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Silicide formation at palladium surfaces. Part II: Amorphous silicide growth at the Pd(100) surface

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Abstract

The morphology and reactivity of the Si/Pd(100) surface is studied by the in-situ combination of scanning tunneling microscopy (STM) and reflection absorption infrared spectroscopy (RAIRS) of adsorbed CO. Si adsorption on Pd(100) is found to be reactive: above 140 K the deposited Si reacts with the substrate to form palladium silicide. In the studied temperature range, 150 K $\leq T \leq$ 600 K, the silicide structure is amorphous. STM and RAIRS measurements reveal an incomplete chemical reaction at the interface with unreacted Si clusters interspersed in a homogeneous film of Pd_2Si. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Silicide formation at metal–semiconductor interfaces has been a very popular research field during the last 30 years [1,2]. Much interest in this subject has arisen from the need of a comprehensive understanding of the mechanisms of Schottky barrier formation, which find numerous applications in semiconductor devices. While most studies have focused on silicide formation on Si substrates upon metal deposition [3–8], we have recently started an experimental effort to characterize silicide formation on metal surfaces, in particular on single-crystal Pd surfaces. One major goal is to learn about symmetries and asymmetries in the early stages of interface formation. In part I of this study we reported a detailed description of Si adsorption and silicide formation at the Pd(110) surface [7,8]. In the present paper we extend our experiments on the Pd/Si interface to the reactive adsorption of Si at the Pd(100) surface.

The contact reaction between Pd atoms deposited on Si substrates is one of the most studied systems [9–16]. The formation of only one silicide compound, Pd_2Si, is observed below 1000 K. The interface is extremely reactive and silicide reaction occurs even at $T = 180$ K [12]. In general, only the formation of amorphous silicide is observed at temperatures below 600 K [1,10,11,13]. The epitaxial condition between the basal plane of Pd_2Si and the Si(111) surface allows the growth of crystalline silicide films on Si(111) upon annealing above $T \geq 600$ K.

Silicide formation upon Si deposition on Pd(110) is in many respects similar to silicide

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formation upon Pd deposition on Si substrates [7,8]. In both cases, the formation of Pd_2Si is observed. The growth scenario depends strongly on the deposition temperature. With increasing temperature, amorphous silicon (<140 K), amorphous silicide (140–320 K) and crystalline silicide (350–600 K) grow on the Pd(110) substrate. The main difference between the two systems (i.e. palladium on silicon and silicon on palladium) is the crystallisation temperature of the grown silicide films. At temperatures slightly above room temperature, a crystalline silicide phase grows epitaxially on the Pd(110) surface.

The aim of the present work is the extension of studies of the Si/Pd interface reaction to the Si/Pd(100) system in order to gain insight into the structure sensitivity of the silicide reaction. A general and comprehensive look should faciltate a microscopic understanding of the contact reaction between Si and the metal to form silicide. As in Ref. [8], Si/Pd(100) surface characterisation is performed by an in-situ combination of scanning tunneling microscopy (STM) and reflection absorption infrared spectroscopy (RAIRS) of adsorbed CO. We profit from the possibility of correlating surface chemical analysis with atomic-level surface structure investigation. Similar to the Si/Pd(110) system, we find a high reactivity, with the onset of silicide formation at temperatures above 140 K. In contrast to this system, silicide films on Pd(100) are always amorphous. No crystalline silicide phase could be grown at the Si/Pd(100) interface.

2. Experimental

The experiments were performed in a UHV chamber (base pressure 10^{-10} mbar) equipped with a variable-temperature STM (100–600 K) and an FTIR spectrometer (Mattson Galaxy 6020) which have been described in detail elsewhere [17]. The Pd(100) crystal was prepared by repeated cycles of Ar-iron sputtering at 700 K, heating in 2×10^{-6} mbar of oxygen at 600 K and subsequent flash annealing at 900 K. The quality of the sample was checked by LEED, AES and STM. Si was evaporated on the well-prepared surface at temperatures between 100 and 600 K by electron-bombardment heating of a Si rod with a typical deposition rate of the order of 4×10^{-4} ML s^{-1}. Calibration of the deposition rate was performed by STM and RAIRS of adsorbed CO [7,8]. All STM measurements were performed in the constant-current mode at a bias of 0.5–2 V bias and a tunneling current of 0.5–1.5 nA. The IR absorption spectra were taken in the reflection geometry with a resolution of 8 cm^{-1}. CO was dosed onto the surface at 100 K, and one monolayer was achieved after an exposure of 20 L.

3. Results

At 100 K, Si deposition is non-reactive, and small Si clusters nucleate at the Pd(100) surface. This is evident from inspection of the vibrational spectra of CO adsorbed at Si/Pd(100) surfaces grown at this low temperature (Fig. 1). The bottom spectrum of Fig. 1 shows a reference spectrum of a monolayer of CO adsorbed on pure Pd(100). The dominant absorption feature is the low-frequency band at 2000 cm^{-1}. This band is assigned to CO molecules adsorbed in the bridge position over two adjacent Pd atoms. From LEED, an ordered $(2\sqrt{2}\times\sqrt{2})R45^\circ$ CO structure was found at $\theta_{CO}=0.5$, and with increasing CO cover-

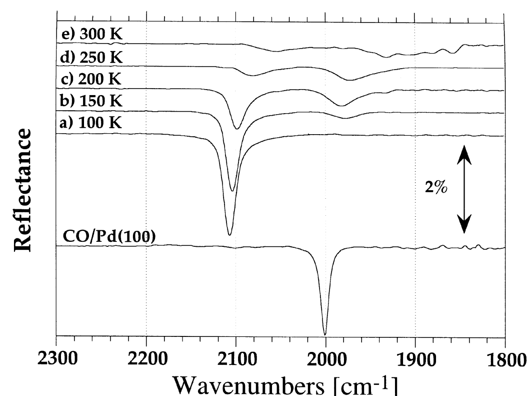

Fig. 1. Infrared spectra of a monolayer of CO adsorbed on Si/Pd(100) after 2.5 ML Si deposition at 100 K and after annealing at the indicated temperatures. The reference spectrum at the bottom characterises CO on clean Pd(100), which reveals a single sharp band at 2000 cm^{-1}.

age several ordered compression structures forming phase/antiphase domains are passed [18]. The heterogenous Si/Pd(100) surface was prepared by the deposition of 2.5 ML Si at 100 K. One single absorption band is observed at 2104 cm^{-1}. The linewidth amounts to 15 cm^{-1}. From the RAIRS measuremnts of CO adsorbed on heterogenous Si/Pd(110) surfaces, this frequency has been assigned to CO adsorbed on amorphous Si [7,8]. The peak maximum is also close to the frequency observed for CO adsorbed on Si(100)-(2×1) (2081 cm^{-1}) [19]. An upright position of CO on top of the Si dimers was inferred for the single-crystal surface. No second absorption band is observed, indicating the exclusive adsorption of CO on amorphous Si. Since there are no hints for Pd atoms mixed up with the topmost layer (cf. the reference spectrum), we must conclude that the surface is completely terminated with Si which has not reacted with the Pd substrate.

Interdiffusion and silicide formation become evident in the infrared spectra upon annealing the $CO/Si_{2.5\ ML}/Pd(100)$ sample. The series of IR spectra in Fig. 1 shows spectra of the remaining CO at the indicated annealing temperatures. Upon annealing the sample to 150 K, the dominant peak shifts slightly to 2100 cm^{-1} and a second broad absorption band appears at 1979 cm^{-1}, indicating the presence of Pd atoms mixed with Si atoms in the topmost layer. The small red-shift of ≈21 cm^{-1} which is revealed with respect to the IR absorption of CO adsorbed on pure Pd(100) is most probably due to finite size effects [20]. The appearance of the Pd absorption band indicates that at 150 K the contact reaction between the deposited Si and the Pd(100) substrate is already activated. This temperature coincides with the silicide formation temperature on the Pd(110) surface. In contrast to silicide formation on Pd(110), the contact reaction on Pd(100) at 150–200 K does not result in a substantial peak shift of the 2104 cm^{-1} band. For the Si/Pd(110) system, silicide formation was characterised by a red-shift of 14 cm^{-1} to 2090 cm^{-1}. As will be discussed below, the absence of this shift can be attributed to a rather incomplete reaction with Si precipitates present in the silicide. Upon annealing to 200 K, the intensity of the "palladium" band at 1979 cm^{-1} increases slightly. It reaches about 25% of the initial infrared absorption of $CO/Si_{2.5\ ML}/Pd(100)$ (bottom spectrum). Thus, about one quarter of the Si atoms in the topmost layer are replaced by Pd atoms from the substrate. Upon annealing to 250 K, a significant red-shift of the high frequency mode to 2081 cm^{-1} is observed. The reduced infrared intensity indicates that about 50% of a monolayer CO has desorbed at 250 K. Since the temperature is far below the desorption temperature for CO/Pd(100) [20], but coincides to the desorption temperature of CO/Si(100) [19], we conclude that a great part of the Si is still unreacted at $T<250$ K. As revealed by the top spectrum in Fig. 1, complete desorption takes place at $T>300$ K. The binding of CO to silicide is obviously much stronger as compared to CO bound to a-Si, and resembles more the adsorption of CO on metallic surfaces.

The surface morphology of the Si/Pd(100) system was studied by STM. Fig. 2 shows a series of STM images representing the surface morphology upon Si deposition at 400, 500 and 600 K. At 400 K, randomly distributed silicide clusters grow at the surface. The clusters are about 25–40 Å in width. These clusters are quite similar to the amorphous structures observed at the Pd/Si(111) and Si/Pd(110) surfaces after submonolayer Pd(Si) depositon at room temperature [13].

At a deposition temperature of 500 K, a quite different surface morhpology is observed. The substrate layer is essentially imaged flat, but the surface appears to be spotted with small protrusions. These protrusions have an average size of 15 Å, and their height corresponds to 10–20% of the Pd(100) step height. In addition, several adislands are found on top of the surface. The surface of the adislands shows the same spotted character as the substrate layer, indicating an identical overall chemical composition. We assume that the silicide in the topmost substrate layer is formed by the incorporation of impinging Si atoms in the layer, while the silicide adislands are formed through the reaction of ejected Pd adatoms with impinging Si adatoms. The source of ejected Pd adatoms is most probably an exchange process between Si atoms with Pd atoms of the substrate layer. This kind of exchange process takes an important role in binary surface alloy formation,

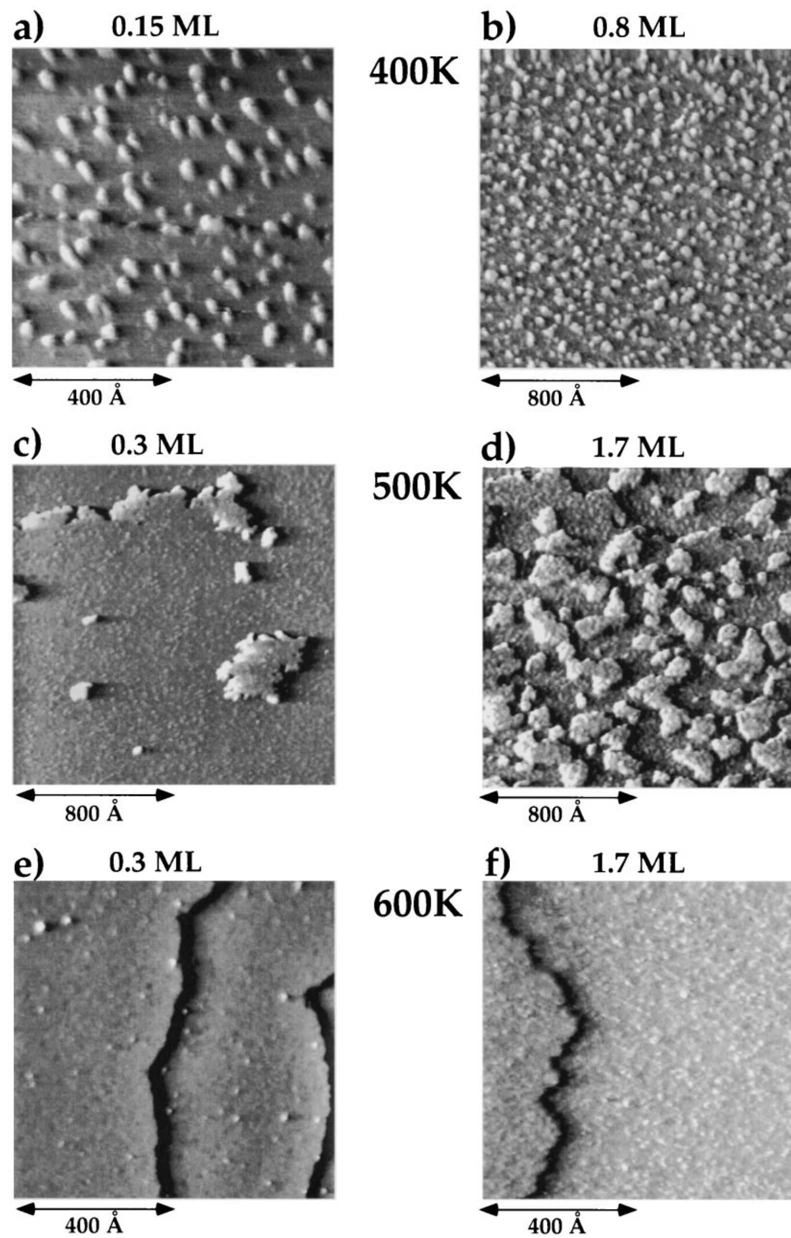

Fig. 2. STM images showing the surface morphology of Si/Pd(100) after Si deposition at 400 K ((a) 0.15 ML, (b) 0.8 ML), at 500 K ((c) 0.3 ML, (d) 1.7 ML) and at 600 K ((e) 0.3 ML, (f) 1.7 ML).

since it facilitates the penetration of foreign atoms into the substrate and the creation of a mixed surface atom composition [21].

Si deposition at 600 K again results in a similar spotted surface. At this temperature, the migration length of Si and Pd adatoms obviously overcomes the average terrace width, resulting in a step flow mode where silicide adislands grow exclusively from step edges. Thus, no isolated silicide adislands are observed.

Diffuse LEED images, which are revealed in the whole temperature range under study ($100\ K \leq T \leq 600\ K$), indicate a non-crystalline surface structure of the heterogenous Si/Pd(100) surface. Below 150 K, amorphous Si grows on the substrate and above 150 K, amorphous palladium silicide is formed, resulting in surface morphologies, as shown in Fig. 2. A particularly interesting aspect of this morphology is the appearance of interspersed protrusions present at all temperatures. In order to reveal their nature, we exploit adsorbed CO as a local chemical sensor probed by vibrational spectroscopy.

Representative RAIRS spectra of a monolayer of CO adsorbed on amorphous silicide are shown in Fig. 3. The IR spectra are presented as a function of the Si dosage. The silicide films were formed upon Si deposition at 400 K (left) and 600 K (right), respectively. We begin with the infrared spectra on the right-hand side. Upon Si deposition, both modes (i.e. the low-frequency mode around $1990\ cm^{-1}$ and the high-frequency mode at $2100\ cm^{-1}$) appear. With increasing Si dosage the intensity of the latter increases over the low-frequency mode at $1990\ cm^{-1}$. The high-frequency band is a chemical fingerprint of the presence of Si in the surface layer [7,8]. At about $\theta_{Si} = 0.8$ ML, saturation is seen. The ratio between the integrated intensities of the two absorption bands remains constant, although the Si dosage increases from 0.8 to 3.8 ML. A constant Si and Pd concentration in the topmost layer is inferred, which is characteristic of a silicide layer of constant stoichiometry. The IR intensities reveal that about 60% of the CO molecules remain adsorbed in the bridge position over two Pd atoms of the silicide film, whereas about 40% of the CO molecules are affected by the presence of Si in the silicide layer. A stoichiometry of Pd_2Si would be consistent with this intensity ratio.

The actual chemical composition of the grown silicide layer depends on the deposition temperature. This is evident when comparing the infrared series of CO adsorbed on silicide grown at 600 K (Fig. 3, right) with the corresponding series characterising CO adsorption on amorphous silicide grown at 400 K (Fig. 3, left). At low Si exposures, the CO absorption spectra of both series are quite similar. The temperature dependence of the chemical composition of the silicide film becomes significant at $\theta_{Si} > 0.8$ ML. Whereas saturation is revealed upon Si deposition at 600 K, the chemical composition of the silicide film grown at 400 K changes continuously (see also Fig. 4). With increasing Si exposure, the absorption band at $1990\ cm^{-1}$ broadens considerably and continously loses intensity in favor of the high-frequency band at $2100\ cm^{-1}$. At $\theta_{Si} = 4.2$ ML, the band has almost vanished, indicating that the topmost layer is nearly Si-terminated and silicide formation is frozen. A bilayer of palladium silicde film seems to be sufficient to block the diffusion of Si and Pd at temperatures ≤ 400 K. The growth of thick silicide films is obviously diffusion-limited. In sili-

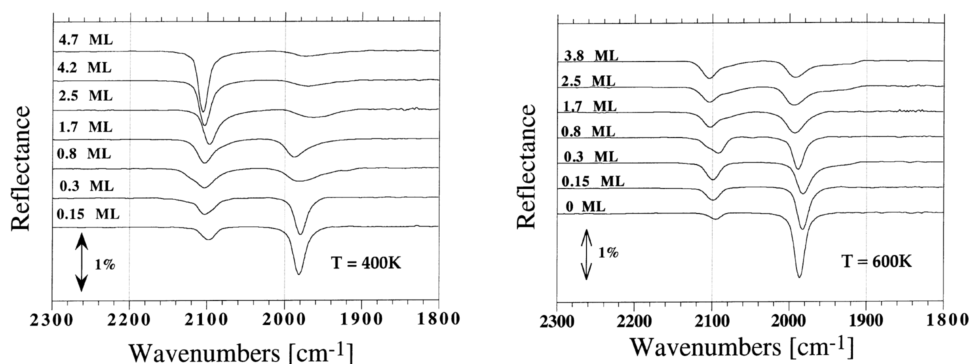

Fig. 3. Infrared absorption spectra of a monolayer of CO adsorbed on Si/Pd(100) after Si deposition at 400 K (left) and 600 K (right). The series show the IR spectra as a function of the Si exposure. 40 L CO was dosed at the surface at 100 K.

cide formation on Si substrates, this phenomenon is known as the "under-reaction" condition, where Pd enrichment is observed in the topmost layer [10,12]. A similar behavior is also observed in silicide formation on the Pd(110) surface [7,8].

Fig. 4 shows the relative infrared intensities of the absorption band at 2100 cm^{-1} of CO adsorbed on the amorphous silicide layer as a function of the Si dosage for three different deposition temperatures. The band intensity is a measure of the Si concentration at the surface. Upon Si deposition at 600 K, a pronounced intensity plateau is observed, consistent with the IR spectra of Fig. 3. At θ_{Si} exceeding 0.8 ML, the saturation composition of the silicide monolayer is revealed: although the Si dosage varies from $\theta_{Si}=0.8$ to $\theta_{Si}=3.8$ ML, the concentration of Pd and Si atoms in the topmost layer remains constant. In contrast, the chemical composition of the silicide films grown at $T=300$ K and $T=400$ K changes continuously with Si exposure. The plotted intensities increase continuously as a function of the Si exposure, indicating a Si enrichment in the topmost layer. Above ≈ 4 ML the values approach unity, indicating Si termination of the topmost layer.

It is worth comparing reactive Si adsorption on Pd(100) with silicide formation on the Pd(110) surface, which has also been studied by STM and RAIRS of adsorbed CO. At deposition temperatures below 350 K, the observed silicide structure is amorphous. The infrared absorption of CO adsorbed on these amorphous films is characterised by two absorption bands. The low-frequency mode at 1990 cm^{-1} is characteristic of CO adsorbed on bridge sites over adjacent Pd atoms in the silicide. A second band at 2090 cm^{-1} is attributed to a mixed Si–Pd_2 site. This band clearly differs from the absorption of CO adsorbed on amorphous Si (2104 cm^{-1}), and thus the distinction between silicide and amorphous silicon is straightforward. On the Pd(100) substrate, this distinction is less simple. The high-frequency mode of CO adsorbed on the saturated silicide film at the Pd(100) substrate is centred at 2100 cm^{-1}, and is thus very close to the absorption of CO/a-Si. The annealing experiment shown in Fig. 5 serves to identify the nature of this mode. The bottom spectrum shows the IR absorption of a monolayer CO on a saturated silicide film grown at 600 K. The infrared absorption of bridge-bound CO on Pd atoms at ~1995 cm^{-1} dominates. The high-frequency mode indicative of the presence of Si is clearly visible at 2100 cm^{-1}. The band is asymmetric and shows a small shoulder around 2090 cm^{-1}. The additional three spectra of the same series show the infrared absorption of the remaining CO upon annealing to the indicated temperatures. At 220 K, the infrared intensity is decreased by about 20%, and the band at 2100 cm^{-1} disappears. The frequency of the disappearing peak and the low desorption temperature indicate that the CO molecules desorb from unreacted Si, where they were weakly bound.

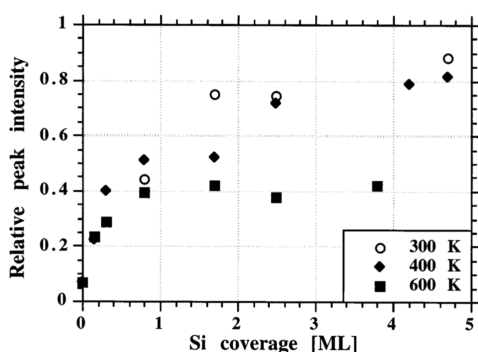

Fig. 4. Relative infrared intensities of the absorption of the high-frequency mode around 2100 cm^{-1} as a function of the Si exposure for three deposition temperatures. ○ 300 K, ◆ 400 K, ■ 600 K.

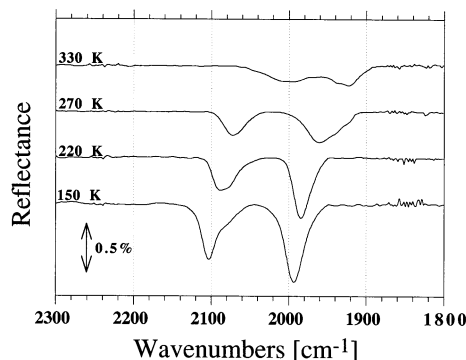

Fig. 5. Infrared spectra of a monolayer of CO adsorbed on palladium silicide prepared upon 1.7 ML Si deposition on Pd(100) at 600 K, recooling to 150 K for the CO dosage (20 L) and subsequent annealing at the indicated temperatures.

A part from the low-frequency band at 1982 cm^{-1}, a high-frequency mode at 2090 cm^{-1} remains, the peak frequency of which is indicative of CO adsorbed on amorphous silicide. With increasing temperature, the intensity of the two remaining absorptions decreases slowly. Complete desorption takes place above 330 K, characteristic of CO desorption from metallic films.

The disappearance of the mode at 2100 cm^{-1} and the amplification of the shoulder at 2090 cm^{-1} upon gentle annealing demonstrates that clusters of unreacted Si are precipitated in the silicide matrix. This explains the unusual morphology seen in the STM images. The small protrusions which are randomly interspersed in the silicide layer are likely to be small clusters of unreacted silicon. Their presence in the silicide surface is the clue to understanding the behavior of the 2100 cm^{-1} band as a function of the Si deposition in Fig. 3. The homogeneous distribution of the Si clusters in the silicide matrix layer produces in the IR spectra a superposition of absorption bands located between 2104 cm^{-1} (CO/a-Si) and 2090 cm^{-1} (CO/a-palladium silicide). Due to the dipole coupling between the adsorbed CO molecules, the high-frequency part will be enhanced over the low-frequency part [22]. Therefore, the high-frequency mode of CO adsorbed on amorphous silicide grown on Pd(100) tends to higher frequencies with a peak maximum around 2100 cm^{-1}, which renders a distinction between a-Si and silicide on Pd(100) difficult.

4. Conclusion

The nucleation and growth of silicide upon Si deposition on Pd(100) has been studied. The Si/Pd(100) interface is very reactive: silicide reaction occurs above 140 K. In the temperature range studied (up to 600 K), the grown silicide layers are amorphous. No crystalline silicide could be grown. The amorphous silicide films have a non-uniform chemical composition. Small Si clusters are randomly interspersed in the silicide film, which has Pd_2Si stochiometry.

Silicide formation at the Pd(100) surface bears similarities to silicide formation on Pd(110). In addition, these two interfacial systems bear similarities to the inverse system, i.e. Pd deposition on Si substrates. In general, Si/Pd interfaces exhibit a pronounced reactivity. The onset of silicide formation is observed at temperatures between 150 and 180 K. The formation of Pd_2Si is observed in all cases. The growth process of thick silicide films is diffusion-limited. At temperatures $\leq$400 K, just a few palladium silicide layers are sufficient to block the interfacial reaction.

The main difference between the systems is the structure of the grown silicide films. On Si substrates, only amorphous Pd_2Si is observed upon Pd deposition at temperatures below 600 K. The epitaxial conditions between the hexagonal basal plane of the Pd_2Si and the Si(111) surface allows the growth of crystalline silicide films at Si(111) upon annealing to temperatures above $T \geq 600$ K. In contrast to the Pd/Si(111) system, no epitaxial condition connects the hexagonal unit cell with the square surface unit cell of Pd(100). In addition, the system has been studied at deposition temperatures just below the crystallisation temperature of Pd_2Si. Thus, amorphous palladium silicide is formed exclusively on the Pd(100) substrate.

Silicide growth on the Pd(110) substrate goes somewhat off line. Although no epitaxial condition connects the unit cell of the Pd_2Si with the rectangular surface unit cell of the Pd(110) substrate, at temperatures slightly above room temperature a crystalline silicide phase can be grown. The symmetry of the open (110) surface promotes the formation of a metastable silicide phase where Si can be incorporated easily in the troughs. The more compact structure of the (100) surface obviously prevents the easy incorporation of Si atoms, and thereby prevents the growth of a crystalline silicide phase.

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