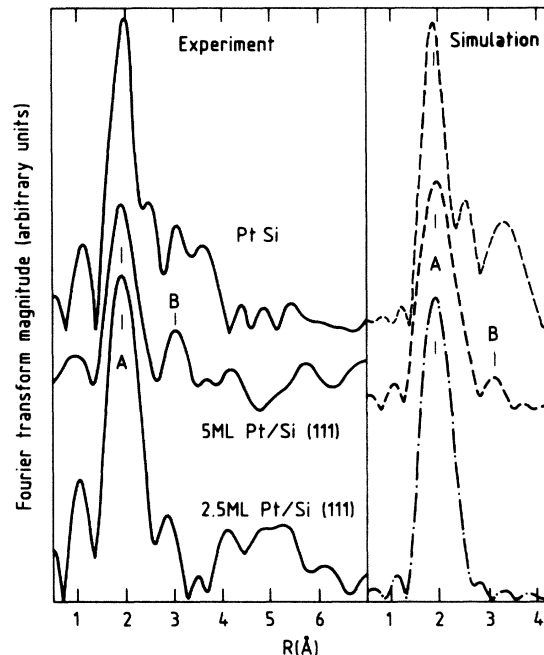


FIG. 3. FT for 2.5 ML (bottom), 5 ML (middle), and for epitaxial PtSi grown *in situ* on Si(111) (top). The right panel presents simulations of the data: 4.5 Si first NN's at 2.49 Å (dot-dashed line); "local" Pt₂Si coordination, i.e., four Pt-Si NN at 2.46 Å and four Pt-Pt second NN at 2.78 Å; PtSi.

Pt/Si (and PtSi) and that of metallic Pt (Fig. 4). The Pt L_3 - L_2 white line intensity ratio¹⁸ is very different for the interface with respect to pure Pt (Ref. 19) and to the silicides. This is a consequence of the Pt $5d$ band rehybridization in the bonding with Si, and its new l and j projections on the $2p$ core holes.

At 5 ML the L_3 - L_2 intensity ratio is larger than for PtSi,¹⁸ qualitatively in agreement with recent Pt₂Si results.²⁰ Peak B in the 5-ML transformed data could contain contributions from first Pt-Pt distances in small Pt

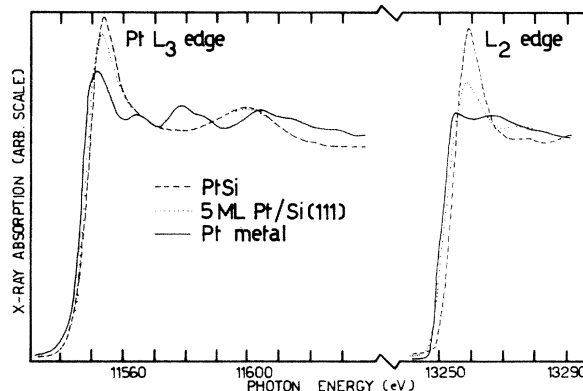


FIG. 4. XARS data for Pt L_3 and L_2 edges in fcc Pt (solid line), PtSi (dashed line), and 5-ML Pt/Si(111) (dotted line). The spectra are normalized below threshold and 30 eV above threshold.

clusters (Pt-Pt = 2.76 Å in fcc Pt). The L_2 resonance spectrum favors a dominant silicidlike phase at 5 ML. The same trends are confirmed in the 9-ML data.

The contribution of these data to our understanding of the growth of the Pt/Si(111) interface can be summarized as follows: After the saturation of the surface interstitial sites, the condensation of further Pt leads to diffusion within the substrate,²¹ and the formation of a Pt-Si solid solution with Pt-Si distances averaging 2.49 ± 0.03 Å and structural disorder at longer range. As the Pt concentration is increased at 5 ML, nuclei of Pt₂Si with coordination limited to the second-neighbor distance are formed. In the diffusion regime, Pt is thought to occupy both substitutional and interstitial diffusing sites (following a kick-out mechanism).²² In our experiment the interface layers are in a high-Pt-concentration regime and local compound nucleation is the dominant driving force for mass transport.

The d empty DOS seen with XARS appears to be broadened and shifted and reduced in amplitude, as in the silicides.²³⁻²⁵ The establishment of a local Pt₂Si coordination is probably responsible for a reduction of the atomic mobility, and this is the likely explanation of the interface

reaction saturation for larger RT deposits.^{3,6} The formation of bulk Pt₂Si requires annealing,⁷ but the interface SEXAFS data show that clusters with Pt₂Si first- and second-shell coordination nucleate within the intermixed Pt/Si(111) interface region already at RT. No evidence of sizeable Pt clusters is found for less than 9-ML Pt/Si(111). In conclusion, we have given the first direct structural description of the Pt/Si(111)7×7 interface formation process at room temperature. At submonolayer coverage Pt chemisorption occupies the surface sixfold interstitial sites introducing stress in the top Si double layer. For higher coverages Pt penetrates within the substrate in a diluted phase within which, upon Pt enrichment, small Pt₂Si-like clusters nucleate.

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¹⁵The first Pt-Si shell of PtSi was isolated by subtracting from the FT of the data (Fig. 3) the simulation of all the Pt-Pt con-

tributions. Phase shifts and amplitudes from this procedure were used to analyze the 0.8-ML Pt-Si data determining the distance at 2.46 ± 0.04 Å, and coordination number 6 ± 2 . The first peak of the 0.8-ML FT, which is not affected by overlap of Pt-Pt contributions, was then backtransformed and the so derived phase and amplitude were used to simulate back the PtSi standard. This cross-checked phase and amplitude determination gives the indicated error bars (± 0.03 Å; ± 1 neighbor) on the final data analysis.

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