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K. Christmann and J.E. Demuth

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Surface Science 4 pages

The Interaction of silicon with a Pd(100) Surface†

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Abstract: The interaction of silicon with a clean Pd(100) surface was studied in UHV using LEED, AES and UV-photoemission. Deposition around 75°C leads to disordered Si layers with little evidence of bulk diffusion or compound formation. Slight warming to ~ 150°C causes the immediate development of a complex LEED pattern indicative of long-range ordering. A pronounced splitting of the Si LVV Auger line as well as the appearance of a photoemission level ~ 2.5 eV below E_f is attributed to the formation of palladium (II) silicide, Pd₂Si. Annealing at 250-500°C leads to decomposition of this silicide as indicated by the destruction of the complex LEED pattern and the disappearance of the Pd₂Si Auger lines. Above 600°C diffusion of silicon into the bulk predominates which leads to a rapid depletion of silicon on the Pd surface as can be followed from both AES and UPS.

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1. Introduction

The reaction between silicon and metals is of considerable practical importance. Traces of Si may easily lead to embrittlement and fracture of many common metals (Fe, Al); whereas larger Si amounts result in silicide formation, important compounds for manufacturing semiconductor device contacts.

Early structural investigations of Si on metal surfaces utilizing LEED have been reported by Jona, e.g., for Al [1], Ni [2] and Be [3] single crystal faces. From these studies it could be inferred that Si strongly reacts with the metal rather than merely forms a normal type of chemisorption bond. Quite recently, Cardillo and Becker [4] investigated the precipitation of Si impurities on a Pt(100) surface by means of LEED/AES and He atom diffraction. They showed that submonolayer concentrations of silicon on this surface readily form Pt(II) silicide Pt_2Si with a surprisingly large long-range order. Similar observations were made with the Pt(111)/Si system [5]. As far as transition metal silicides are concerned, an extensive data body exists [6], in particular for palladium(II)silicide, Pd_2Si , and some other silicides of Ni, Pt, Co, Rh, V, and Ti. AES studies on these compounds by Roth et al [7] revealed a nice correlation between the Auger lineshape and the bonding state character of the Si atoms in the silicide, in that silicides with a low heat of formation (e.g., Pd_2Si) exhibit the least covalent bonding and give rise to a pronounced Si LVV Auger line splitting. Experimental [8] and theoretical studies [9] into the electronic structure of Pd_2Si showed that this silicide has properties very similar to a metal with low lying, filled 4-d states.

In the following paper, we report on a combined LEED, AES and UPS study on the reaction of silicon with a clean Pd(100) surface with the aim to follow the silicide formation as a function of temperature.

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2. Experiment

The measurements were carried out in a turbo-molecular pumped stainless steel uhv system (base pressure below 8×10^{-11} torr), equipped with four-grid LEED optics (Varian), quadrupole mass filter (UTI), a differentially pumped He discharge resonance lamp and a double pass cylindrical mirror analyser. AES was performed using the LEED gun as a source of high-energy electrons (typical beam current $20 \mu\text{A}$, energy 2 keV) and the LEED optics as a RF type analyzer. The modulation voltage was as low as 2 V ptp in order to give sufficient resolution of the Si LVV Auger transition region. UV-photoemission data were taken using electron counting technique, the pass energies employed corresponded to energy resolutions of 100 meV (He I) and 250 meV (He II). The photon beam was incident at an angle of $\sim 75^\circ$ with respect to the CMA axis and $\sim 40^\circ$ with respect to the surface normal.

Silicon deposition was achieved using an electronically regulated evaporation source [10]; the Si deposited from a tungsten boat was of very high purity (99.999%). A fairly large Si source — substrate distance ($\sim 50 \text{ mm}$) was chosen in order to provide a uniform deposition over the entire area of the Pd crystal surface. The Pd crystal was prepared and cleaned by cycles of argon sputtering and oxygen treatments as is described in more detail elsewhere [11]. The temperature was recorded via a chromel-alumel thermocouple spot-welded onto the rear of the crystal.

3. Results and Discussion

a) LEED

In contrast to what is observed with Ni, Al, or Be[1-3], submonolayer deposition of Si on Pd(100) at room temperature does not lead to long-range ordering, i.e., no LEED *extra* spots are obtained from the Si covered Pd(100) surface. However, even small amounts of Si cause the background intensity to increase considerably until after deposition of ~ 2 -3 Si layers the integral order Pd beams disappear completely. Careful warming of this covered surface up to 150°C , produces a complex LEED pattern (fig.1) with numerous sharp spots even at the lowest attainable electron energies, thus indicating a large unit mesh with a surprisingly pronounced long-range order.

At this temperature, the Si atoms already react with the palladium surface to form palladium silicide. As this is an exothermic process ($\Delta H_f, \text{Pd}_2\text{Si} = 0.45 \text{ eV}$ [7]), the excess of the heat of formation gives the Si atoms sufficient mobility that they can form a well-ordered phase with pronounced long-range periodicity. It should be noted that Cardillo and Becker [4] made almost exactly the same observations with a Pt(100) surface reacting with Si. From their He scattering data they came up with a structural model of the surface silicide which actually exclusively consisted of Pt_2Si . From our AES data (cf. sect. 3b) we have good reasons to be-



Fig. 1. LEED pattern formed by Pd_2Si on a Pd(100) surface; $E = 85 \text{ eV}$.

lieve that the related silicide, Pd_2Si , is formed on the Pd surface which causes the observed complex LEED pattern. (This pattern is more complicated than the $(6\sqrt{2} \times 6\sqrt{2}) R 45^\circ$ pattern obtained by Cardillo et al. for the Pt(II)silicide).

Raising the temperature beyond 300°C irreversibly destroys the extra LEED pattern without evidence of other intermediate ordered structures, until finally the clean Pd(100) pattern is restored. As the Si does not desorb (all our attempts to get Si TD spectra failed) only rapid bulk diffusion of Si can account for this observation.

b) Auger electron spectroscopy

Fig. 2 shows a family of Auger spectra taken after successive Si depositions at 75°C without further annealing. At very low Si coverages (below $\sim .1$ ml) small features appear at 79 and 86.5 eV. Increasing Si coverages cause mainly the latter peak to grow, and after about half a monolayer of Si a shoulder appears around 90 eV. Further deposition into the monolayer range and above makes this shoulder grow almost exclusively (with the 86.5 eV structure remaining constant) until finally the typical Auger spectrum of silicon is obtained. Simultaneously, the Pd MNN transitions (main peak at 331 eV) lose their intensity continuously until they disappear after roughly 5 Si layers have been deposited. No attempt was made to analyze the Auger data in terms of absolute Si concentrations because of the lack of a second independent measure for the number of Si atoms in the surface.

If the Pd surface covered with Si in this way is carefully subjected to annealing around 150°C , the one huge Si LVV-line at 92 eV shrinks considerably, and after a couple of minutes a new spectrum (shown in fig. 2 as a dotted line) is obtained: The 86.5 eV transition now is completely separated from the 92 eV line that actually has shifted down to 91.2 eV and has a distinct satellite around 96 eV. In addition to that, two other peaks are observed at 75 and 80.6 eV. A comparison of this spectrum with that reported by Roth et al [7] for bulk Pd_2Si clearly reveals that these spectra are practically identical. With the occurrence of these new Auger features we also observed the complex LEED pattern as well as the development of a new UPS level (cf. sect. 3a and c, respectively). Higher annealing temperatures (above 200°C) again lead to alterations in the silicon Auger spectrum: the peak at 96 eV disappears, and the 91.2 eV line decreases progressively, whereas the 86.5 eV transition gets the predominant feature. At this stage, the Pd_2Si LEED pattern has disappeared completely, and the photoemission spectra more and more resemble the clean Pd spectrum (cf. sect. 3c).

Even higher annealing up to 700°C drives the Si completely into the bulk, and the Auger spectrum of the clean Pd finally is restored.

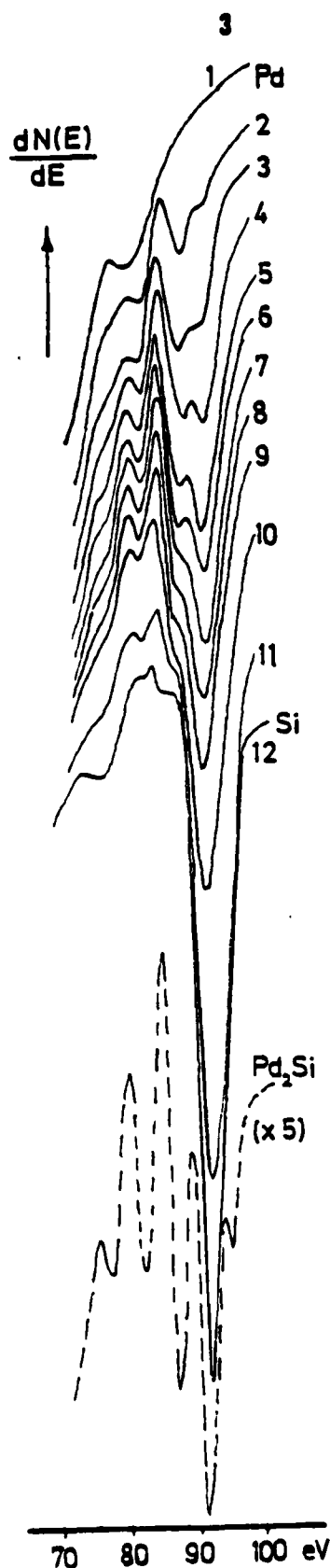


Fig. 2. Sequence of AES curves displaying the Si LVV transition energy region. The Si deposition increases in going from spectrum 1 to 12.

c) UV photoemission

Photoemission spectra were taken at $T = 75^\circ\text{C}$ with He I radiation (21.2 eV) as a function of silicon deposition. As the deposition proceeds, a preferential attenuation of the d-band features near the Fermi edge occurs (the Pd d-states at 2.3 eV below E_f are little affected). For ~ 5 deposited Si layers we no longer observe d-band emission at E_f ; new (weak) features appear at 3.2 eV and 7 eV below E_f that are characteristic of clean Si. The total work function change that accompanies the Si deposition was determined to be approximately -600 meV. This fairly small value indicates little charge transfer in forming a silicon-palladium bond, actually electronic charge is withdrawn from the Si atoms to fill Pd d states. This observation is in agreement with calculations by Lang and Williams [12] for Si atoms interacting with a jellium surface. In contrast to AES, annealing at 150°C does not produce dramatic changes in the photoemission curves. A single, fairly broad level appears near the clean Pd emission maximum, i.e., at 2.5 eV below E_f , along with a single shoulder around 4.2 eV below E_f . Photoemission studies by Rubloff et al [8,9,13] on Pd_2Si produced by subsequent Pd deposition on a clean Si(111) surface showed that in going from Si to Pd_2Si the above mentioned maximum in the EDC continuously shifts from 3.5 eV to ~ 2.7 eV below E_f as the Pd_2Si is formed progressively. We therefore interpret the observed UPS curve as being caused by Pd_2Si precipitated on a background of clean Pd, although the vicinity of the Pd_2Si and Pd density of states maximum render a clear distinction quite difficult. We also note that we have occasionally observed UPS features near 6.5 eV and 10.2 eV below E_f , which arise from the presence of oxygen in the silicon layer. This oxygen competitively reacts with the Si to form SiO_2 at 150°C , and the observed photoemission levels correspond very well with UPS results on the valence levels of amorphous SiO_2 reported by DiStefano and Eastman [14]. Higher annealing temperatures cause the Pd_2Si photoemission maximum at 2.5 eV to shift to 2.3 eV where it is more characteristic of the Pd d-band emission of the clean surface.

4. Conclusions

We have shown that the reaction of silicon with a clean Pd(100) surface at 150°C leads to the formation of palladium(II)silicide at the interface. There was no evidence from both AES and UPS measurements for any further formation of a silicide with different stoichiometry, i.e., with a lower Si : Pd ratio. At elevated temperatures ($T > 500^\circ\text{C}$) the bulk diffusion of silicon causes Pd_2Si compound decomposition and the rapid depletion of Si on the palladium surface.

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