Chapter 1
Introduction

1.1 Overview

Binnig and Rohrer et al. developed scanning tunneling microscopy (STM) at the IBM Zürich Research Laboratory in 1981. It is used to observe surfaces on the atomic scale. The power of STM has introduced the new age of nanotechnology. The motion of atoms, the structure of surfaces and growth behaviors in real space of several materials are now feasible.

Given the need for stable electric contacts and better performing semiconductor-based devices, understanding epitaxial growth and the reactions of metal with SiGe-based materials are very important. Therefore, metal films on semiconductors should be grown atomically flat, with uniform thickness.

In this work, STM is used to study the deposition of Pb on the Si(111) surface. The low reactivity and solubility of Pb in the bulk of Si make the Pb/Si(111) system an appropriate model for studying the metal/semiconductor system. However, the phase diagram of Pb/Si(111) is very complex, depending

on coverage, temperature and the experimental annealing procedure. For instance, when Pb is deposited on Si(111) with a coverage of 1/6 ML, a so-called mosaic phase (or γ phase) is observed[1,2]. When the Pb coverage slightly exceeds 1/3ML, 1/3ML-($\sqrt{3}\times\sqrt{3}$) phase and (1×1) phase[3] are observed. With a coverage between 1 and 4/3ML, a hexagonal incommensurate phase (HIC) and a striped incommensurate phase (SIC) are observed[4,5]. The phases of the Pb/Si(111) system vary not only with the Pb coverage, but also with the temperature. For example, when the 1/3ML-($\sqrt{3}\times\sqrt{3}$) phase and the (1×1) phase are cooled below ~250K, (3×3) and ($\sqrt{7}\times\sqrt{3}$) phases are formed. However, the SIC phase does not undergo a phase transition, even at 50K. The atomic model proposed by Hwang *et al.* indicates that the HIC and the SIC phases are composed of three Pb atoms at the T1 sites toward either at the H3 or T4 sites[6,7]. Therefore, based on the trimers model of Hwang *et al.*, the Pb coverages of HIC and SIC phases are 1ML rather than between 1 and 4/3 ML.

Hupalo *et al.* recently proposed the "devil's staircase phase diagram" of the Pb/Si(111) system with a Pb coverage of between 1 and 4/3ML. The phase diagram is derived using the 1-D Ising theoretical model, and established theoretically for the Pb/Si(111) system. However, the presence of defects in any experiment is inevitable. Accordingly, the effect of defects on the phase transition is observed *in situ* and discussed in the first part of this investigation. The staircase phase diagram is also obtained from experimental results.

The presence of corner holes makes the Si(111)-(7×7) surface imperfect. Earlier studies[8] indicate that a quantum-well state may not be present on the site of the corner hole of the Si(111)-(7×7) surface. The effect of this fact on the nucleation properties and the growth behaviors of Pb deposited on the Si(111) surface are experimentally examined.

In the incommensurate phase (IC) of the Pb/ Si(111) system, unlike on the Si(111)7×7 surface, quantum-well states are observed everywhere[9]. The homogeneity of electronic properties can be exploited to grow atomically flat Pb films. The growth behavior of Pb deposited on the IC phase at low temperature (55K, 100K and 140K) is studied. The third part of this thesis presents experimental observations.

When Pb is deposited on the IC phase at ~200K, Pb grows in preference to Pb islands. In the incommensurate phase of the Pb/ Si(111) system, quantum Pb islands have been grown, and found two yield distinguishable image contrast patterns [10]. Contrast patterns vary with the applied bias and the thickness of the Pb islands, originating mainly from the electronic effect. Type I Pb islands, with a strong image contrast, act as templates for the nucleation of nanoclusters (or nanopucks). The fourth section of this work presents the results. Ag nanopucks are grown in highly ordered two-dimensional arrays on Type I Pb islands in a pronounced wide plateau region between ~70K and ~150K. The substrate strongly affects the growth

behavior. Scaling theory does not elucidate the growth behavior. Thus, the trapping strength of the substrate is quantified. The quantitative results reveal that the trapping powers of Type I and Type II for Ag nanopucks differ markedly. This investigation considers the growth behavior of Ag to elucidate the bi-layer oscillatory characteristic of Pb islands. Furthermore, *dI/dV* measurements of Ag nanopucks nucleated at different sites exhibit the same characteristic.

dI/dV measurements indicate that *x*-, *y*-confinement must be involved in determining the electronic properties of Ag nanopucks. Therefore, the last section on experimental results addresses the electronic structures of Ag nanopucks. The site-dependent characteristics of the electronic structures and the size-, shape-dependent properties are examined. The effect of the substrate on the electronic structures of the Ag adsorbates is also investigated.

1.2 Principles of scanning tunneling microscopy (STM)[11]

The most important physical effect in STM is the electronic tunneling effect. In quantum mechanics, within a classically forbidden region, the

wavefunction $\varphi(z)$ has the solution $\varphi(z)=\varphi(0)e^{-\kappa z}, \kappa=\frac{\sqrt{2m(U-E)}}{\eta}$ which satisfies Schrödinger's equation,

$$-\frac{\eta^2}{2m}\frac{d^2}{dz^2}\varphi(z)+U(z)\varphi(z)=E\varphi(z).$$

Therefore, the probability density, $p \propto |\varphi_n(0)|^2 e^{-2\kappa z}$, must be non-zero to enable the barrier to be penetrated. When a bias voltage V is applied, the tunneling probability density near the Fermi level is proportional to the tunneling current

$$I \propto \sum_{E_F-eV}^{E_F} |\varphi_n(0)|^2 e^{-2\kappa z} .$$

1.3 STM operating modes[11-13]

STM is typically used in two modes. Involve different control parameters. These two modes are respectively interaction between the tip and the sample, and the control of the tip with a fixed *z* position. When the interaction between the tip and the sample is constant, the STM is in "the constant current mode". When the *z* position is fixed, it is in "the constant height mode".

(a) Constant current mode

In this mode, during scanning, the interaction between tip and sample is set with a fixed current I_0 and bias voltage V_0 to cause a constant tunneling current to flow between these two electrodes. Therefore, the *z*-position of the tip responds to the interaction intensity between the tip and the sample from the sample : the separation of the tip from the sample is constantly adjusted via a feedback loop system, which forces the piezoelectric driver of the tip. Accordingly, a topographical image can be obtained by recording the height of the tip as a function of position.

The constant current mode is properly applied when the investigated surfaces are not flat on the atomic scale. The surface features can be elucidated according to the sensitivity of the piezoelectric driver. However, the disadvantage of this mode is the limited scan speed governed by the finite response time of the feedback loop.

(b) Constant height mode

The constant height mode is utilized to increase the scan speed significantly. In constant height mode, the time constant of the feedback system is made long or eliminated. The tip can be rapidly scanned at constant height over the surface of the sample. Thus, the variations in the tunneling current are recorded as a function of position to yield a topographic image. However, although turning off the feedback loop system provides the great advantage of

faster scanning, it also makes the constant height mode effective only for relatively flat samples.

(c) Current image tunneling spectroscopy (CITS)

STM yields not only the topographic image but also information on local electronic spectroscopic properties. Electronic spectroscopy elucidates the local density of electronic states of interest and is very important in surface science and nanoscience. Current image tunneling spectroscopy (CITS)[14] is particularly elegant. The polarity of the applied bias voltage, V, between the sample and the tip determines whether the tunneling current flows into the unoccupied states of the sample (positive sample bias) or out of the occupied states (negative sample bias). The tunneling current I comprises all of the tunneling probability associated with the sample states in the interval *eV*, and can be represented as

$$I \propto \sum_{E_F - eV}^{E_F} |\varphi_n(0)|^2 e^{-2\kappa z}.$$

The local density of states (LDOS) $\rho_S(Z,E)$ is defined as

$$\rho_S(z,E) \equiv \frac{1}{\varepsilon}\sum_{E-\varepsilon}^{E} |\varphi_n(z)|^2.$$

for a small value ε. Therefore, the relationship between the tunneling current and the LDOS can be written as,

$$I \propto V\rho(o, E_F)e^{-2\kappa z}.$$

The sample wavefunction is

$$\varphi(z) = \varphi(0)e^{-\kappa z},$$

$$\text{so} \quad I \propto \sum_{E_F - eV}^{E_F} |\varphi_n(0)|^2 e^{-2\kappa z} = \sum_{E_F - eV}^{E_F} |\varphi(z)|^2 = \rho_s(z, E_F)eV.$$

The tunneling current I can thus be expressed in terms of the formula,

$$I \propto \rho_s(z, E_F)V.$$

Finally, a series of data on the applied bias and the tunneling current yields the dI/dV data, and the electronic properties of the LDOS between $E_F - eV$ and E_F.

1.4 Si(111) 7×7 reconstructure[11]

Silicon (Si) is the simplest and most effective semiconductor substrate used in STM experiments. The Si crystal has the so-called diamond structure[15,16]. Each Si atom has four valence electrons and each forms four sp^3 orbitals, which in the form of a regular tetrahedron. The most natural cleavage plane is the (111) plane. Clearly, after the (111) plane is cleaved on the surface, the Si atoms have a dangling bond perpendicular to the (111) surface. The

dangling bond orbitals are half- filled, so many unsaturated bonds are present on the surface, and the nascent Si(111) is unstable. Hence, the unstable nascent Si(111) surface is reconstructed even at room temperature to become a Si(111)-2×1 surface. Heating the Si(111) surface in an ultrahigh vacuum reconstructs the metastable Si(111)-2×1 surface to a more stable structure Si(111)-7×7[11]. The Si(111)-7×7surface is complex and no model thereof was available until Takayanagi *et al.* provided one in 1985[17]. They developed the DAS model, incorporating nine dimers (D), 12 adatoms (A) and a stacking fault layer (S) in a unit cell.

1.5 Pb phases on Si(111) surface

Properties of metal/ semiconductor systems are very important in nanotechnology and nanoscience. However, for many metal/ semiconductor systems, determining which metals do not react with the semiconductor, and finding metals that can form flat and uniformly thick films under the stress effects of lattice mismatch[18-20], are difficult. Pb deposited on Si has been a preferred metal/ semiconductor system for scientists because of the low reactivity and solubility of Pb in Si. However, when Pb is adsorbed on the Si(111) surface, the system exhibits various phases, depending on coverage, temperature and annealing history[21-24]. The Si(111)7×7 surface can be transformed into a 1×1 bulk-terminated structure if further annealing is

performed following the deposition of Pb on Si(111)7×7 surface.

The Pb phases on the 1×1 bulk-terminated interface differ with the coverage of the deposited Pb: the phase diagram of the Pb/Si(111) system is complex[2-7,25-30]. Figure 1.1. presents the phase diagram of Pb/Si(111). As the coverage of Pb increases, the phases of Pb deposited on Si(111) are, in order, the γ phase, the $\frac{1}{3}ML(\sqrt{3}\times\sqrt{3})$ with a coexisting 1×1 phase, and incommensurate phase (IC).

In this thesis, the growth behaviors of Pb on three phases of Pb deposited on an Si(111) surface are studied. Three conditions are considered: (i) no further annealing; Pb is deposited on the Si(111)7×7 surface without further annealing; (ii) ≤ 1ML Pb deposited on Si(111)7×7, followed by annealing at ~480°C for a few seconds, such that the $\frac{1}{3}ML(\sqrt{3}\times\sqrt{3})$ and the 1×1 phase coexist at room temperature; (iii) slightly more than 1ML Pb is deposited on Si(111)7×7 surface, followed by annealing at ~480°C for one second to generate a IC phase.

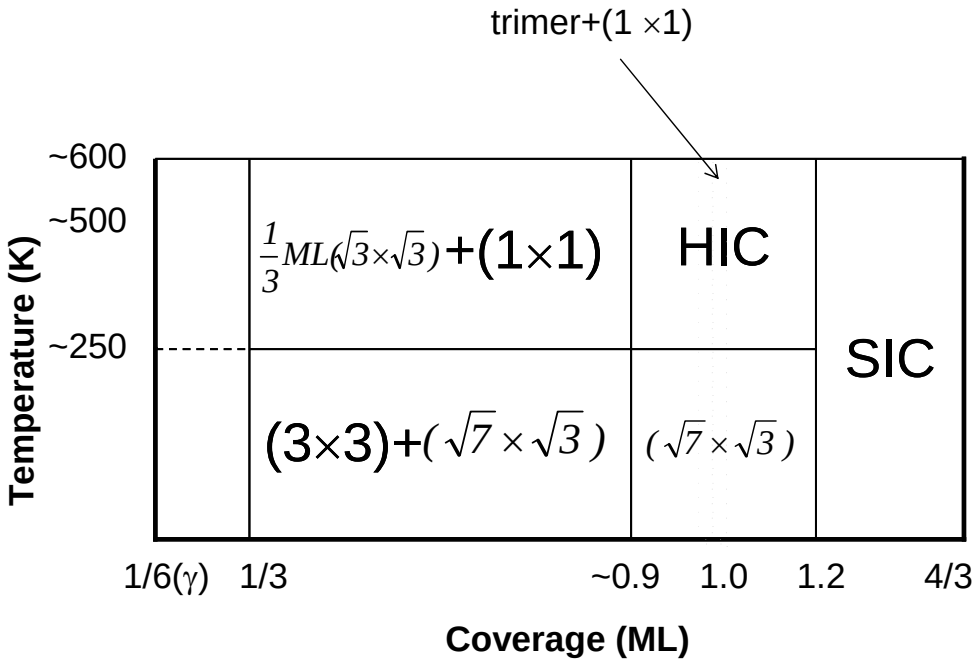

Fig. 1.1: Overview the phase diagram of Pb deposited on Si(111) surface for coverage between 1/6 and 4/3 ML[25]. The HIC is indicated the hexagonal incommensurate phase, and the SIC is represented the striped incommensurate phase.