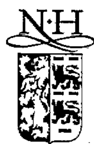

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# CO vibrational spectroscopy at heterogeneous Si/Pd(110) surfaces

Nicolas Wälchli *, Elisabeth Kampshoff, Klaus Kern

*Institut de Physique Expérimentale, EPFL, CH-1015 Lausanne, Switzerland*

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**Abstract**

The growth and reaction of Si on the Pd(110) surface has been studied by scanning tunnelling microscopy (STM) and reflection absorption infrared spectroscopy (RAIRS) of chemisorbed CO. Below 140 K the Si deposition on the substrate is nonreactive and amorphous Si clusters grow. The resonance frequency of adsorbed CO on these clusters is centred at 2104 $cm^{-1}$. Above 140 K Si reacts with the substrate to form palladium silicide. Below room temperature the silicide films are amorphous while above 320 K the silicide grows in well shaped crystalline islands. The vibrational spectrum of CO adsorbed on crystalline palladium silicide films is characterised by two absorption bands: a high frequency mode at 2074 $cm^{-1}$ and a low frequency mode at 2000 $cm^{-1}$. The assignment of these two vibrational bands is discussed.

*Keywords:* Carbon monoxide; Infrared absorption spectroscopy; Metal–semiconductor interfaces; Palladium; Scanning tunneling microscopy; Silicon; Vibrations of adsorbed molecules

Silicide formation is an important subject in semiconductor device physics [1–3]. Numerous studies have concentrated on the silicide formation on Si substrates upon metal deposition. Much less is known on the inverse scenario, silicide formation at metal surfaces. In the present paper we report on a STM and RAIRS study of the growth of Si and silicide on the Pd(110) surface in the temperature range $100\,K < T < 600\,K$. The chosen method, the in situ combination of STM and RAIRS, offers a unique possibility of correlating surface chemical analysis with atomic-level surface structure. This is particularly important in the case of very reactive systems like Si/Pd. As chemical sensor we use the CO molecule which is adsorbed onto the well prepared and characterised heterogeneous surfaces. The internal stretch vibration which is easily accessible with RAIRS reacts quite sensitively to the chemical nature of its surrounding and is thus a valuable probe of the surface chemical composition.

The experiments were performed in a UHV chamber (base pressure of $10^{-10}$ mbar) equipped with a variable temperature STM (100–600 K) and a FTIR spectrometer (Mattson GALAXY 6020) [4]. The Pd crystal was prepared by repeated cycles of Ar ion sputtering at 700 K, heating in $2 \times 10^{-6}$ mbar oxygen at 600 K and subsequent flash annealing at 900 K. Si was evaporated on the well prepared surface at temperatures between 100 and 600 K by electron bombardment heating of a Si rod. Typical deposition rates were of the order $5 \times 10^{-4}$ ML $s^{-1}$. All STM measurements were performed in the constant current mode at 0.5–2 V

* Corresponding author. Fax: +41 21 693 3604.

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bias and 0.5–1.5 nA tunnelling current. The IR absorption spectra were taken in reflection geometry with resolution of 8 $cm^{-1}$. CO was dosed onto the surface at 100 K; a monolayer was achieved after exposure of 40 L.

Relatively little is known about the adsorption of CO onto semiconductor surfaces [5–7]. On the Si(100)(2 × 1) surface CO molecules adsorb non-dissociatively [6,7]. The infrared absorption at 2081 $cm^{-1}$ is very close to the gas phase value indicating that the interaction of CO with the substrate is weak [7]. It is assumed that the CO molecule adsorbs in an upright position on top of the Si dimers. The molecule already desorbs at 220 K. On the Si(111)(7 × 7) surface CO does not chemisorb at temperatures above 100 K [7].

On the other hand, the interaction of CO with metal surfaces is extensively studied and reasonably well understood. On the Pd(110) substrate the CO molecule is adsorbed in a short bridge site on adjacent Pd atoms [8–10]. The CO/Pd(110) monolayer reveals a (2 × 1) superstructure with p2mg symmetry. The infrared absorption of the internal stretch is centred at 2000 $cm^{-1}$. The CO molecules desorb at about 350 K [11].

Up to now there is no information available concerning the adsorption of CO on heterogeneous silicon/metal surfaces. Fig. 1 shows the infrared spectra of a monolayer CO adsorbed onto different heterogeneous Si/Pd(110) surfaces at 100 K. The series depicts the dependence of the CO vibration on the Si deposition temperature. In order to facilitate the interpretation of the data we have added spectra of CO on amorphous Si, a-Si, (a) and on clean Pd(110) (f) as references. The IR absorption of CO adsorbed on a-Si is centered at 2104 $cm^{-1}$ and is 39 $cm^{-1}$ red-shifted with respect to the gas phase. The infrared absorption of CO adsorbed on the clean Pd(110) surface shows a more significant red-shift of about 150 $cm^{-1}$ with respect to the gas phase value indicating the strong interaction of CO with the metal surface. The peak maximum is centered at 2000 $cm^{-1}$.

The adsorption of CO on the heterogeneous surfaces is in general characterised by two well separated absorption bands. Below 140 K Si does not react with the Pd(110) surface and the Auger spectrum shows one single peak at 92 eV indicating

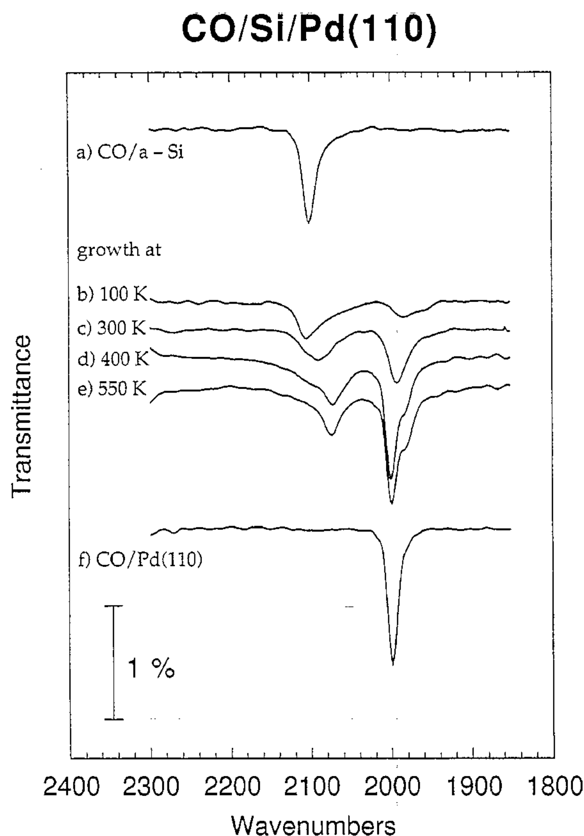


Fig. 1. Infrared spectra of a monolayer CO adsorbed on amorphous Si (a), on Si/Pd(110) after deposition of 1.2 ML Si at 100 K (b), at 300 K (c), at 400 K (d) at 550 K (e) and of a monolayer CO adsorbed on clean Pd(110) (f). A monolayer was achieved after dosing 40 L CO at 100 K.

the absence of silicide formation [12]. The unreactive deposition at low temperatures is confirmed by the vibrational spectrum of Fig. 1b. The high frequency mode here is observed at 2104 $cm^{-1}$; i.e. it shows no significant shift with respect to the a-Si spectrum in Fig. 1a indicating the absence of any reaction with the Pd substrate. The low frequency mode around 2000 $cm^{-1}$ is assigned to CO adsorbed on the remaining, uncovered Pd substrate sites (compare with Fig. 1f). Note that the Si deposited at 100 K grows in a three-dimensional mode. Although the amount of Si deposited on the surface exceeds 1 ML the Pd substrate is not yet completely covered. Both vibrational bands of CO on the Si/Pd(110) surface are inhomogeneously broadened indicating that the clusters of amor-

phous Si and the remaining patches of Pd substrate sites are small and randomly distributed. Above 140 K the deposition of Si on Pd(110) is reactive. Auger spectroscopy shows multiple peak shape features around 92 eV characteristic for palladium silicide formation [12]. The three representative spectra of CO adsorbed on the silicide/Pd(110) surface (Figs. 1c–1e) are quite similar. They show two distinct absorption bands: a low frequency band at 2000 $cm^{-1}$ and a high frequency band at 2074 $cm^{-1}$ (d,e) and 2090 $cm^{-1}$ (c), respectively. The low frequency mode is once again assigned to the CO bound in the bridge position to Pd atoms of the uppermost layer, while the high frequency mode indicates the presence of silicide. The silicide formation is evident by comparing the spectra with the analogous spectrum of amorphous Si on Pd(110) in Fig. 1b. The frequency has shifted by 30 $cm^{-1}$ upon Si deposition at and above 400 K and by 14 $cm^{-1}$ upon deposition at room temperature.

Comparing the IR data to the STM topographs in Fig. 2 shows that the band at 2074 $cm^{-1}$ is characteristic for crystalline silicide while the broad vibrational band at 2090 $cm^{-1}$ corresponds to CO adsorption on small amorphous silicide clusters. As shown in the uppermost STM image (Fig. 2a) small silicide clusters form at room temperature. They are 10–40 Å in width and they are randomly distributed at the surface. It is possible to assume that both, the surface inhomogenity as well as the amorphous character of the silicide, are responsible for the anomalously large linewidth of the infrared absorption in Fig. 1c. Above 320 K the silicide grows in well shaped monocrystalline islands. The corresponding infrared absorptions in Figs. 1d and 1e reveal an appropriate narrow lineshape. The crystalline silicide islands nucleate in the first substrate layer as well as on top of the substrate (Fig. 2b). They have a rhomboid shape. The island size can be increased by Si deposition at elevated temperatures as demonstrated in Fig. 2c. A section of a silicide island covers nearly the whole STM image. LEED measurements confirm the monocrystalline structure of the silicide grown above 320 K. A $\begin{pmatrix} 1 & 1 \\ 4 & 0 \end{pmatrix}$ LEED superstructure with two domains is inferred. The silicide islands grown at 550 K show a characteristic pattern of protrusion stripes running along the $[\bar{1}12]$ direction. The lines are interpreted as misfit dislocations indicating a partial relief of compressive strain in the silicide layer. By comparing Figs. 2b and 2c it becomes obvious that the surface area covered with silicide is quite different although the amount of deposited Si is identical. This is due to two competing reaction channels for the deposited Si: it can react with Pd surface atoms to form palladium silicide and it can also diffuse into the Pd substrate without reaction. The competition between both channels is controlled by the depos-

Fig. 2. The growth of palladium silicide on Pd(110) at 300 K (a), at 400 K (b) and at 550 K (c). The Si deposition at the surface is 0.4 ML.

ition temperature. More comprehensive information concerning the Si subsurface diffusion and the silicide formation is given in Ref. [13].

We now focus on the crystalline silicide grown at 550 K. As shown in Fig. 3 (left side) the silicide grows two-dimensional up to monolayer completion (deposition of about 1.2 ML) but continues to grow three-dimensionally upon further Si deposition. The corresponding CO spectra are shown at the right hand side. The bottom spectrum (0.2 ML Si deposited) is dominated by the absorption band at 2000 cm$^{-1}$ corresponding to CO adsorbed in Pd bridge configuration atoms in the uppermost layer (compare with Fig. 1f). The submonolayer Si

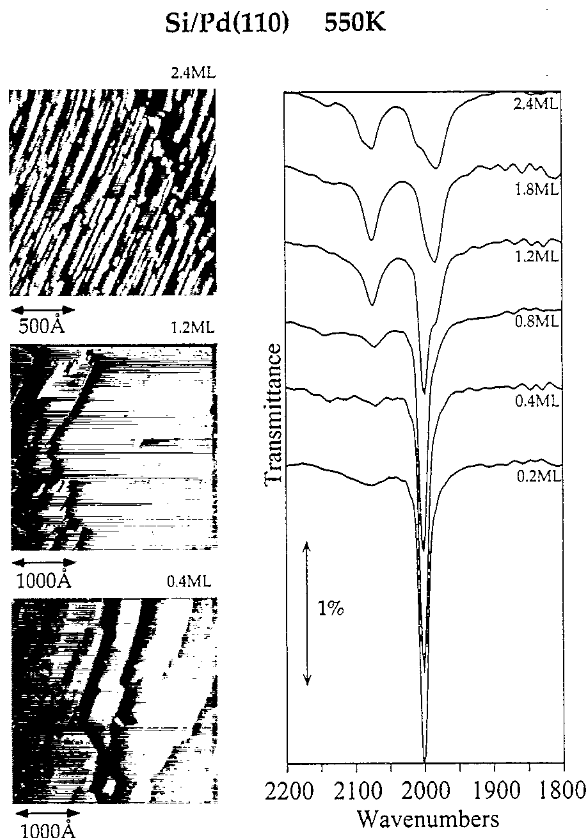


Fig. 3. Left: the growth of crystalline palladium silicide on Pd(110) at 550 K; the Si deposition at the surface is 0.4, 1.2 and 2.4 ML, respectively. Right: The infrared spectra of a monolayer CO adsorbed on crystalline palladium silicide grown at 550 K. The amount of deposited Si is indicated in the figure. A monolayer CO was achieved after dosing 40 L CO at 100 K.

deposition is accompanied by the appearance of a second absorption band at 2074 cm$^{-1}$. The intensity of this absorption increases with increasing Si dosage while the intensity of the initial absorption at 2000 cm$^{-1}$ slowly decreases. Upon completion of the silicide monolayer the intensity of the high frequency absorption saturates. The maximum value of its relative intensity with respect to the integrated absorption of the whole spectrum amounts to about $I_{rel} \approx 40\%$ indicating that a large number of CO molecules still adsorb on the crystalline silicide layer in bridge position over adjacent Pd atoms. There is no significant frequency shift visible due to silicide formation. With the onset of the silicide growth in the second layer a third band appears in the form of a low frequency shoulder of the main absorption peak at 2000 cm$^{-1}$. A deconvolution reveals a peak maximum at 1980 cm$^{-1}$. With increasing Si deposition the intensity of this absorption increases in disfavour of the absorption at 2000 cm$^{-1}$. After deposition of more than 2 ML Si this band dominates the spectrum. Since this absorption band is observed with the silicide growth in the second layer and since the absorption around 2000 cm$^{-1}$ decreases simultaneously it is possible to assume that this band is due to CO molecules adsorbed on the Pd atoms in the second silicide layer. The frequency indicates also a bridge position. The chemical redshift of 20 cm$^{-1}$ might be reasonable because the Pd atoms in the first silicide layer are mainly bound to Pd atoms of the bulk whereas the Pd atoms of the second layer are exclusively surrounded by silicide. In the uppermost spectrum of Fig. 3 after deposition of 2.4 ML a small shoulder around 2100 cm$^{-1}$ arises indicating the onset of the unreactive Si growth on top of the silicide layer.

We now turn to the assignment of the absorption at 2074 cm$^{-1}$. We did thermal desorption experiments in order to clarify the origin of this mode. The infrared spectra in Fig. 4 represent the remaining CO molecules from a silicide surface prepared by depositing 2.4 ML Si at 400 K. The bottom spectrum in Fig. 4 is quite similar to the uppermost one in Fig. 3 indicating an analogous, crystalline surface morphology as revealed upon Si deposition at 550 K. The CO molecules corresponding to the small shoulder at 2100 cm$^{-1}$ are the first desorbing

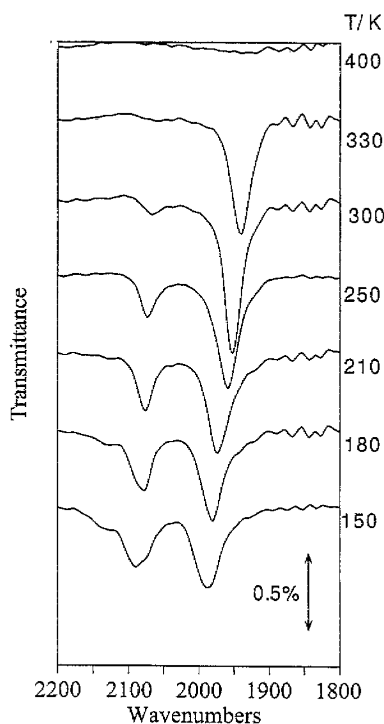


Fig. 4. The infrared spectra of CO adsorbed on palladium silicide grown at 400 K upon deposition of 2.4 ML Si and after annealing the CO layer at the indicated temperatures.

species. The temperature of about 200 K corresponds to CO desorbing from the reconstructed Si(100)(2×1) surface. Consequently a small amount of unreacted Si already exists in the third silicide layer grown at 400 K. Upon further annealing the intensities of the remaining two absorptions at 2074 and 2000 $cm^{-1}$ slowly decrease. At an annealing temperature of 300 K both absorptions are still visible. Complete desorption takes place above 300 K. This temperature roughly coincides with the measured desorption of CO from the Pd(110) surface [11]. Since the band at 2074 $cm^{-1}$ decays at about 300 K well above the desorption temperature of CO/Si(100) it is likely to assume that the corresponding CO species is also bound to Pd atoms. For the assignment of the absorption at 2074 $cm^{-1}$ we consider the two most likely adsorption configurations (1) a bridge bound CO molecule above a mixed Si–Pd adsorption site and (2) a CO molecule in an on top position over a Pd atom in the silicide. The occupation of a mixed adsorption site has already been observed for CO/CuNi(111) [14]. The resonance frequency of CO adsorbed in a mixed adsorption site would be expected between 2000 (CO/Pd(110) bridge) and 2081 $cm^{-1}$ (CO/Si(100) bridge) which would be consistent with the absorption at 2074 $cm^{-1}$. But simultaneously this peak frequency agrees very well with the measured IR absorption (between 2060 and 2090 $cm^{-1}$) of CO linearly bound on top of the Pd atoms of the (110) surface [10,11]. Thus, an unambiguous assignment of the 2074 $cm^{-1}$ mode of CO on the palladium silicide is not possible. Further investigations especially of the atomic structure of the grown silicide will be helpful.

The CO stretch vibration has been shown to be very sensitive to the local bonding arrangement on the heterogeneous Si/Pd(110) surface. Below 140 K the Si deposition on the substrate is nonreactive. This is confirmed by RAIRS. The infrared absorption of CO onto the three-dimensional grown Si is centered at 2104 $cm^{-1}$ and identical with CO adsorbed on a-Si. Reactive Si deposition on the Pd(110) surface above 140 K is accompanied by a red-shift of the CO absorption band indicating the formation of palladium silicide at the surface. The IR absorption spectra imply the existence of two distinct adsorption sites of CO adsorbed to the crystalline palladium silicide. A large fraction of CO molecules are still adsorbed in bridge position over two adjacent Pd atoms in the silicide layer. The thermal desorption experiments reveal that Pd atoms are also involved in the bonding of the second CO species.

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