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Structural Chemisorption of Co onto Si(111) 7 × 7.

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Abstract. – Based on SEXAFS results for 0.5, 1 and 2 ML (monolayers) of Co deposited onto Si(111) 7 × 7 at room temperature, we obtain the structure of the chemisorption in this model system. The 7 × 7 order of the substrate determines the chemisorption geometry and coordination numbers for the first 0.7 ML of Co. At 2 ML a Co-rich overlayer covers the interface.

The chemisorption of transition metals on Si(111) represents an intriguing problem in spite of the large experimental and theoretical effort which is devoted to its study. Transition metals/silicon interfaces are usually called reactive interfaces implying that the interface chemistry must be related to the capability of these systems to form stable compounds, often in epitaxy on the substrate. The chemisorption, in this sense, is viewed as the metastable precursor stage of the nucleation of stable silicon-silicide interfaces [1]. Along with the better understanding of the Si(111) 7 × 7 surface [2], new accurate experiments, mostly STM, have recently shown the complexity of chemisorption patterns of metal atoms on this surface.

In this letter we present the results of a study of the local structure of the chemisorption of cobalt on Si(111) 7 × 7 at 300 K, by surface-EXAFS experiments.

Co was deposited by means of a radiation-shielded quarz-calibrated e-beam evaporator onto atomically clean Si(111) surfaces which showed a sharp 7 × 7 LEED pattern in a vacuum of $1 \cdot 10^{-8}$ Pa. Coverages are defined with respect to the Si(111) density. The Si(111) wafers (n-type) were annealed by direct ohmic heating. Auger spectroscopy was used to monitor the Co MVV/Si LVV peak ratio and surface cleanliness: no contaminants were detected in the as-deposited interfaces. SEXAFS [3] measurements were obtained by

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exciting the Co $1s$ core level (K-edge = 7707 eV) up to 500 eV of energy above threshold with synchrotron radiation from the DCI storage ring, monochromatized by a Si(311) double-crystal device, and by collecting all the ejected electrons with a channeltron. The polarization dependence of the SEXAFS amplitudes was exploited in the 0.5(1) ML Co/Si(111) 7 × 7 sample by orienting the surface normal either perpendicular to the X-ray polarization vector or at $\approx 72°$. Thicker deposits were measured at $\approx 45°$ incidence angle. The polarization-dependent SEXAFS spectra are displayed in fig. 1, along with the relevant
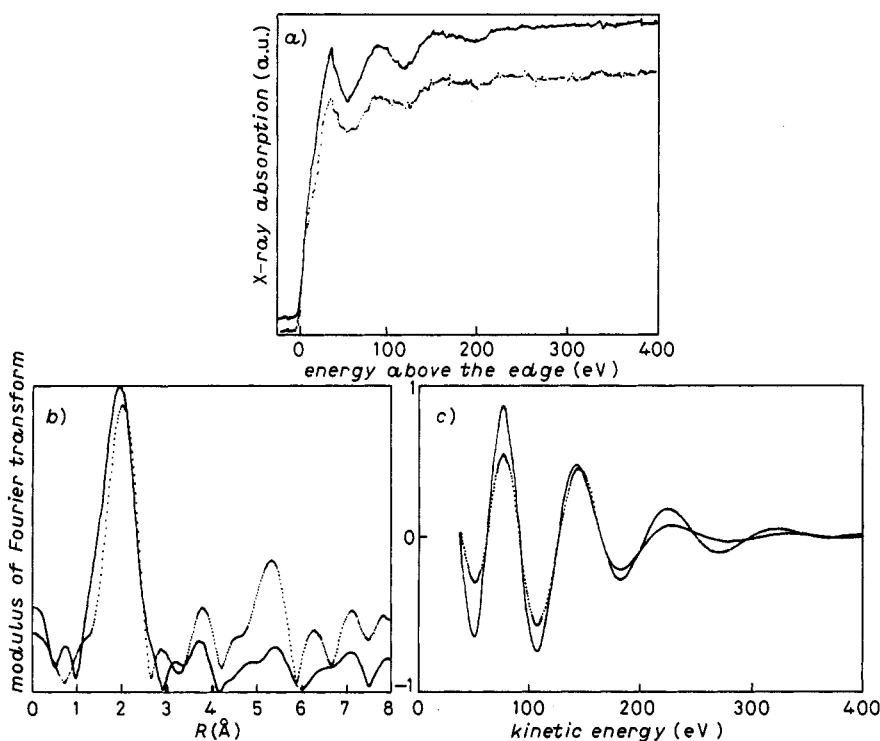

Fig. 1. – a) Polarization-dependent SEXAFS data for 0.5 ML Co/Si(111) 7 × 7; b) magnitude of the Fourier transform of the data; c) Fourier filtered EXAFS signal of the first neighbour shell. —— 90 degrees, $\cdots$ 18 degrees.

steps of the data analysis. The polarization-dependent SEXAFS coordination number is $N^* = 3 \sum_i N_i \cos^2 \alpha_i$, where N_i is the number of neighbours of the i-th neighbour shell whose bonds form the angle α_i with the $\boldsymbol{E}$ vector of the X-rays. Standard Fourier analysis [3] of the $\chi(k)$ EXAFS functions extracted from the data, was done in the $k = (3.2 \div 10)$ Å^{-1} range.

The deposit of 0.5 ML of Co onto the Si(111) 7 × 7 surface produced Auger peak-to-peak ratio of 0.11(2) and the LEED pattern showed blurred 7 × 7 streaks between the 1 × 1 spots. The $\chi(k)$ SEXAFS function obtained at normal incidence contains information on the Co environment in the interface plane: it can be readily fitted with a one-shell function corresponding to Si nearest neighbours at a distance of 2.31(2) Å and $N_\parallel^* = 6.8(5)$. Due to the identical first layer distance as in CoSi$_2$ we checked the N^* value by the amplitude ratio method [3] against the $\chi(k)$ of a bulk CoSi$_2$ standard measured under identical conditions. The envelope of the backscattering amplitude function ($A(k)$) (fig. 1) is qualitatively identical to that obtained for the first shell of the standard: this allows to exclude that in the

interface plane Co adatoms might occupy first-neighbour positions at similar distances as Si first neighbours. If this was the case, the SEXAFS amplitudes would have been affected by the sum of Co-Si and Co-Co contributions in phase opposition to each other [4] and the envelope of $A(k)$ would differ significantly from that of $CoSi_2$. A similar one-shell analysis as above fails to explain the peak in the Fourier transform of the glancing incidence data, *i.e.* of the data sensitive to the Co environment perpendicular to the interface plane. In this latter case a two-coordination shell function must be considered giving a best fit of the data for $N_\perp^* = 3.7(5)$ Si nearest neighbours at 2.31(3) Å plus $N_\perp^* = 2.4(5)$ Co neighbours at 2.56(3) Å with Debye Waller factors larger than in both $CoSi_2$ and bulk Co. The envelope of $A(k)$ clearly shows the shift of the maximum towards larger k values typical of the presence of Co-Co backscattering. The derived N^*s and bond lengths (d) for the interfaces are summarized in table I and compared to the crystallographic values for $CoSi_2$ [2]. The ratio of polarization-dependent Co-Si coordination numbers is $N_\parallel^*/N_\perp^* \approx 1.84$, whilst Co-Co neighbours are only present perpendicular to the interface.

TABLE I. – *Results of the polarization-dependent coordination numbers N^*, bond lengths d and increases of room-temperature Debye-Waller factors (with respect to $CoSi_2$ and to h.c.p. Co) for the chemisorption of 0.5, 1 and 2 ML of Co onto Si(111) 7 × 7 at room temperature. The experimental errors are indicated in parentheses.*

Co on Si(111) 7 × 7:	0.5 ML		bulk $CoSi_2$	
	Co—Si	Co—Co	Co—Si	Co—Co
$N_\parallel^*$	6.8(0.5)	0(1)	8	12
$d_\parallel$ (Å)	2.31(0.02)	—	2.31	3.78
$\Delta\sigma_\parallel^2 (10^{-3} Å^2)$	1.0(5)	—	—	—
$N_\perp^*$	3.7(0.5)	2.4(0.5)	8	12
$d_\perp$ (Å)	2.31(0.03)	2.56(0.03)	2.31	3.78
$\Delta\sigma_\perp^2 (10^{-3} Å^2)$	0.0(1)	0.2(1)	—	—

Co on Si(111) 7 × 7:	1 ML		2 ML	
	Co—Si	Co—Co	Co—Si	Co—Co
N^* 45°	4(0.5)	3.6(0.5)	3(0.5)	4.5(0.5)
d 45° (Å)	2.32(0.03)	2.55(0.03)	2.32(0.03)	2.55(0.03)
$\Delta\sigma^2 (10^{-3} Å^2)$	2.5(5)	2.5(5)	6(1)	2.5(5)

Although the measured Co-Si distance is the same as in $CoSi_2$, the strongly polarization-dependent value of the coordination number can only be explained with the coexistence of two kinds of chemisorption sites. In fact a $CoSi_2$-like first shell would imply 8 Si nearest neighbours with isotropic distribution, *i.e.* $N^* = 8$ both at normal and glancing incidence. The lack of Co-Co signal at the $CoSi_2$ second-neighbour distance (3.78 Å) excludes a $CoSi_2$-like description too. We therefore find $CoSi_2$-like first neighbour distances but non–$CoSi_2$-like coordination numbers. The intrinsic anisotropy of the chemisorbed layer is further shown by the presence of Co neighbours only perpendicular to the surface at a distance 2.5% larger than in h.c.p. and amorphous [5] cobalt which escludes microclustering of Co. Furthermore, the permanence of 7 × 7 order in the LEED pattern from the 0.5 ML Co/Si(111) system imposes to consider a chemisorption model compatible with the maintainance of the 49-atom rhombic domains.

The above experimental facts impose to consider a two-layer thick interface in which the Co adatoms take two kinds of chemisorption sites at equal distances with silicon: a «buried» layer of Co highly coordinated with Si, and a layer of Co surface atoms having a Si environment of lower symmetry. By following this hypothesis the in-plane N^* can be explained as the average of Co in sixfold interstitial sites ($H6$) in Si which contribute $N_{\parallel}^* = 8$ (as in $CoSi_2$) and top-layer-Co in threefold atop ($T4^*$) sites, $i.e.$ just «half» of the buried sites, contributing $N_{\parallel}^* = 4$. If the $T4^*$ sites are just on top of the occupied sixfold interstitial sites then a Co-Co vertical bond of 2.56 Å is readily explained (fig. 2). The $N_{\perp}^*$ Co-Co for a single
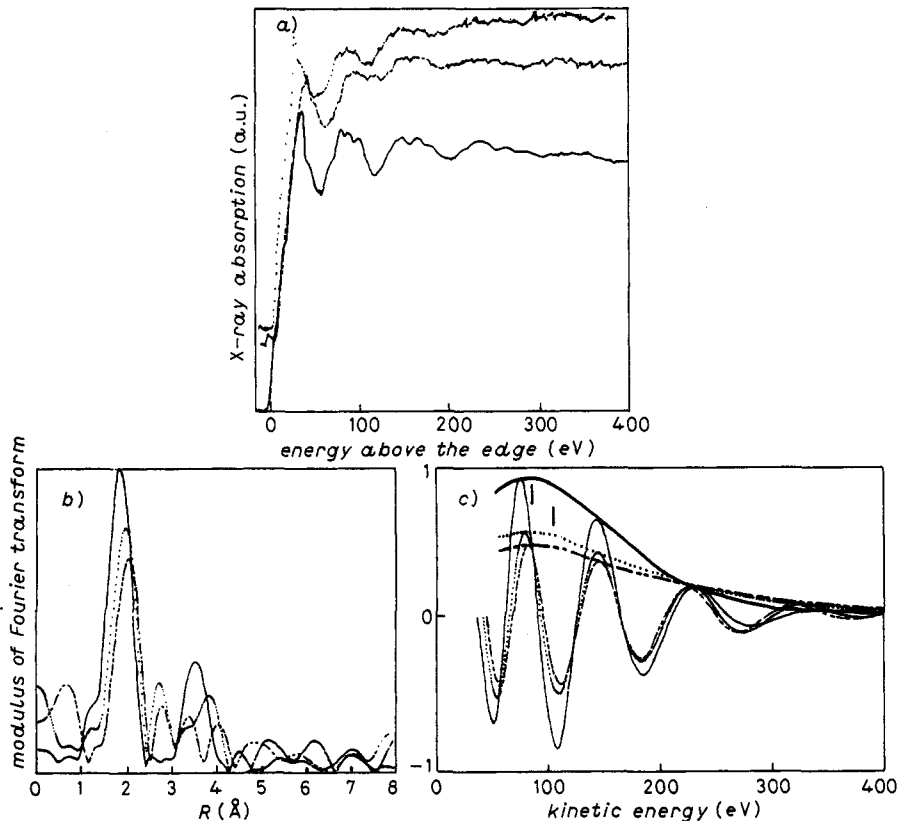

Fig. 2. – As fig. 1 but data measured at 45 degrees of incidence angle for 1 ML Co/Si(111) 7 × 7 at room temperature (dots); 2 ML Co/Si(111) 7 × 7 (dashed lines); and bulk $CoSi_2$ (solid lines).

vertical bond contributes $N_{\perp}^* = 4$. The additional information from LEED further conditions the chemisorption model: we show in fig. 2 the dimer-atom-stacking-fault model for the Si(111) 7 × 7 surface [2] and, below it, the representation of the chemisorption of Co into $H6$ sites within the Si(111) bilayer, and $T4^*$ sites on top of the occupied $H6$ sites, both in the regular and stacking-fault parts of the surface. By considering a proportion of 58% of simple $H6$ and 42% of $H6 + T4^*$ complexes, one accounts for the measured coordination numbers. This means that at the coverage of 0.5(1) ML about 0.35 ML of Co occupy the $H6$ interstitial sites within the top Si(111) bilayer which must undergo locally a vertical expansion of 0.8(1) Å. The remaining 0.15 ML of Co are hosted in the $T4^*$ positions forming three bonds with Si and a vertical bond with the underlying $H6$ Co. The Co-Si bond length implies that

the three Si(111) atoms lying between the *H*6 and the *T*4* Co atoms are contracted in their relative interatomic distance (which is a Si-Si second-neighbour distance) by 2.5%. The saturation of the occupancy of the *H*6 chemisorption sites at 0.35 monolayers can be easily related to the 7 × 7 reconstruction of the substrate. If one disregards the Si adatoms on the 7 × 7 surface one counts 20 bulklike honeycombs per 49-atom surface unit cell, half of which are in stacking fault with the substrate, plus large circular holes at the corners and oval holes along the edges and the short diagonal (fig. 2*a*)). The Si honeycombs provide 0.4 ML of *H*6 chemisorption sites, with the local geometry shown in fig. 2*b*) for both the regular half, and the stacking-fault half of the 7 × 7 unit cell. The large hollow sites at the corners and edges of the 7 × 7 unit cell cannot host Co in a high-coordination configuration with bond distances of 2.31 Å. The filling of all of the *H*6 sites leaves to the extra Co atoms the *T*4*. The displacement of the Si 7 × 7 adatoms along with the vertical displacement and the lateral stress in the Si atoms shared by the *H*6 and *T*4* Co adatoms are likely the causes of the blur of the LEED pattern, but do not modify the overall periodicity of the reconstructed substrate. The role played by the 7 × 7 reconstruction in determining the chemisorption geometry of a silicide-forming metal, and consequently the growth mode of the interface, is here directly derived from surface structural data. Recent STM data [6] for the chemisorption of Pd on Si(111) 7 × 7 showed aggregation of structurally unresolved islands only on the faulted half of the 7 × 7 unit cell: the islands were attributed to a silicidelike precursor of the reacted interface nucleating selectively on the faulted sites. Similar results have been shown for Cu/Si(111) 7 × 7 [7]. SEXAFS cannot distinguish between the faulted and unfaulted sites of fig. 2*b*) since the differences in the radial distribution of neighbours starts only in the third-nearest-neighbour shell. The site occupation values indicate unambiguously that both faulted and unfaulted sixfold interstitial sites are occupied for the chemisorption of 0.5 ML of Co.
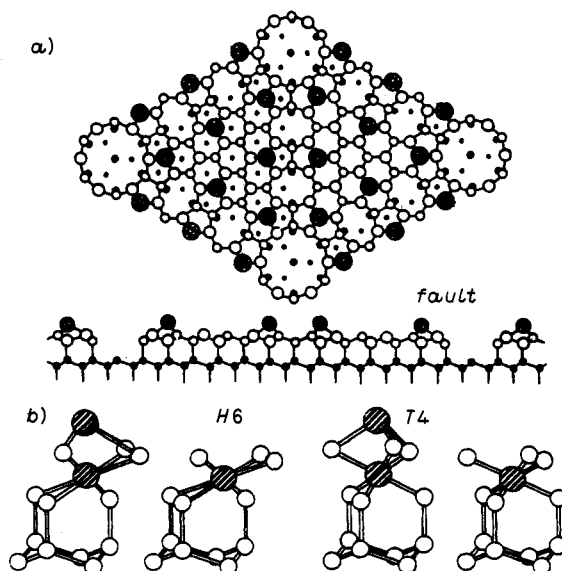

Fig. 3. – *a*) Top and side view of the dimer-atom-stacking-fault model for the Si(111) 7 × 7 surface, the Si adatoms are cross-hatched; *b*) model for the chemisorption of Co (large hatched atoms) on Si(111) 7 × 7 at room temperature implying the occupation of sixfold interstitial sites, *H*6, and threefold atop site, *T*4*. Saturation coverage corresponds to 0.81 ML.

The crossover from chemisorption to interface formation at room temperature was then studied by increasing the Co coverage. A deposit of 1 ML Co/Si(111) 7 × 7 gave an Auger ratio of 0.20(2) and a strongly attenuated 1 × 1 LEED pattern. The SEXAFS results are fitted with a two-shell function implying a reduction of the average Co-Si coordination at 2.32(3) Å and a strong increase of Co-Co coordination at 2.55(3) Å. These results are compatible with the saturation of the $T4^*$ sites, i.e. a total of 0.81 ML of Co in $H6 + T4^*$ chemisorption sites, followed by the formation of Co-rich environments. At 2 ML the SEXAFS data are again well fitted with a two-shell function corresponding to the same Co-Si and Co-Co distances as above, with a stronger relative weight of Co-Co contribution, and larger structural and/or dynamical disorder (table I). We interpret the average coordination numbers measured at this stage as representative of a structurally complex interface between the chemisorption layer and the metallic Co overgrowth which is clearly observed at still higher coverages. EXAFS simulations have been done to compare the interface data with the known silicide structures (Co_2Si_3, $CoSi$, Co_2Si, Co_3Si) as well as with the Co diffusion in the Si adamantane interstitial site (Co-4Si at 2.35 Å and Co-6Si at 2.71 Å); none of these hypotheses explain the data. We conclude that there is no homogeneous onset of silicide nucleation for such thin Co deposits at room temperature. We associate the results to the overgrowth of a Co-rich layer on top of the interface layer whose local structure may not change with respect to the chemisorption regime. Medium-energy ion scattering experiments [8] showed, for similar coverages, that the number of displaced Si atoms did not increase with respect to the typical value of the 7 × 7 surface in agreement with our observation of weak perturbation of the substrate in the chemisorption regime, and up to 2 ML of Co adsorption. We stress that although the sixfold interstitial chemisorption has been observed before in related systems like Ni/Si(111) 7 × 7 [4], Pt/Si(111) 7 × 7 [9], and V/Si(111) [10], it was always associated to structural disruption of the substrate surface and to the onset of epitaxial growth of silicides or to reactive intermixing. Our results for Co/Si(111) 7 × 7 show instead that the structure of the chemisorbed layer is ruled by the substrate surface 7 × 7 structure and that this hinders the nucleation of a silicide at room temperature. Previous conclusions on the Co/Si interface growth at monolayer thicknesses were based largely on the results of spectroscopic studies of the electron states [11]. The measure of Co-Si bond length identical to $CoSi_2$ at the interface explains the qualitative similarities observed in the density of states, but our results show that the chemisorption structure is not precursor of the epitaxial growth of $CoSi_2$ in the sense that the chemisorption sites are not the nucleation sites of $CoSi_2$ [12] and the growth of the Co/Si(111) 7 × 7 interface at RT is not found to proceed via sequential homogeneous nucleation of bulk phases. Structural studies of thicker, unannealed, Co overlayers on Si(111) showed the coexistence of grains of $CoSi$ and Co_2Si along with $CoSi_2$ and unreacted Co [8, 13].

In conclusions we have shown, by SEXAFS, that the chemisorption of Co on Si(111) 7 × 7 at room temperature implies sixfold and threefold chemisorption sites. We have then developed a model that relates the chemisorption to the surface reconstruction of the substrate: strong chemisorption bonds are formed into the sixfold interstitial sites available in the 7 × 7 domains (0.4 ML of Co), and on top of these sites in $T4$ symmetry for a total of 0.81 ML of Co. Extra Co atoms condense in a metastable Co-rich environment.

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