Reactions at the Si / Pd(110) interface

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1. Introduction

Silicide formation has been studied extensively, both because of its practical importance in semiconductor technology and because epitaxial silicide films provide well-defined model systems for basic studies of interface reactions [1,2]. Numerous experimental studies have concentrated on the Pd_2Si system which has the advantage to grow epitaxially on the Si(111) surface [3]. Much has been learned of this fascinating system, however a complete microscopic understanding of the mechanisms for silicide formation at the interface is still lacking.

In this contribution we report in situ scanning tunneling microscopy (STM) results on silicide formation on the Pd(110) surface. The reaction scenario is found to depend strongly on the deposition temperature, which determines the competition between Si bulk diffusion and silicide formation. At room temperature amorphous silicide clusters nucleate. These clusters are not stable but dissolve progressively with time. Above 320 K, crystalline Pd_2Si is formed which grows in well shaped islands. The crystalline silicide is also unstable at elevated temperatures.

2. Experimental

The experiments were carried out in a UHV chamber (base pressure 2×10^{-10} mbar) equipped with a variable temperature STM (150 K - 600 K), an AES with cylindrical mirror analyser and a reverse view LEED [4]. The Pd(110) crystal was prepared by cycles of 800 eV Ar^+ ion sputtering at 300 K and 700 K, heating at 650 K in a 10^{-6} mbar O_2 atmosphere and flash annealing at 900 K. The surface quality was controlled by STM, LEED and AES. STM images reveal large terraces with an average size of ≈ 1000 Å. The Pd(110) surface has a rectangular unit cell of dimensions 3.89 Å × 2.75 Å. One monolayer (ML) is defined as the surface density of Pd atoms, i.e. 1 ML = 9.35×10^{14} atoms cm^{-2}. Evaporation of Si on the well prepared Pd(110) surface was achieved by electron bombardement heating of a Si rod. Typical deposition rates were of the order of 2×10^{-4} ML s^{-1}.

3. Results and Discussion

At low temperatures (< 200 K) Si does not react with the Pd(110) surface. A high density of very small Si clusters nucleates on the surface. The Auger spectrum shows only one single peak at 92 eV clearly demonstrating the absence of silicide formation [5]. Upon increasing the deposition temperature to 300 K amorphous

silicide clusters are formed at the Pd(110) surface upon deposition of Si. The clusters have a typical size of 10 Å - 50 Å and are uniformly distributed at the surface. This is demonstrated in fig. 1a showing an STM image taken immediately after deposition of ≈ 0.01 ML of Si on Pd(110) at 300 K. Auger spectroscopy of the room temperature deposits shows multiple peak shape features around 92 eV characteristic for Pd_2Si formation [5]. The corresponding LEED pattern is diffuse indicating that the clusters have no crystalline structure but are amorphous. This behavior is analogous to the initial growth of palladium silicide on Si(111) at room temperature where also the formation of amorphous Pd_2Si clusters has been observed [6].

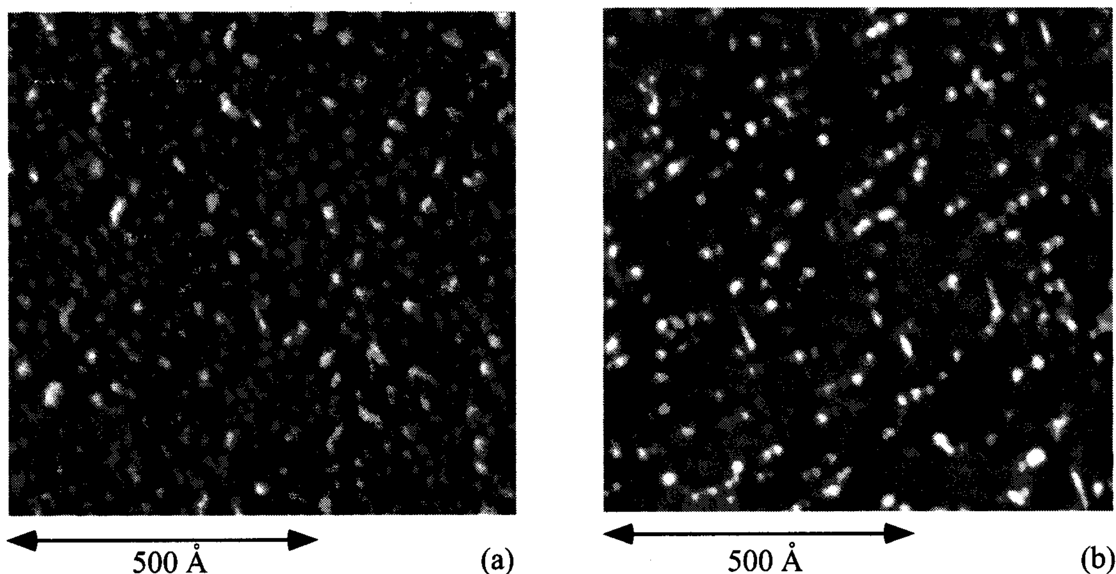
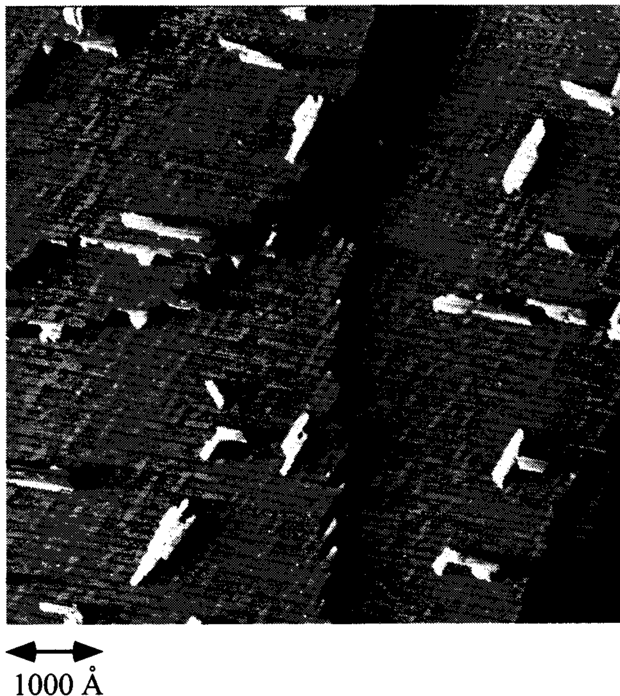


Fig. 1 : The growth (a) and dissolution (b) of amorphous palladium silicide clusters on Pd(110) at 300 K. The STM image in (a) has been recorded immediately after deposition and the image in (b) 30 minutes later. The Si coverage is ≈ 0.01 ML.

The amorphous silicide clusters on Pd(110) are not stable at 300 K. The clusters disappear progressively with time as we notice on the STM image in fig. 1b which has been taken 30 minutes after deposition. The STM measurements suggest that the silicide clusters decompose and the Si atoms diffuse into the Pd bulk via an exchange mechanism with Pd substrate atoms. This is documented in fig. 1b which clearly shows the presence of substrate holes, mostly one layer deep. The holes are elongated along the [$\bar{1}$10] direction and are mostly mon- or diatomic in width. Besides these holes and some of the left silicide clusters we can identify Pd atoms which are arranged as short chains running also along [$\bar{1}$10]. A likely scenario to explain this morphology is the following. The unstable silicide clusters decompose at 300 K and the liberated Si adatoms exchange their place with Pd atoms of the top surface layer. In a second step a Pd atom in the surface layer is ejected to create a vacancy, which then can be filled by a Pd atom from the second layer exchanging its place with the incorporated Si atom. The formed vacancies as well as the kicked out Pd atoms can diffuse and form islands. Due to the anisotropic structure of the substrate, vacancy-islands and Pd-adislands are elongated along [$\bar{1}$10]. This mechanism ensures an efficient bulk diffusion of Si and is compatible with the morphology seen in fig. 1b.

Above about 320 K the reaction scenario is quite different. As example we show in fig. 2 an STM image characterising the silicide formation at 400 K. Two kinds of well shaped silicide islands are formed: one embedded in the first Pd layer and the other on the Pd(110) surface, one step height above. The Auger spectrum reveals the same multiple peak shape as seen at 300 K, which is characteristic for Pd_2Si. Both island types are elongated. There are two domains visible which are oriented along the diagonal $[\bar{1}12]$ and $[\bar{1}1\bar{2}]$ directions of the Pd(110) unit cell. The adislands and the embedded islands show the same distinct orientations. The silicide islands have a crystalline structure and grow epitaxially on the Pd(110) substrate indicated by a sharp $\begin{pmatrix} 1 & 1 \\ 4 & 0 \end{pmatrix}$ superstructure with two domains.



1000 Å

Fig. 2 : The growth of crystalline palladium silicide islands on Pd(110) at 400 K. The Si coverage is 0.13 ML.

Obviously the embedded silicide islands are formed by the reaction of Pd in the surface layer with penetrating Si atoms, while the adislands are formed through reaction of ejected Pd adatoms with Si adatoms. The density of the embedded silicide islands is much higher than that of the adislands. This can easily be understood because the flux of Si atoms arriving at the Pd surface is much larger than the « effective flux » of Pd adatoms ejected onto the surface due to the Si-Pd exchange. The nucleation probability of embedded silicide islands via Si-Pd exchange is thus much higher than the probability that a Si and a Pd adatom meet and nucleate an adisland.

We note that also the crystalline silicide islands are not stable at elevated temperatures. At temperatures of 500 K the islands decompose on a minute time scale while at room temperature typical decay times are of the order of hours. The silicide phase can however be stabilized by quenching to 200 K or below.

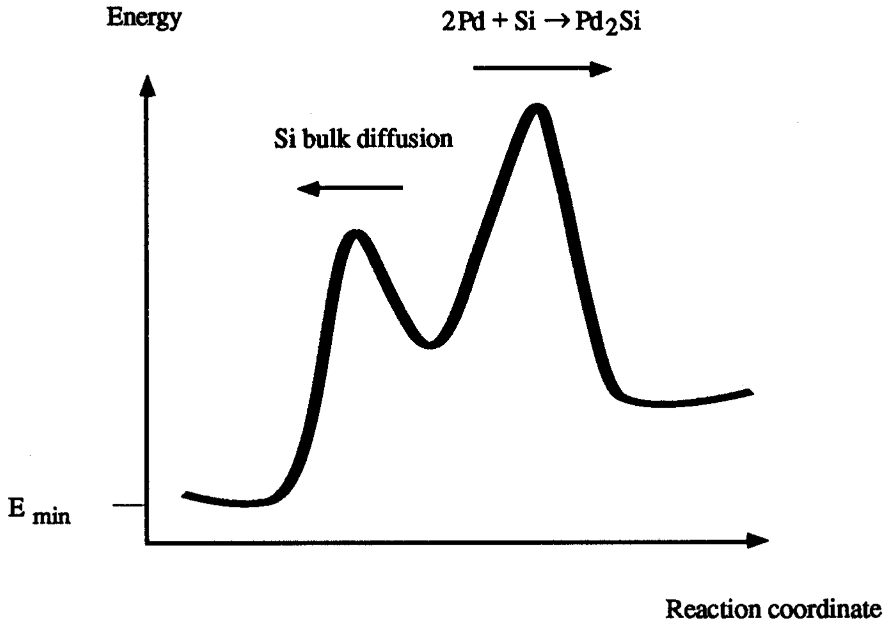


Fig. 3 : Schematic potential diagram describing the Si/Pd(110) system.

The observed reaction behavior at the Si/Pd(110) can be understood qualitatively by the schematic potential diagram shown in fig. 3. Si deposited on the Pd surface has two reaction channels, the diffusion into the bulk or reaction with the metal to form a silicide. The energetic ground state of the system is the complete dissolution of Si in the Pd bulk. This state is achieved through bulk diffusion of the Si atoms via a Si-Pd exchange mechanism. Typical activation barriers for these exchange diffusion processes are of the order of 1 eV or below [7]. The chemical reaction to form Pd_2Si is likewise activated whith a barrier of about 1.3eV [8]. As the reaction rates depend exponentially on the barriers, bulk diffusion is always prefered with respect to chemical reaction. At very low temperatures both channels are frozen and Si clusters are stable. With increasing temperature first bulk diffusion becomes active. Only at elevated temperatures silicide formation becomes significant. However, because the silicide phase is not the global minimum, the only way to stabilize the formed silicide is the rapid quenching below the threshold for bulk diffusion.

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